Statistical Physics: a jogging course (2019 version)[1]

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Yoshi Oono oono@me.com

You can use the following notes as your elementary calculus check list:

https://www.dropbox.com/home/ApplMath?preview=AMII-ElementaryCheckList.pdf.

Also you can use the following notes as your elementary linear algebra re-introduction:

http://www.yoono.org/Y_OONO_official_site/P427_S19_lectures_files/P427LinearAlgebra.pdf

This is an introductory statistical thermodynamics course hopefully covering most topics that those who graduate from physics should know. I wish to connect elementary gas kinetics and Brownian motion smoothly to equilibrium statistical thermodynamics. Thus, as is clear, this course emphasizes three levels of description of the world, *microscopic*, *mesoscopic* and *macroscopic* descriptions. It is also emphasized that the latter two are closely related to large deviation and the law of large numbers, respectively.

Needless to say, it is not very easy to cover these topics within one semester, so the course is a jogging course. As an undergrad course in the US it is a bit challenging. If 1/3 of the participating students think interesting and rewarding, the course is a success.[2]

Self-study guide

(1) The best way to study is not to work when you do not wish to. If you wish to,

[1]While the previous version was, upon the suggestion of Cambridge University Press, expanded into a full year course for advanced undergrads and published as *Perspectives on Statistical Thermodynamics* (Cambridge UP, 2017), but Cambridge and I agreed that I can continue to use the original lecture version for my own course. This is a version with DISCUSSION problems added.

[2]⟪**Another Faraday effect**⟫ V. Arnold said, "M. Faraday arrived at the conclusion that Lectures which really teach will never be popular; lectures which are popular will never teach. This Faraday effect is easy to explain: according to N. Bohr, "clearness and truth are in a quantum complementarity relation." [Tribute to Vladimir Arnold: Arnold in his own words, Notices AMS **59**, 378 (2012)] The quotation is from p379.

concentrate on the study at least 15 minutes.[3]
(2) When you work, work as actively as possible, because effective learning is always 'active learning';[4] Think what you would do if you encounter the problem as the first person in the world.

Since I learned mathematics and physics without attending any course (beyond 200 in the US level) (because I was a wet chemist), I certainly wished to have books with filled details and with all the problems solved. Thus, these lecture notes may be followed without pencil and paper. However, I learned some will power was needed to use such books effectively, because 'muscle building' always requires some load. Therefore, always try to guess the next line or step in the derivation/transformation of formulas before reading the lines. Footnotes with $*$ are devoted to the derivation of marked formulas or to more detailed explanations. The reader can regard them as solutions to technical quizzes.

About every two sections accompanies one Discussion (table after the contents) related to the two sections covered in the preceding week of lectures; Discussion is a set of problems you can solve, discussing with your friends before reading the full solutions with further remarks. After Discussion comes a 'Homework = Exercise' to test your understanding that consists of problems often closely related to the ones in Discussion.

Even with Homeworks and Discussions, there is not enough space to give all the representative elementary problems. Therefore, to augment the book, I urge the reader to **consult the following two problem books**:

R. Kubo, H. Ichimura, T. Usui and N. Hashitsume, *Thermodynamics* (North Holland, 1968),
R. Kubo, H. Ichimura, T. Usui and N. Hashitsume, *Statistical Mechanics* (North Holland, 1990 paperback).

I learned thermal physics from these books. All the problems are fully solved, but many of them are not very easy. Try to solve at least the problems in [A] of these books. These books will be (collectively) quoted as Kubo's problem book (because the original Japanese version is a single book).

[3]Because in your brain cells new coding and noncoding RNAs require at least about this order of time to be transcribed.

[4]Read: Brown, P. C., Roediger III, H. L. and McDaniel, M. A. (2014). *Make it stick: The science of successful learning*, Cambridge (MA): The Belknap Press.

The international system of units (SI)

The official reference page is https://www.bipm.org/en/measurement-units/.
"This decision, made at the 26th meeting of the General Conference on Weights and Measures (CGPM), means that from 20 May 2019 all SI units are defined in terms of constants that describe the natural world. This will assure the future stability of the SI and open the opportunity for the use of new technologies, including quantum technologies, to implement the definitions."

The seven defining constants of the SI and the seven corresponding units they define are as follows:

Defining constant	Symbol	Numerical value	Unit
cesium hyperfine frequency	$\Delta\nu_{\mathrm{Cs}}$	9 192 631 770	Hz
speed of light in vacuum	c	299 792 458	m/s
Planck constant	h	6.626 070 15 $\times 10^{-34}$	J·s
elementary charge	e	1.602 176 634 $\times 10^{-19}$	C
Boltzmann constant	k_B	1.380 649 $\times 10^{-23}$	J/K
Avogadro constant	N_{A}	6.022 140 76 $\times 10^{23}$	mol^{-1}
luminous efficacy of visible radiation	K_{cd}	683	lm/W

The units in the table are: $\mathrm{Hz} = \mathrm{s}^{-1}$, $\mathrm{J} = \mathrm{kg{\cdot}m^2s^{-2}}$, $\mathrm{C} = \mathrm{A{\cdot}s}$, $\mathrm{lm} = \mathrm{cd{\cdot}m^2}$ and $\mathrm{W} = \mathrm{kg{\cdot}m^2s^{-3}}$.

The definitions of the basic units we need are s, kg, and m defined as follows:

$$1\ \mathrm{s} = 9,192,631,770/\Delta\nu_{\mathrm{Cs}}, \tag{0.1}$$

$$1\ \mathrm{m} = \frac{9,192,631,770}{299,792,458}\frac{c}{\Delta\nu_{\mathrm{Cs}}} \simeq= 30,663,319\frac{c}{\Delta\nu_{\mathrm{Cs}}}, \tag{0.2}$$

$$1\ \mathrm{kg} = \frac{h}{6.62607015 \times 10^{-34}}\ \mathrm{m^{-2}s}. \tag{0.3}$$

Historically, $N_{\mathrm{A}} = R/k_B$ and k_B is the energy corresponding to one kelvin of thermal energy to be equal to 1.380649 $\times 10^{-23}$ J. R is the gas constant. Now, both N_{A} and k_B are defined numerically as in the above table. This determines the units K (kelvin) and mole.

You must realize that time or the unit of time is extremely special. This means that we do not have any natural universal quantity such as h, c or e to determine time or length.

Contents

Discussions

Discussions are problem sets that you can work out while discussing with your friends. Full solutions with remarks and comments are with them, so after discussions please look at them critically.

1 Outlook of the course

Summary
∗ Science is an empirical endeavor.
∗ Science and religion have fundamental conflict.
∗ Our world allows microscopic, mesoscopic and macroscopic descriptions.
∗ The law of large numbers and deviations from the law allow us to understand macroscopic and mesoscopic worlds.

Key words[5]
Three levels of description: Microscopic, mesoscopic, macroscopic

What you should do
∗ Reflect on what science should be.

Now, everybody knows that the materials we see around us are made of atoms and molecules. We could even see them by, for example, atomic force microscopes. However, only 50 years ago no one could see atoms.[6] About 100 years ago the existence of atoms was still disputed.

1.1 Atomisms, ancient and modern

The idea that the world is made of indivisible and unchanging minute particles (*atomism*[7]) is, however, not a very creative idea.[8] After all, it seems that there are only two choices: (i) the world is infinitely divisible and continuous or (ii) the world is made of indivisible units separated by void (and various easy ideas in between). Ancient Greek and Indian philosophers reached atomism. Some philosophers may have favored atomism, because it avoided paradoxes associated with continuum (say,

[5] You must be able to explain these words (hopefully to your lay friends).

[6] Are you really sure you can see them today? First of all, what do we mean by 'see'? Thus, the answer is not as straightforward as we naively expect, even if it is affirmative.

[7] atom ← *atomos*: *a* = "not", *tomos* = "cutting"

[8] ⟪**Appreciate asking questions; appreciate Anaximander**⟫ As we will see soon, the ancient atomism is not quite correct as a scientific idea, since important ingredients to make it as a part of natural science are missing due to the limitation of mere philosophical considerations. However, we should appreciate these philosophers for asking the questions that led them to these ideas. We must appreciate those who have asked new questions. In this sense, according to Carlo Rovelli, Anaximander was the first scientist: "I do not wish to overstate the importance of Anaximander. In the end, we know very little about him. But twenty-six centuries ago, on the Ionian coast, somebody opened a new path to knowledge and a new route for humanity." (C. Rovelli, *The first scientist: Anaximander and his legacy* (Westholme, Yardley 2007; English version 2011 (translated by M. L. Rosenberg)), location 187, Introduction.

Zeno's paradox; perhaps even irrational numbers could be avoided).

Leucippus (5th c. BCE) is usually credited with inventing atomism in Greece.[9] His student Democritus systematized his teacher's theory. The early atomists tried to account for the formation of the natural world by means of atoms and void alone. The void space is described simply as nothing, or the negation of body. Atoms are, by their nature, intrinsically unchanging, but can differ in size, shape, position (orientation), etc. They move in the void and can temporarily make clusters according to their shapes and surface structures.[10] The changes in the world of macroscopic objects were understood to be caused by rearrangements of the atomic clusters.

Thus, atomism explains changes in the macroscopic world without creating new substance. Also all the macroscopic phenomena are naturally ephemeral ('the second law of thermodynamics'?).[11]

The most decisive difference between the modern atomism and the ancient atomism is that the latter is devoid of dynamics.[12] Indeed, the ancient atomism allowed motions to displace atoms and to change their aggregate states, but no special meaning was attached to movements themselves (quite contrary to the modern thermal motion which we will learn soon).[13]

1.2 Two enemies of empiricism

As noted in **1.1** the modern science has two pillars: the fact-seeking empirical part (in the narrow sense) and the fact-organizing part (based on the phylogenetic learning). These pillars are vulnerable, if we are not vigilant enough (to check (i) and (ii) in **1.4**), to naive versions of 'just-so empiricism' and 'metaphysical influences'.

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[9] `http://plato.stanford.edu/archives/win2011/entries/atomism-ancient/` S. Berryman, "Ancient Atomism," *The Stanford Encyclopedia of Philosophy* (Winter 2011 Edition), Edward N. Zalta (ed.).

[10] No 'interatomic' forces were conceived. That is, it seems that they imagined interactions between contacting bodies (atoms) but they never thought about forces through the void space. Interactions without contact (through void) seem to be a Newtonian novelty as we will see in Lecture 2.

[11] Since atomism understands that the world orders emerge from rearrangements of atoms, logically this implies that we human beings as natural phenomena are also understood as special arrangements of atoms. Consequently, ancient atomists were critical against institutionalized religions; atomism and secular humanism are rather harmonious as can be seen in Epicurus. If you read Epicurus (e.g., `http://epicurus.net`), you will realize how 'modern' his various views are.

It is natural and legitimate to ask whether God is or Gods are made of atoms. If God exists in or with the universe, It is made of atoms; if not, It has no effect on the universe, so irrelevant to us.

[12] Recall that even the Archimedean mechanics was essentially statics.

[13] Epicurus grants atoms an innate tendency to move downward through the infinite cosmos. The downward direction is simply the original direction of atomic fall. Interestingly, however, he allows atoms occasionally to exhibit a slight, otherwise uncaused (stochastic!) swerve from their downward path to avoid 'ordered parallel motion.'

'Just-so empiricism' means just what we observe is a reliable empirical fact. We always need to reflect on what we (can) actually observe (because often what we see is influenced by our metaphysical framework). The metaphysical biases come from Zeitgeist and various traditional ideas including religions. In a certain sense the former may be a more serious threat, because most scientists are unaware of the prejudices they are raised with.[14]

1.3 What was beyond philosophers' grasp?

The idea that everything is made of irreducible units is, as we have just argued, rather natural; if not infinitely divisible, there must be a unit. However, it is hard to identify what the actual unit is without empirical information. Notice that no one ever imagined that we are made of cells:[15] Recognize that the *cell theory* is one of the two pillars of biology (the other is Darwinism). We should clearly recognize that this indicates the limitation of philosophers who are not empirical enough. The lack of the idea of 'molecule' from the ancient atomism is also an example of this limitation. Perhaps, it is a sign of progress to recognize that the world does not have the structures we 'naturally' expect.[16]

Mechanics is also beyond philosophers' grasp. Therefore, modern atomism was beyond the reach of any philosopher.

We must respect empirical facts. Science is an empirical endeavor. At the same time, however, as you recognize from the works of Newton, Maxwell, Darwin, and others, 'pure empiricism' is not at all enough to do good science.[17]

1.4 What is science?

The question what science is does not have any definitive answer. However, its spirit, especially its empirical backbone, consists of

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[14]⟪**Question the Zeitgeist**⟫ We usually believe that the smaller the scales the more fundamental the phenomena. Thus, the study of extremely small scales of the world is regarded as the fundamental physics. How is this really scientific? Notice that the idea is closely related to the 'just-so empiricism' and its uncritical extension. Thus, we must critically review what we really empirically know.

As to the 'metaphysical influences', recently, Sabine Hossenfelder eloquently questioned the practice in high-energy physics. See S. Hossenfelder, *Lost in Math: how beauty leads physics astray* (Basic Books, New York, 2018).

[15]You should know that the discovery of nucleus by Brown (of Brownian motion) was a key to the proposal of the cell theory by Schwann and Schleiden in 1839.

[16]Kepler's discovery that the circular orbit is not natural may be an example; this was never accepted by Galileo.

[17]That is, as Confucius said: 'he who learns but does not think, is lost.' 'he who thinks but does not learn is in great danger.' (*Analect*, Book 2). You can read more excerpts here (Analect excerpts in English/Old Chinese).

(i) the humility that constantly makes us reflect on whether we really know and whether our methodology and logic are sound, and
(ii) the resultant skepticism.[18]

This science spirit must be universal beyond us human-beings wherever there are intelligence and conscience; Science is a conscientious and intelligent way of life.[19]

1.5 Never forget fundamental conflict between science and religion

As seen in **1.4** there is a fundamental conflict between science and religion; the latter demands the unconditional acceptance of certain propositions. Thus, the faithful can never emancipate himself from the burden of self-deception.

Unfortunately, a fundamentally wrong point of view can be found even in Physics Today.[20] There, it is argued that there was deep and constructive mutual engagement of science and religion as exemplified by Newton.[21] "Throughout most of history, scientific investigation has gone hand in hand with a commitment to theism, at least in the three Abrahamic faiths."

However, this simply demonstrates that any (wrong) motivation would do, if one is serious/genius (See the next **1.6**).

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[18] Also, the skepticism applied to itself is crucial: to cut the chain of skepticism off at appropriate positions and 'to experiment.' I took these statements from Y Oono, *The Nonlinear World* (Springer 2011), mainly Chapter 5.

Unscientific attitudes and political radicalism are correlated: Read M. Rollwage, R. J. Dolan, S. M. Fleming, Metacognitive Failure as a Feature of Those Holding Radical Beliefs, Current Biology **24**, 4014 (2018). Radical participants—on both ends of the political spectrum—showed reduced insight into the correctness of their choices.

[19] ⟪**Faith is evil**⟫ "Faith is an evil precisely because it requires no justification and brooks no argument." [R. Dawkins, *The God Delusion* (Houghton Mifflin Company, 2006) Chap. 8]. "Even mild and moderate religion helps to provide the climate of faith in which extremism naturally flourishes." "The take-home message is that we should blame religion itself, not religious extremism as though that were some kind of terrible perversion of real, decent religion." "Voltaire got it right long ago: 'Those who can make you believe absurdities can make you commit atrocities'."

"As long as we accept the principle that religious faith must be respected simply because it is religious faith, it is hard to withhold respect from the faith of Osama bin Laden and the suicide bombers." "What is really pernicious is the practice of teaching children that faith itself is a virtue."

S. Weinberg said: "Religion is an insult to human dignity. With or without it, you'd have good people doing good things and evil people doing evil things. But for good people to do evil things, it takes religion."

[20] T. McLeish, Thinking differently about science and religion, Physics Today 71(2) 10 (2018). He claims, "Maintaining the view that science and religion are in conflict does no one any favors and is hurting science." He is right, IF you do not care about fundamental consistency and integrity of ones intellectual life.

[21] As you can read in R. Ilffe, *Priest of Nature*, the religious worlds of Isaac Newton (Oxford, 2017), Newton was dead serious about showing that the central Christian doctrine of the Trinity was a diabolical fraud. His atomism is deeply related to this.

1.6 Let us not underrate the importance of error

Stefan Zweig wrote in a biography of Magellan, noting that "he planned and acted in honest error": Let us not underrate the importance of error. Through the promptings of genius, guided by luck, the most preposterous error may lead to the most fruitful of truths. In every branch of science, hundreds of highly important discoveries have been the outcome of erroneous hypotheses.

We simply note that Newton was unable to pursue intellectual self-consistency because of the shackles of the Zeitgeist.

Let us go back to narrower topics:

1.7 How numerous are atoms and molecules?

How many water molecules are there in a tablespoonful (15 cm^3) of water? Although we should discuss how to determine the size or mass of an atom (see Section 7), let us preempt the result.

Suppose one person removes one molecule of water at a time from the tablespoonful of water, and the other person use the tablespoon to scoop out the ocean water to the outer space. If they perform their operations synchronously, starting simultaneously, which person will finish first?[22] With a simple calculation you will realize that the number of molecules in a spoonful of water is comparable (the ratio is less than ca. 3) to the amount of ocean water measured in tablespoons.

Imagine you scoop out water of a 50 m swimming pool. You will not even try to start.

1.8 Why are molecules so small?

Thus, molecules are numerous. They are numerous because they are tiny. Why is an atom so tiny? This is not a meaningful question, however, because being small or being large is only relative; we cannot say whether a 1 m stick is long or short without comparing it with something else.[23] Let us compare our size with the atom size.[24] The above question properly understood is: why is the size ratio between atoms and us so big? Do not forget that we human beings are products of Nature.

[22]What if the tablespoons are replaced with teaspoons (5 cm^3)?

[23]To recognize this trivial fact is the first step to *dimensional analysis*, an important way of thinking in physics. Read "Introduction to Dimensional Analysis ". In these lectures dimensional analytic explanations will be attempted whenever dimensional analysis can be used.

[24]You might recall Protagoras, who said: Man is the measure of all things. However, the original meaning of this statement seems to have been much more restricted, because the word 'things' in the original only meant things human beings created (ideas, feelings, social entities, etc., not stars, mountains, etc.). See `http://en.wikipedia.org/wiki/Protagoras`.

Therefore, to compare us with atoms does not imply anthropocentric prejudice. Let us try to understand our size relative to atoms.

1.9 Why are we made of so many atoms?

Large animals, or, more generally, the so-called *megaeukaryotes*, are often constructed with repetitive units such as segments.[25] The size of the repeating unit is at least one order larger than the cell size. Consequently, the size of 'advanced' organisms must be at least 2-3 orders as large as the cell size.

Thus, the problem is the cell size.[26] We are *complex systems*,[27] so we have our parents and the crucial information and materials required to build us comes from the preceding generation. Since there is no ghost in the world, information must be carried by a certain thing (no ghost principle). Stability of the thing requires that information must be carried by polymers. What polymer should be used? Such a question is a hard question, so we simply imagine something like DNA. 'No ghost principle' tells us that organisms require a certain minimal DNA length. This seems to be about 1 m. As a ball its radius is about $0.5 \sim 1$ μm. This implies that our cell size (eukaryotic cell size) is ~ 10 μm ($= 10^{-5}$ m).

Thus, the segment size is about 1mm, and the whole body size is about 1 cm (this is actually about the size of the smallest vertebrates[28]). If we require a good eyesight, the size becomes easily one to two orders more, so intelligent creatures cannot be smaller than ~ 1 m. That is, the atom size must be 10^{-10} as large as our size.

We have, at least roughly, understood why atoms are small or why we are big.

[25]It may well be the case that the so-called biocomplexity achieved by Metazoa is due to segments, or a modular scheme to build a body.

[26]There is almost no paper discussing the cell size seriously, but recently a relevant paper appeared: Marshall WF et al., BMC Biology **10**, 101 (2012). It is an interesting collection of articles discussing relevant topics to cell size, but no relation with the required information is discussed. However, it has been recognized well that the amount of the DNA in a cell (the so-called C-number) is well correlated with the cell size (see for a summary, T. R. Gregory, "Coincidence, coevolution, or causation? DNA content, cell size, and the C-value enigma," Biol. Rev. Camb. Philos. Soc. **76**, 65-101 (2001)). Thus, we may safely claim that the lower bound of the cell size is determined by the amount of DNA.

Interestingly, if a very small body must be constructed, nucleusless cells are used to make the nervous system (see Wasp neurons lacking nuclei Nature **480**, 294 (2014)).

[27]The so-called complex systems studies study spontaneous formation of certain (ordered) structures from disorder. Thus, they study only pseudo-complex systems, because spontaneous emergence is a telltale sign of simplicity. In contrast, you did not spontaneously emerge, because to make you was not very simple. Pasteur realized the fundamental complex nature of life: life comes only from life, and never emerges spontaneously within a short time. Thus, unfortunately, no books with titles containing the word 'complexity' really discuss complexity. See, e.g., Chapter 5 of Y. Oono, *The Nonlinear World* (Springer, 2012).

[28]For example, Scherz et al., Morphological and ecological convergence at the lower size limit for vertebrates highlighted by five new miniaturised microhylid frog species from three different Madagascan genera. PLoS One **14**, e0213314 (2019).

1.10 Our world is lawful to the extent of allowing the evolution of intelligence

We have discussed, with the aid of atomism and cell theory, that science is an empirical endeavor and that no correct world view is obtainable solely with philosophical meditations without observing the world.

Who observes the world? We observe the world and are making science, so we must be at least slightly intelligent. To be intelligent at least we are $10^{9\sim 10}$ as large as the atom. But our large size is not enough. The world must have allowed our intelligence to evolve.

If there is no lawfulness at all, or in other words there is no order in the world,[29] then intelligence is useless; calculation is useless. We use our intelligence to guess what happens next from the current knowledge we have. If in a certain world organisms' guesses using their intelligence are never better[30] than simple random choices (say, following a dice), then intelligence would not evolve;[31] recall that the human brain is the most energy consuming very costly organ.[32] This means that the macroscopic world (the world we observe directly on our space-time scale) must be at least to some extent lawful with some regularity;[33] we believe in the lawfulness of the world to the extent that we are superstitious.[34]

However, if the law or regularity is too simple, then again no intelligence is useful. If the world is dead calm, no intelligence is needed. The world must be just right (the Goldilock principle or the principle of moderation). The macroscopic world we experience is not violent but not dull.[35]

1.11 Microscopic world is unpredictable

In contrast, we know the world of atoms and molecules (the microscopic world) is a

[29] 'Order' may be understood as redundancy in the world; knowing one thing can tell us something about other things simply because everything is not totally unrelated.

[30] Here, 'better' means it is more favorable to the reproductive success of the organisms.

[31] You will not study, if your grade is randomly assigned.

[32] Its weight is 2% of the body weight, but it consumes about 20% of the whole body energy budget.

Even our growth rate when we are very young seems to be considerably reduced to develop our brains. See C. W. Kuzawa et al., Metabolic costs and evolutionary implications of human brain development, Proc. Natl. Acad. Sci., **111**, 13010 (2014).

[33] Our logical brain must be a reflection of the logical nature of the environment we evolved. This must be parallel to the fact that many fishes have hydrodynamically optimal shapes. Water obeys hydrodynamics, not because fishes swim in it!

[34] Mistaking correlation as causality is an important ingredient of superstition.

[35] This is the meaning of the statement appearing later that the world is macroscopically phenomenologically describable.

busy and bustling world. They behave quite erratically and unpredictably (despite deterministic nature of mechanics) by at least two reasons, chaos and external disturbances.

Maxwell clearly recognized that molecules behave erratically due to collisions. Perhaps the simplest model to illustrate the point is the *Sinai billiard*. A hard ball (or rather you can imagine an ice hockey puck) is moving on the flat table, which has a circular obstacle on it. The ball hit the obstacle and is bounced back specularly (see Fig. 1.1).

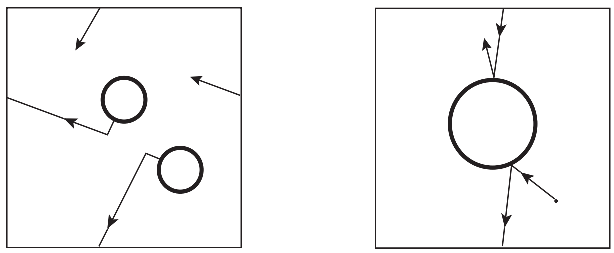

Figure 1.1: Sinai billiard: **Left**: a motivation. Two hard elastic discs (pucks) are running around on the table with a periodic boundary condition (if a disk disappears from one edge, it reappears from the opposite edge with the same velocity), colliding from time to time with each other. This is a toy model of a confined gas. **Right**: If the dynamic of the center of mass (CM) of one disk is observed from the CM of the other disk, the former may be understood as a ballistic motion of a point mass with occasional collisions with the central circular obstacle. This is called the *Sinai billiard*, and is known to be maximally chaotic.

Roughly speaking, a small deviation of the direction of the particle is doubled upon specular reflection at the central circle, so, for example, to predict the direction of the particle after 100 collisions is very hard.[36] Imagine what happens if there are numerous such particles colliding with each other. Thus, predictions would be absolutely impossible. Further worse, it is very hard to exclude the effects of the external world, in which we do not know what is going on at all. E. Borel pointed out that the trajectory of a molecule after a very short time can be totally altered, if one gram of mass moves by 1 cm on Sirius (11 ly away from us) due to the change in gravitational field. This implies that you cannot even breath if you wish to study the 'intrinsic behavior' of a collection of atoms.[37]

1.12 Kinetic theory

As discussed in **1.11** the microscopic world is full of noise, and everything looks stochastic, even though the intrinsic mechanics is not at all stochastic. Consequently, it is traditional that the microscopic world is handled with *Kinetic Theory* that grafts space-time local collision dynamics (in many cases binary collision dynamics) and the

[36]It is convenient to remember that $2^{10} \simeq 10^3$, so $2^{100} \simeq 10^{30}$.

[37]Quantum mechanically, subtle entanglements are easily lost by perturbation, so the system is much more fragile than the classical counterpart.

statistical description of one particle properties (e.g., its position and momentum).

This line of approach was developed into quite a sophisticated theory by Boltzmann and subsequent researchers. The theory allows us to understand time-dependent changes of a system, but since it is very hard to discuss simultaneous multiple collisions, it can study only dilute systems; it is almost hopeless to study condensed matter (e.g., liquid) honestly within the framework of kinetic theory,[38] so in this notes we do not discuss the theory at all.

1.13 Why our macroscopic world is lawful: the law of large numbers

The world on the scale of atoms is full of noise. We know our scale is quite remote from the atomic scale. The time scales are also disparate; the time scale required to describe molecular dynamics is 0.1 fs $= 10^{-16}$ s, but the shortest time span we can recognize must be longer than 10 μs $= 10^{-5}$ s. Lawfulness must come from suppression of noise. Our size is crucial to suppress noise; even if particles in a small droplet undergo quite erratic motion, if many particles are averaged, the erratic effect would disappear. This statement may be formally expressed as follows.

Let X_n be random variables.[39] Here, n is the suffix to specify the nth variable; we consider a collection of numerous (N) such variables, and X_n is the nth among them. Then,

$$\sum_{n=1}^{N} X_n = Nm + o[N], \tag{1.1}$$

where m is the average value (= expectation value) of X_n.[40] This is the *law of large numbers*,[41] the most important pillar of probability theory and the key to understanding the macroscopic world (see Section 4).

You may imagine outcomes of coin tossing as an example: $X_n = 1$ if the nth outcome is a head; otherwise, $X_n = 0$. By throwing a coin N times, we get a 01 sequence of length N, say, $0100101101110101\cdots001$. You can guess the sum is roughly $N/2$, where N must be sufficiently large. This is the law of large numbers. We clearly see the importance of our being big (relative to atoms).

[38]The latest summary of difficulties may be found in Isabelle Gallagher, From Newton to Navier-Stokes, or how to connect fluid mechanics equations from microscopic to macroscopic scales, Bull. Amer. Math. Soc. **56**, 65-85 (2019).

[39]We will discuss what we wish to mean by 'random variables' more carefully later, but here, you have only to understand them as variables that take various values in an unpredictable fashion.

[40]⟪***o***⟫ This standard symbol means higher order small quantities. In the limit being discussed, if $X/Y \to 0$, then we write $X = o[Y]$, which is read: compared with Y, X is a higher order small quantity in the limit being discussed. This does not mean X and Y themselves are infinitesimal. For example, $N^{0.99}$ is $o[N]$, if N is large (in the $N \to \infty$ limit), because $N^{0.99}/N = N^{-0.01} \to 0$.

[41]There are weak and strong laws of large numbers, but in statistical physics, generally we do not need any distinction. The formulation here is in the strong version.

1.14 We live in a rather gentle world

You might object, however, that being big may not be enough; we know violent phenomena in the macroscopic world like turbulence or perhaps the cores of galaxies. If the variances are too big, perhaps we may not be able to expect the expectation values to settle within a reasonable narrow range.[42] Also even if the expectation value eventually converges, needed N in the law of large numbers should not be too big; if you can recognize the regularity of the world only after averaging the observations during 1000 generations, probably the law of large numbers cannot favor intelligence very much. Thus, as already discussed above, the world in which intelligence can emerge cannot be too violent. We emerge in the world in which the law of large numbers hold rather easily at large scales to allow macroscopic laws (actually the world very close to no change from the molecular point of view). We live in the world where space-time scale is not only quite remote from the microscopic world of atoms and molecules, but also the extent of nonequilibrium is not too large.[43]

Now, an outline of our main topics:

1.15 Thermodynamics and statistical mechanics

The macroscopic world close to equilibrium[44] can be described *phenomenologically* by *thermodynamics*. Here, 'phenomenologically' implies that what we observe directly can be organized into a single logical system without assuming any entities beyond direct observations. Thermodynamics is distilled from empirical facts observable on our scale, so it is the most reliable theoretical system we have in physics.[45]

As we will learn in Lecture 13, statistical mechanics obtains the Helmholtz free energy A (which will be explained in detail later; Lecture 11) as

$$A = -k_B T \log Z, \tag{1.2}$$

where k_B is the Boltzmann constant, T is the absolute temperature, and Z is the

[42] Technical terms in this sentence will be explained in Section 3.

[43] We need a stable simple macroscopic laws for feeble minds to work (recall the intelligence must evolve). Our macroscopic world is so lawful that some of us can even believe in the benevolence of God.

[44] Intuitively, you may consider a system is close to equilibrium, if all the rapid changes (from our point of view) in it have subsided.

[45] Needless to say, classical mechanics, electromagnetism, quantum mechanics, etc., are also reliable theoretical systems based on our empirical observations. While thermodynamics is used with conscious recognition of its limitations (applicable only to macroscopic systems in equilibrium), other theories are (were) often regarded valid unconditionally (i.e., without clear recognition of their valid domains). In this sense these theories are less reliable. We must learn a lesson from the history that classical electrodynamics was regarded as the ultimate theory until it was recognized not to work in the microscopic world. Now, it is believed quantum mechanics is correct on all scales, and so is the general theory of relativity. Therefore, the current big issue is to unify these two, but we must admit that empirical facts recede from the foreground.

(canonical) *partition function*

$$Z = \sum e^{-H/k_B T}. \tag{1.3}$$

Here, H is the system Hamiltonian (the energy function or energy operator in quantum mechanics) and the summation is over all the *microscopic states*. We will discuss thermodynamics and its relation to statistical mechanics in Lecture 12, and then will learn how to use it subsequently.

1.16 Thermodynamic singularity and phase transition

We all know at least intuitively what a phase transition is. Think, for example, freezing or boiling of water. Some properties change sharply when such transitions occur. That is, thermodynamic quantities have singularities. In particular, the Helmholtz free energy A becomes singular (Section 24).[46]

Since $e^{-H/k_B T}$ is a smooth function of T (> 0), if Z given by (1.3) consists of finitely many summands, strictly speaking, nothing singular can happen in A as a function of T. This could mean that no phase transition occurs statistical-mechanically. However, if the system under study is very big (ideally, infinitely big, in the so-called *thermodynamic limit*), A (per particle or volume) can lose smoothness as a function of T; the sum of infinitely many smooth functions need not be smooth. Thus, *phase transitions* can be explained statistical-mechanically in the large-system size limit (in the so-called thermodynamic limit; Section 24).

1.17 Mesoscopic world

What does the world look like if we observe it on the scale intermediate between the microscopic and the macroscopic scales? In (1.1) the $o[N]$ term becomes not ignorable. That is, *fluctuation* cannot be ignored. This is the world where *Brownian g* dominates, where unicellular organisms live and where the cells making our bodies function. Intelligence is useless, because fluctuation is still too large and prevents agents from predicting what would happen. The best strategy is to wait patiently for a miracle to happen, and if it happens, to cling to it. Molecular motors just do this, crudely put.

In the mesoscopic world, the average of what we observe is consistent with our macroscopic observation results; *Onsager's regression hypothesis* asserts this. However, if we observe individual systems, observables fluctuate a lot around the expected macroscopic behaviors. Although we will not have time to go into statistical mechanics of such slow macroscopic changes, we will discuss Brownian motion and will give an informal discussion of transport phenomena (Sections 6-7).

[46] Mathematically, for example, it could lose differentiability.

1.18 Law of large numbers and probability

We are interested in statistical mechanics, so no one would doubt the relevance of probability theory. What is probability? We will discuss this later (Lecture 3), but let us proceed intuitively. We take statistics, and we know if the number of samples is increased, then statistical results become more reliable. This is just the law of large numbers **1.13** we have already encountered . The law of large numbers can be written as

$$P\left(\left|\frac{1}{N}\sum X_i - m\right| > \varepsilon\right) \to 0 \tag{1.4}$$

as $N \to \infty$, however small positive ε we choose, where P denotes *probability* of the *event* in the parentheses. That is, if we obtain an empirical expectation value $(1/N)\sum X_n$ using N samples, its deviation exceeding ε from the true average value becomes increasingly unlikely as N is increased, however small positive ε we choose. If a system is in equilibrium, this limit describes the world of macroscopic equilibrium governed by thermodynamics.

1.19 Large deviation and fluctuation

Now, we ask what happens between the microscopic and macroscopic scales, so we cannot take N very large. We should study how the above probability goes to zero as a function of N. This is governed by the *large deviation principle*:

$$P\left(\frac{1}{N}\sum X_i \sim x\right) \sim e^{-NI(x)}, \tag{1.5}$$

where I is called the *large deviation function* (or *rate function*), and may be approximated with a quadratic function when x is close to the true expectation value m:

$$I(x) \simeq \frac{1}{2V}(x-m)^2. \tag{1.6}$$

Here, V is a positive constant (corresponding to variance) and m is the expectation value, where $I(m) = 0$ implies the law of large numbers. (1.6) means that mesoscopic noise is usually Gaussian. That is, with the aid of a Gaussian noise w whose average is zero and variance V/N, we can write

$$\frac{1}{N}\sum X_i = m + w. \tag{1.7}$$

As we will see later (Lecture 18), I is related to the decrease of entropy from equilibrium due to fluctuations, and the above relation is useful in understanding fluctuations we can observe spatially locally in a system (Einstein's theory of thermodynamic fluctuations).

1.20 Time coarse-graining and Langevin equation

Even if the system reaches a state without any macroscopic change (i.e., an equilibrium state), molecules and atoms continue to jump around, so the mesoscopic world is not quiet and remains time-dependent even in equilibrium (that is, even if macroscopically the system is quiet). Thus, we observe Brownian motion (Lecture 7). It is well known that the trajectory of a Brownian particle is quite erratic and almost nowhere differentiable. However, we know molecules and atoms obey ordinary mechanics, so the time derivative of their positions must be well defined. This implies that the time derivative $\delta X/\delta t$ at the mesoscopic scale is not really the true mechanical derivative.[47] It is a time average of the true time derivative during a short span of time δt (perhaps $\sim 10^{-6}$ s, which is, however, very long for atoms; recall the time scale difference): the following definition must be very natural:

$$\frac{\delta X}{\delta t} = \frac{1}{\delta t}\int_t^{t+\delta t} ds \left(\frac{dX}{dt}(s)\right)_{true} = \frac{X(t+\delta t)-X(t)}{\delta t}. \tag{1.8}$$

Onsager's regression hypothesis implies that if $\delta X/\delta t$ is averaged over many observations (for example, repeating the same experiment under the same condition many times), the result (in the following formula, taking the average is denoted by $\langle\ \rangle$)

$$\left\langle \frac{\delta X}{\delta t} \right\rangle = F(X) \tag{1.9}$$

should describe the time dependence of macroscopic nonequilibrium phenomenology (macroscopic laws). Therefore, if we apply the large deviation principle to the time average (in the present context δt corresponds to N of (1.5)[48]), we may write

$$P\left(\frac{\delta X}{\delta t} \sim \dot{X} \,\middle|\, t\right) \sim e^{-\delta t I(\dot{X})}, \tag{1.10}$$

where the large deviation function reads

$$I(\dot{X}) \simeq \frac{\Gamma}{2}(\dot{X} - F(X))^2, \tag{1.11}$$

Γ being a positive constant. This implies that the time derivative on the mesoscopic time scale obeys the equation quite parallel to (1.7):

$$\frac{\delta X}{\delta t} = F(X) + \text{noise}. \tag{1.12}$$

Such equations with the noise terms are called the *Langevin equations*. Here, the noise amplitude is represented by Γ^{-1}. As we will learn later, the magnitude of the noise must be chosen appropriately to describe the equilibrium fluctuations correctly. This correct relation is provided by the *fluctuation-dissipation relation*. For example, the relation tells us a relation between the diffusion constant of a Brownian particle and the temperature, which is practically important in actual experiments. This course will cover at least the intuitively understandable aspect of this relation.

[47] That is, the 'infinitesimal displacement' δX and the 'infinitesimal time' δt are not truly mechanically (= microscopically) infinitesimal, but only look infinitesimal on the mesoscopic scale.

[48] or, more precisely, if we write the infinitesimal time on the microscopic time scale as dt, N in (1.5) corresponds to $\delta t/dt$.

Discussion 0

D0.1 [Hume, Smith, Watts, $\cdots$ and Scottish Renaissance]
David Hume is the key thinker who emphasized the source of our knowledge is our experiences (i.e., the source lies outside our mind). Then, Emanuel Kant realized that we still need some organization principle that is innate to every rational being. Konrad Lorenz emphasized that this innate 'a priori' is the result of 'phylogenetic learning,' that is, the result of evolution. In short, we are rational because the world is rational just as fish is hydrodynamical because water is hydrodynamical.[49]

We should clearly recognize that Adam Smith and David Hume were very close friends.[50] They knew Watt; especially, Smith's description of the division of labor is influenced by this relation; Smith's ideas on free economy came from Hume and Hume's ethics came from Smith. Furthermore, S. J. Gould claims, "I would advance the even stronger claim that the theory of natural selection is, in essence, Adam Smith's economics transferred to nature."[51]

The cultural background of thermodynamics was the Scottish Renaissance.

D0.2 [No absolute truth]
All the truths we accept as such are relative to our experiences. In this sense there is no absolute truth. "God and truth are two sides of the same coin. Life and mental well-being are hindered by both..."[52]

[49] Read K. Lorenz, "Behind The Mirror: A Search for a Natural History of Human Knowledge" (Houghton Mifflin 1978).

[50] Read D. C. Rasmussen, "THE INFIDEL AND THE PROFESSOR DAVID HUME, ADAM SMITH, AND THE FRIENDSHIP THAT SHAPED MODERN THOUGHT (Princeton University Press, 2018).

[51] in S. J. Gould "Structure of Evolution Theory" (Belknap Press of Harvard UP, Cambridge, MA, 2002) p122.

[52] D./ L. Everett, "Don't Sleep, There Are Snakes: Life and Language in the Amazonian Jungle" (Vintage Departures, 2008) p272. Recommended.

2 Atomic picture of gases

Summary[53]
∗ The biggest discovery about gases was the discovery of atmospheric pressure and vacua.
∗ Gay-Lussac gave key empirical facts: $PV \propto T$, the law of constant temperature (for adiabatic free expansion) and the law of combining volumes.
∗ Bernoulli related temperature and (translational) kinetic energy of molecules, but to make kinetic theory precise, we need probability.

Key words
Law of partial pressure, D. Bernoulli's kinetic theory, equipartition of energy,

What you should be able to do[54]
∗ Explain the law of constant temperature.
∗ Roughly reproduce Daniel Bernoulli's logic.
∗ Derive the equipartition of energy (for the translational motion).

The following books are recommended for a historical background:
S. G. Brush, *Statistical Physics and the Atomic Theory of Matter, from Boyle and Newton to Landau and Onsager* (Princeton UP, Princeton, 1983) esp., Chapter 1.
D. Lindley, *Boltzmann's Atom, The great debate that launched a revolution in physics* (The Free Press, New York, 2001).

2.1 Aristotelian physics and Galileo's struggle

According to Aristotle's (384-322 BCE) physics,[55] the four properties, hot, cold, dry and wet were irreducible properties, which corresponded to four elements of Empedocles (ca 490-430 BCE), fire, water, earth and air, respectively. The crucial point is that what we observe directly by our sense has a direct materials basis.

This type of ideas is called '*thingification*' or 'reification.' Chemistry is naturally under its spell;[56] one might say genomic biology is struggling to emancipate itself

[53] Historical comments in these lectures are heavily dependent on Y. Yamamoto, *Historical Development of Thoughts of Heat Theory* [in Japanese] (2007-8).

[54] This summarizes what you should be able to do in practice. Most things required in this course are practical.

[55] Originally, 'physica' meant study of nature.

[56] Needless to say, the modern chemistry never thinks color and odor are the properties of the

from this.[57]

Even *Galileo* (1564-1642) was initially under this influence, but later he clearly established the mechanical view of Nature, asserting that what we could feel (e.g., color, odor, etc.) existed only in the relation between the sensing subjects and the sensed objects and was thus subjective and secondary; only the (geometrical) shapes, numbers, configurations (positions) and movements (position changes) of substances were objective and were primary properties.

2.2 Archimedean mechanics

Mechanics, or more precisely, studying Archimedes was the key for Galileo and Descartes to overcome the Aristotelian 'physics'. Archimedes gave them the conviction that the natural laws could be formulated mathematically; indeed the world is mathematically constructed.

2.3 Could Galileo conceive kinetic theory of gases?

Then, you might think Galileo could have invented a kinetic theory of gases and could have conceived warmth as 'thermal motion.'

This is 'partially' correct. Galileo conceived a special substance 'fire particles,' whose vigorous motion was regarded as heat/warmth. It seems that he wished to distinguish 'microscopic motion' from 'macroscopic motion.' The relation between motion and heat was in a certain sense recognized thanks to the fire arms, but it may not be surprising that the relations of heat to the ordinary 'slow' motions and to the motions of bullets may not have been identified.[58]

2.4 Boyle: the true pioneer of kinetic theory of heat

Boyle (1627-1691) was the first to accept the principle that matter and motion were the primary things, and was truly free from the Aristotelian 'reificationism.' He correctly asserted that there were microscopic and macroscopic motions. The former was sensed as heat but could not be sensed by us as motion; the only motion we could sense as such was the 'progressive motion of the whole' (i.e., the systematic motion),

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substances themselves, but still it tends to explain properties of substances in terms of the properties of the atoms and molecules more or less directly. For example, if you find an acidic organic compound, you would likely think of COOH.

[57] e.g., such a superstition that there is a gene (as *FoxP2*) governing the capability to speak).

[58] Galileo never seems to have paid attention to the frictional heat, but even if he noted this, it would not have been so trivial to go from there to the idea of converting heat to systematic motion. As we will see later, it is doubtful that even Thomson clearly understood the relation when Clausius established thermodynamics.

which could not be felt by us as warmth even if it was vigorous. Thus, Boyle paved the way to the discussion of mutual convertibility of heat and (macroscopic) motion. Boyle was the true pioneer of the motional or the kinetic theory of heat.

2.5 Discovery of atmospheric pressure and vacua

The biggest discovery of modern physics about gases was the discovery of atmospheric pressure and vacua by Torricelli (1608-1647), Pascal (1623-1662) and von Guericke (1602-1686). This was a discovery demarcating the medieval and the modern ages, its importance only second to heliocentrism. Do not forget that even Galileo explained the impossibility of sucking water up more than 10 m in terms of the competition of gravity and the abhorrence of vacua by air.

Within the Aristotelean system, air and fire were regarded essentially light elements, having the tendency to go away from the earth. Therefore, the idea of mass (or weight) of air could not possibly be born. The discovery of vacua decisively discredited Aristotle.

2.6 Daniel Bernoulli and modern dynamic atomism

Thus, a modern dynamic atomic theory should be possible at any time, and indeed, Daniel Bernoulli's (1700-1782) gas model[59] (1738[60]) was the first fully kinetic model. We will discuss a simplified version (ignoring the size of atoms) in a modern fashion shortly.

However, the success of Newtonian universal gravity almost derailed atomism based on mechanics. Bernoulli's work was forgotten for a hundred years.

2.7 Newton derailed kinetic theory of heat completely

Newton (1642-1727) tried to explain Boyle's law (i.e., PV = constant, where P is the pressure, and V the volume) in terms of (repulsive) forces acting between particles. The idea of forces among particles was a novel idea actually deviating from the tradition of mechanistic theories. For Newton's contemporary scientists (and also for himself), introduction of gravitational force that explains the solar system was so impressive that the take-home lesson of the Newton's success was a program to find forces that explain various phenomena as you can clearly read in author's preface to *Principia*.[61]

[59] This was in his book on hydrodynamics.

[60] J S Bach, *Mass in B minor* (BWV 232; about 110 min) was the same year.

[61] Newton wrote in author's preface to *Principia* as follows: "I wish we could derive the rest of the phenomena of nature by the same kind of reasoning from mechanical principles; for I am induced by many reasons to suspect that they may all depend upon certain forces by which the particles of bodies, by some causes hitherto unknown, are either mutually impelled towards each other, and

Crudely put, somehow, Galileo's fire particle, Newton's ether,[62] and the 'pure elemental fire' of Boerhaave (1668-1738) were understood as analogues. Newton's repulsive (springy) molecules were imagined due to the clouds of such particles surrounding the molecules.

2.8 A hundred year hiatus of kinetic theory and a lesson

For about 100 years, the Newton's program **2.7** stifled the kinetic attempts.

You may have been surprised by this episode, but you will learn in your real life how vulnerable the so-called scientists are to the current trend/fashion and authority. This is quite unscientific, you might say. It is not surprising that the unfathomable gap between science and religion is not properly recognized by many scientists.

Remember that fish advected by the stream is dead.

2.9 Between Bernoulli and Maxwell

Between Daniel Bernoulli (ca 1740) and the birth of the modern kinetic theory (due to Maxwell (1831-1879) ca 1860) were the general acceptance of chemical atomic theory (ca 1810) and the birth of physics in the *modern sense*.[63] Also during this period crucial empirical facts were accumulated, making kinetic theory almost the sole consistent explanation of gasses.

2.10 Dalton

Dalton (1766-1844) asserted the *law of partial pressure*:[64] the total pressure of a gas mixture is simply the sum of the pressures each kind of gas would exert if it were occupying the space by itself. As illustrated in Fig. 2.1, it is very naturally explained from the atomic point of view.

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cohere in regular figures, or are repelled and recede from each other; which forces being unknown, philosophers have hitherto attempted the search of nature in vain; but I hope the principles here laid down will afford some light either to this or some truer method of philosophy.' (*Principia*, author's preface, May 8, 1686).

[62]Newton's philosophical starting point was New Platonism of Cambridge and Alchemy; both presupposed that the world is activated by the active principle. Ether was understood as the protoplast created by God to 'entrust' His own activity. Initially, Newton conceived a pan-etherial cosmology. See R. Ilffe, *Priest of Nature*, the religious worlds of Isaac Newton (Oxford, 2017).

[63]It is more experimental and mathematical rather than speculative with dedicated laboratories and professionally trained 'scientists.'

[64]Dalton arrived at his atomic theory not very inductively as is stressed by Brush on p32; Dalton's writings are sometimes hard to comprehend due to arbitrary thoughts and their outcomes being nebulously mixed up with real experimental results (Yamamoto *loc. cit.* p194), quite different from well-educated Gay-Lussac.

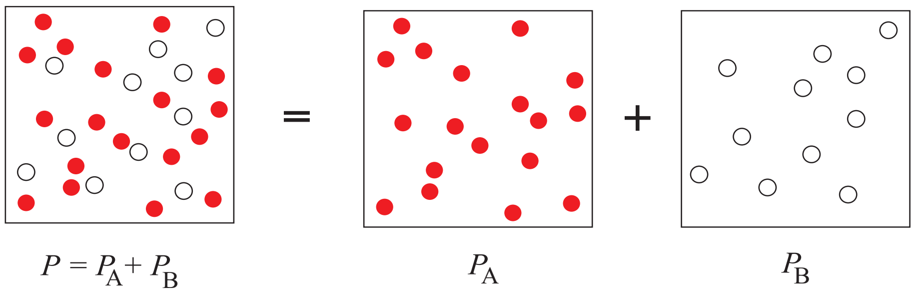


Figure 2.1: The law of partial pressure due to Dalton

2.11 Gay-Lussac and three laws

Gay-Lussac (1778-1850) then established three important laws (ca 1810[65]):
(i) The law of thermal expansion of gases (also called *Charles' law*; $P \propto T$ if V is constant).
(ii) The *law of constant temperature* under adiabatic expansion: if a gas is suddenly allowed to occupy a much larger space by displacing a piston, there is practically no temperature change. You can simulate this nicely using `http://falstad.com/gas/` with the free expansion setup.
(iii) The *law of combining volumes*: in gas phase reactions the volumes of reactants and products are related to each other by simple rational ratios implying that 'particles' cannot generally be atoms.[66]

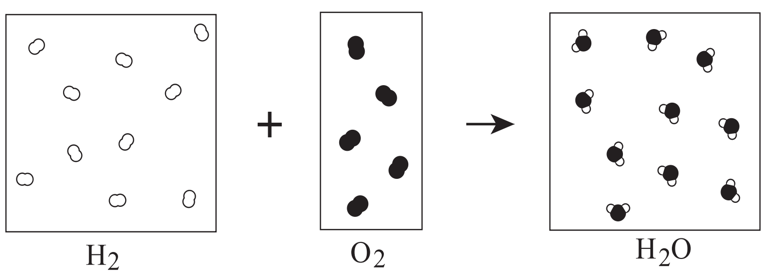


Figure 2.2: The law of combining volumes indicating that generally gases are made of molecules instead of atoms. The figure illustrates $2H_2 + O_2 \rightarrow 2H_2O$.

2.12 Avogadro

[65][1810: Napoleon married Marie Louise of Austria; Chopin was born; Beethoven Piano Trio *Archduke* (Istomin-Stern-Rose)] Notice that Gay-Lussac was the first generation of professional scientist trained professionally to be a scientist. He was a product of French Revolution.

[66]But Dalton rejected this interpretation, saying, Gay-Lussac's experiments were inaccurate, etc. This clearly indicates that Dalton was a metaphysicist more than a physicist.

In 1811[67] Avogadro (1776-1856) proposed *Avogadro's hypothesis*: every gas contains the same number of *molecules* at the same pressure, volume, and temperature.

However, the molecular theory was not generally accepted until 1860, when Cannizzaro (1826-1910) advocated Avogadro's proposal in the Karlsruhe Congress (However, Clausius accepted this by 1850;[68] actually, Cannizzaro was triggered by Clausius' kinetic theory paper a year before[69]).

2.13 Build your intuition through simulation

http://falstad.com/gas/ is an excellent site to play with a gas dynamic model in java with a heater/cooler, with or without gravity, etc.

2.14 Daniel Bernoulli's kinetic theory

Let us look at Daniel Bernoulli's work.

The (kinetic interpretation of) pressure P on the wall is the average momentum given to the wall per unit time and area by the gas. Consider the wall perpendicular to the x-axis (see Fig. 2.3).

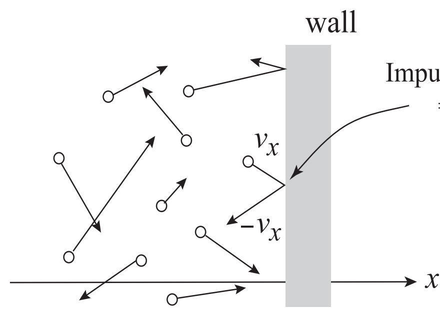


Figure 2.3: Bernoulli's theory (or mechanical model of gas). Particles are so small that they are assumed not to collide with each other.

Let us proceed step by step. Assume that the mass of each particle is m, and that the number density of the particles is $n = N/V$, where V is the volume of the (uniform) gas and N the total number of particles:
(i) For a single particle with velocity $\boldsymbol{v} = (v_x, v_y, v_x)$ hitting the wall ($v_x > 0$) in the figure, the momentum given to the wall upon collision (= the impulse) must be

[67][1811: New Madrid earthquake, J. Austin published *Sense and Sensibility*.] This year Stevens started the first steam-powered ferry service between New York City and Hoboken. As will be noted later again, recognize how thermal physics had been left behind its practical applications.

[68]Brush p51

[69]C. Cercignani, "The rise of statistical mechanics," in *Chance in Physics*, Lect. Notes Phys. **574** (edited by J. Bricmont, D. Dürr, M. C. Gallavotti, G. C. Ghirardi, F. Petruccione and N. Zanghi) p25 (2001). This article gives a good summary of Boltzmann's progress.

$2mv_x$.
(ii) The total momentum given to the wall in one second is the force on the wall in the x-direction, whose magnitude is equal to PA, where A is the area of the wall. For a particle moving toward the wall to hit it within the next one second, it must be within distance v_x from the wall. Therefore, to contribute to the pressure the particles with the x-component velocity around v_x[70] (> 0) must be in the volume of $A \times v_x$.
(iii) Let $n(v_x)$ be the number density of the particles with its x-component velocity around v_x. Then, the contribution of such particles to the pressure (times the wall area) must be $n(v_x) \times Av_x \times 2mv_x$ according to (i) and (ii).
(iv) Therefore, summing over all the incoming particles, we get

$$PA = \sum_{v_x > 0} 2n(v_x)Amv_x^2. \tag{2.1}$$

That is,

$$P = \sum_{v_x>0} 2n(v_x)mv_x^2 = \frac{\sum_{v_x>0} 2n(v_x)mv_x^2}{\sum_{v_x>0} n(v_x)} \sum_{v_x>0} n(v_x) = 2n_+ m\langle v_x^2 \rangle_+, \tag{2.2}$$

where n_+ is the number of particles with positive v_x, and $\langle \ \rangle_+$ means the average over molecules with positive v_x (to hit the wall).[71]
(v) We do not expect the mean square velocity of the left-going and right-going particles are different, so $\langle v_x^2 \rangle_+ = \langle v_x^2 \rangle$ (henceforth $\langle \ \rangle$ generally implies averaging, or calculation of expectation values) and $n_+ = n/2$ (just half of the particles move to the right; notice that we have used the law of large numbers!). Therefore,

$$P = nm\langle v_x^2 \rangle. \tag{2.3}$$

(vi) Using the isotropy of the gas, we expect $\langle v_x^2 \rangle = \langle v_y^2 \rangle = \langle v_z^2 \rangle$, so $\langle \boldsymbol{v}^2 \rangle = \langle v_x^2 \rangle + \langle v_y^2 \rangle + \langle v_z^2 \rangle = 3\langle v_x^2 \rangle$. Therefore,

$$P = \frac{1}{3} mn\langle \boldsymbol{v}^2 \rangle. \tag{2.4}$$

Or, recalling $n = N/V$, we have

$$PV = \frac{2}{3} N\langle K \rangle, \tag{2.5}$$

where K is the kinetic energy of a single gas particle. This equation is called *Bernoulli's equation*.

[70] We must write it to be in $[v_x, v_x + dv_x)$, precisely, but let us proceed as informally as possible.
[71] The astute reader should have noticed that the law of large numbers **1.13** is (implicitly) used here.

Comparing this with the equation of state of an ideal gas $PV = Nk_BT$,[72]

$$\langle K \rangle = \frac{3}{2} k_B T. \tag{2.6}$$

2.15 Equipartition of kinetic energy

Let us see that all the particles in a gas consisting of particles with different masses have, on the average, identical translational kinetic energies. That is, (2.6) holds for any particle in a gas mixture (if it is 'in equilibrium'). As we will learn later, this is almost self-evident, if we know the basic statistical mechanics, but we should also be able to have elementary understanding. It may be inconvenient if you cannot drive a good car at a high speed on a highway, but if you cannot walk, you will not be able to explore the places where nobody has ever been.

Consider a two particle collision process. In equilibrium (i.e., if, on the average, you cannot discern any change),

$$\langle \boldsymbol{w} \cdot \boldsymbol{V} \rangle = 0, \tag{2.7}$$

where $\boldsymbol{w}$ is the relative velocity and $\boldsymbol{V}$ is the center of mass velocity. If we write these in terms of the velocities of two particles $\boldsymbol{v}_1$ and $\boldsymbol{v}_2$ and their respective masses m_1 and m_2, we have

$$\boldsymbol{w} \cdot \boldsymbol{V} = (\boldsymbol{v}_1 - \boldsymbol{v}_2) \cdot \frac{(m_1 \boldsymbol{v}_1 + m_2 \boldsymbol{v}_2)}{m_1 + m_2} = \frac{(m_1 v_1^2 - m_2 v_2^2) + (m_2 - m_1)\boldsymbol{v}_1 \cdot \boldsymbol{v}_2}{m_1 + m_2}. \tag{2.8}$$

We know $\langle \boldsymbol{v}_1 \cdot \boldsymbol{v}_2 \rangle = 0$, so we get the equality of the average kinetic energies.

The gas mixture can be simulated here: `http://www.falstad.com/gas/` and choose Setup: 2 (random speed). Small particles look really fast. Look at the energy distributions.

Notice that Bernoulli's formula and equipartition of translational kinetic energy imply that even if all the particles in an ideal gas (non-interacting particle system) are with different masses, still the ideal gas law holds.

Question. We have demonstrated the equipartition law, but we can give any initial condition to the gas. Do you believe that the equipartition law eventually holds even if the initial condition does not satisfy the law? □

[72]Here, the modern notations are used; what they knew at that time was that $PV \propto NT$, but they could not find N.

Discussion 1

D1.1 [Very elementary questions]
(1) The unit of pressure is 'pascal' Pa. Write this in terms of s, kg and m. [1 atm = 101,325 Pa.][73]

(2) What is the total kinetic energy of the gas in the room where you are now? You must supply reasonable values for P, T, etc.

Can you supply an explanation/illustration that makes the number more intuitively understandable?

(3) Estimate the number of molecules in the air of the discussion room. You may assume the standard ideal gas equation of state $PV = Nk_BT$ with the accepted value for the Boltzmann constant $k_B = 1.380662 \times 10^{-23}$ J/K. Clearly recognize that without knowing this constant, you cannot get the number of molecules. Thus, a fundamental question of physics is how to measure this value. This is (historically) the topic of Brownian motion (Section 7).

(4) Suppose all the air molecules are condensed to a point mass of mass $M = Nm$ (without any internal structure), where m is the (average) mass of the gas molecule. What is the speed of the point mass, if it has the same (total) kinetic energy $\mathcal{K}$ as obtained in (2)?

You cannot answer this question without knowing the mass of air in the room.[74] Let us use the air density = 1.2 kg/m^3.

Now, compare it with the mean square velocity ($\sqrt{\langle \boldsymbol{v}^2 \rangle}$) of the molecules. What is your observation?

(5) It is usually taught that the kinetic theory of gases was a triumph of atomism, but is it really so? Consider the limit $N \to \infty$, keeping $M = Nm$ constant. What do you obtain?

What is the logical conclusion of this observation?

(6) Suppose you place a sphere of radius 1 m in the room. How many air molecules collide its surface on the average in one second?

First outline how to obtain the formula for the number N_C of molecules colliding a one side of a plane with unit area on the average in one second in terms of the

[73] **⟪How to write units⟫**
∗ Units are always with upright fonts, e.g., volume V m^3, or distance L km.
∗ There must be a space between the quantity (number) and the unit, e.g., 32 mK (32 millikelvins) or 25.2 kg.
∗ The products of different units must be separated with a center dot, e.g., mg·s for milligram times second. Notice that m·g means meter times gram.
∗ When fully spelled as 'pascal', 'newton' or 'coulomb', all the units start with lower case letters. In this case you need plural 's', e.g., 3.2 Pa is spelled out 3.2 pascals.

[74] This tells you how important it is that you can make a vacuum. Creating vacua was important only second to heliocentrism, as noted in the lecture notes **2.5**.

quantities appearing in **2.14**.

We may be able to estimate N_C later more accurately, but here let us assume that we know only (the modern interpretation of) Daniel Bernoulli's kinetic theory.

What can you say or is there any way to estimate the number of particles impinging on the sphere approximately?

Solution.
(1) Since the pressure is force/area, Pa = N/m^2, where N is newton and N = kg·m/s^2. Therefore, Pa = kg/m·s^2.
How to write units: As explained in footnote 67, notice that units are never italicized. You must know how to correctly write units. The numerical value and the unit must be separated by a space. k (kilo) must not be in upper case. Distinct units in product must be separated by ' · '; mK is 'milikelvins' and m·K is 'meter times kelvin'.

(2) According to Bernoulli's equation (2.5), $PV = (2/3)N\langle K\rangle$. Therefore, the total kinetic energy is given by

$$\mathcal{K} \equiv N\langle K\rangle = \frac{3}{2}PV = \frac{3}{2}101,325V = 1.52 \times 10^5 V \text{ J}. \tag{2.9}$$

Here, a reasonable value V must be supplied in m^3 to use the unit J (= joule).

If the room is 20 m × 10 m × 3 m, $\mathcal{K} = 9 \times 10^7$ J. The average US car weighs 4,000 lb = 1,800 kg, so this means $\mathcal{K}$ is the kinetic energy of a car running at 300 m/s (1,000 km/h or 670 mph). This is about the energy available from burning 1 kg of gasoline (46.7 MJ/kg) [cf. 1 gallon of gas = 2.86 kg].

(3) Let V be the volume of the room, the air pressure P and its temperature T. Thus, $N = PV/k_BT$. P should be in pascals. Note: 1 atm = 1.013×10^5 (101,325, precisely) Pa. Here, T must be room temperature, 300 K. Thus,

$$N = \frac{PV}{k_BT} = \frac{101,325}{1.380662 \times 10^{-23} \times 300}V = 2.45 \times 10^{25}V. \tag{2.10}$$

In elementary courses we are told that 1 mole of gas occupies 24.5 liters of volume under a similar condition:[75] $2.45 \times 10^{25} \times 24.5 \times 10^{-3} = 6 \times 10^{23}$, our calculation is reasonable.

(4)

$$\mathcal{K} = \frac{1}{2}Mv^2 = \frac{1}{2}1.2Vv^2 = \frac{3}{2}101,325V, \tag{2.11}$$

so

$$v^2 = 3 \times 101,325/1.2 = 253,312.5 \;\Rightarrow v = 503 \text{ m/s}. \tag{2.12}$$

Since $\langle K\rangle = m\langle v^2\rangle/2$,

$$\mathcal{K} = \frac{1}{2}Nm\langle v^2\rangle = \frac{1}{2}M\langle v^2\rangle. \tag{2.13}$$

[75] More precisely, 22.3 liters under 1 atm and 273 K.

Thus, $\sqrt{\langle \boldsymbol{v}^2 \rangle}$ is just the same!

Imagine 'M' is divided into 100 equal (actually, need not be equal) particles. Then, the ideal gas consisting of these 100 particles gives exactly the same equation of state, the Bernoulli equation.

(5) We get just the same Bernoulli's equation. Thus, Bernoulli's theory could be interpreted simply as a means to study continuum, so the success of kinetic theory cannot tell us anything about the reality of atoms.

(6) According to Bernoulli the total number of particles colliding on the surface in Fig. 2.3 in the lecture notes is given by (see (ii) in **2.14**):

$$N_C = \sum_{v_x > 0} n(v_x) v_x. \tag{2.14}$$

From symmetry, the answer to (6) is $4\pi N_C$.

To estimate (2.14) accurately, we need $n(v_x)$, which we will discuss only in Section 5. We can rewrite (2.14) as

$$N_C = \sum_{v_x > 0} n(v_x) v_x = \frac{\sum_{v_x > 0} n(v_x) v_x}{\sum_{v_x > 0} n(v_x)} \sum_{v_x > 0} n(v_x) = \langle |v_x| \rangle \frac{1}{2} n. \tag{2.15}$$

$\langle |v_x| \rangle$ and $\sqrt{\langle v_x^2 \rangle} = \sqrt{\langle \boldsymbol{v}^2 \rangle}/\sqrt{3}$ should be of the same order.[76] Thus, our estimate is

$$N_C \approx \frac{1}{2\sqrt{3}} n \sqrt{\langle v^2 \rangle} = \frac{1}{2\sqrt{3}} \frac{N}{V} \sqrt{\frac{2N\langle K \rangle}{M}} = \frac{1}{2} \frac{N}{V} \sqrt{\frac{PV}{Nm}} = \frac{1}{2} \frac{P}{k_B T} \sqrt{\frac{P}{\rho}}. \tag{2.16}$$

Here, $\rho = 1.2$ kg/m^3. Using the result in (3)

$$N_C \approx \frac{1}{2} 2.45 \times 10^{25} \sqrt{\frac{1 \times 10^5}{1.2}} = 1.2 \times 10^{25} \times \sqrt{8.25 \times 10^4} = 3.4 \times 10^{27}. \tag{2.17}$$

Thus, the answer is about 4×10^{27}.

D1.2 [Does gravity matter?].
The actual room is influenced by the gravitational field of the earth.

(1) What is the potential energy difference of an oxygen molecule between the floor and the ceiling?

(2) Estimate the ratio of this potential energy and the kinetic energy. Is it the order of 1%, 0.1 %, or $\cdots$? Is it ignorable? [Think of 0.1% of T.]

Solution.
(1) Let h be the height of the ceiling. Then,

$$hmg = h \times 9.8 \times (32 \times 10^{-3}/6.02 \times 10^{23}) = 5.2 \times 10^{-26} h \text{ J}. \tag{2.18}$$

[76] Can you tell which must be larger? Recall Cauchy's inequality.

(2) The ratio is $mhg/(mv^2/2) = 2gh/v^2 \sim 50/5 \times 10^4 \sim 0.1$ %. This corresponds to ~0.5 K. If such a difference exists, we cannot ignore it in a big lecture room.

(3) ['open ended' discussion topic] If a particle climbs up from the floor to the ceiling, its kinetic energy would be converted into its potential energy, so the particle would slow down.

Can you conclude that the temperature at the ceiling must be cooler (to the order estimated in (2)) than on the floor (after the air in the room settles down to time-independent state = equilibrium state)?

This is not a very trivial question, so I wish you to guess the answer, supplying plausible supportive arguments.

Comments

Naively speaking, we may expect that the air is cooler near the ceiling than near the floor. Indeed, there was a very famous scientist who concluded the existence of the temperature difference. Actually, there is no temperature difference due to external field. I wish to prove this later, but it is not very trivial, so here, I wish you to discuss (i) what is the likely situation, $\Delta T = 0$ or not?; (ii) Give justifying or plausibility arguments for your guess.

A relatively elementary exposition, assuming Boltzmann/Maxwell distribution:[77] In Fig. 2.4 the number in each box indicates the number density with a given kinetic energy due to v_z.

$$e^{-\beta m v_z^2/2} dv_z \propto \frac{1}{\sqrt{\varepsilon}} e^{-\beta\varepsilon} d\varepsilon. \tag{2.19}$$

Thus the number density of particles around energy ε is proportional to $e^{-\beta\varepsilon}/\sqrt{\varepsilon}$; we get the table 2.4, where $r = e^{-\beta mgh}$.

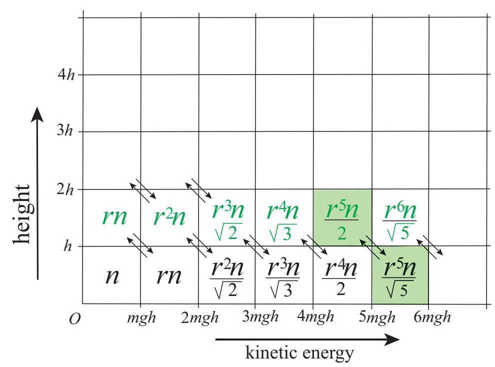


Figure 2.4:

Let us study the equilibrium between different heights (say, the green blocks between lower cell with energy $kmgh$ (with number density n') and the cell (with kinetic energy $(k-1)mgh$ and with the number density n'') one h higher into which the particle can move from the original box. This transition should be proportional to v_z, so proportional to $\sqrt{\varepsilon}$ (i.e., going

[77] This is taken from H. Ezawa, "Who saw the atom?" (Iwanami 2013; original 1976) p305-

up $\sqrt{k}$ or down $\sqrt{k-1}$). Therefore, in equilibrium

$$n'\sqrt{kmgh} = n''\sqrt{(k-1)mgh}, \tag{2.20}$$

where $n' = nr^k/\sqrt{k}$, so we get $n'' = nr^k/\sqrt{k-1}$. The outcome is the green results in the table. Note this is r (the Boltzmann factor due to mgh) times the Maxwell distribution (the lowest row). Thus, the second row must have the same temperature.

Of course, we can understand this from the canonical distribution trivially (Section 13), but we cannot use it here, since no logic to justify its use is given yet.

D1.3 [Law of partial pressure from the kinetic point of view].
Demonstrate Dalton's law of partial pressurewith the kinetic theory of D. Bernoulli. If you think this is too trivial, you can skip it.

Solution.
Trivial.

D1.4 [Ideal gas in $\mathfrak{d}$-space].
What is Bernoulli's equation of state in $\mathfrak{d}$-dimensional space? Again, a trivial question, right?

Solution.
Almost trivial; you have only to replace '3' with $\mathfrak{d}$. For such cases you need not write down obvious things repeatedly, but you must be able to explain why it is trivial.

D1.5 [Equipartition-related]
(1) In an equilibrium[78] mixture ideal gas maintained at temperature T are two molecules, 1 and 2, with mass m and M, respectively. Suppose $m/M = 0.31$. What is the ratio between the mean square relative velocity of these two molecules and the mean square velocity of molecule 1?

(2) What is $\langle (1/2)m(\boldsymbol{v}_1 - \boldsymbol{v}_2)^2\rangle$ in the $M/m \to \infty$ limit? The answer should be obvious, so state your answer first with your supporting argument and then confirm it, using the formulas you should have used to answer (1).

Solution.
(1) Let the velocity of molecule i be $\boldsymbol{v}_i$. The relative velocity is $\boldsymbol{w} = \boldsymbol{v}_1 - \boldsymbol{v}_2$. We wish to compute

$$\langle \boldsymbol{w}^2\rangle = \langle \boldsymbol{v}_1^2\rangle + \langle \boldsymbol{v}_2^2\rangle - 2\langle \boldsymbol{v}_1\cdot\boldsymbol{v}_2\rangle. \tag{2.21}$$

[78] We have not clearly defined what 'equilibrium' is, but here you may understand that the system is isolated and left alone for a sufficiently long time. The molecules move in a mutually unrelated manner, and, in particular, the equipartition of energy holds.

Since two molecules are statistically independent, and since their mean velocities must be zero ($\langle \boldsymbol{v}_1 \cdot \boldsymbol{v}_2 \rangle = \langle \boldsymbol{v}_1 \rangle \cdot \langle \boldsymbol{v}_2 \rangle = \mathbf{0} \cdot \mathbf{0} = 0$),

$$\langle \boldsymbol{w}^2 \rangle = \langle \boldsymbol{v}_1^2 \rangle + \langle \boldsymbol{v}_2^2 \rangle. \tag{2.22}$$

Now, we use the equipartition of the translational kinetic energy

$$\frac{1}{2} m \langle \boldsymbol{v}_1^2 \rangle = \frac{1}{2} M \langle \boldsymbol{v}_2^2 \rangle = \frac{3}{2} k_B T. \tag{2.23}$$

Therefore,

$$\langle \boldsymbol{w}^2 \rangle = \frac{3}{m} k_B T + \frac{3}{M} k_B T. \tag{2.24}$$

Thus, the ratio is

$$\frac{\langle \boldsymbol{w}^2 \rangle}{\langle \boldsymbol{v}_1^2 \rangle} = \frac{(3/m)k_B T + (3/M)k_B T}{(3/m)k_B T} = \frac{m+M}{M} = 1.31. \tag{2.25}$$

(2) $\langle \boldsymbol{w}^2 \rangle$ must be identical to $\langle \boldsymbol{v}_1^2 \rangle$ of molecule 1, so the answer is $3k_B T/2$, since the 'heavier' molecule 2 is not moving at all! The ratio above goes indeed to 1 in the desired limit.

Exercises 1

E1.1 [How big is N_A]
Propose a way to show/illustrate how big Avogadro's constant N_A (or, more generally, the number of molecules in a macro object) is. My 'spoon performance' **1.7** was an example. One more illustration:
The total number of cells in human bodies on the earth at present is still less than N_A, even if you include your beloved gut microbes.

E1.2 [Otto von Guericke 1654]
The Magdeburg hemispheres[79] has a 50 cm diameter. One of them had a tube connection to attach the pump, with a valve to close it off. When the air was sucked out from inside the hemispheres, and the valve was closed, the hose from the pump could be detached, and the hemisphere were held firmly together by the air pressure of the surrounding atmosphere. Estimate the force required to separate the hemispheres.

Soln.
The 'opened-up' illustration of the Magdeburg hemisphere system is in Fig. 2.5:

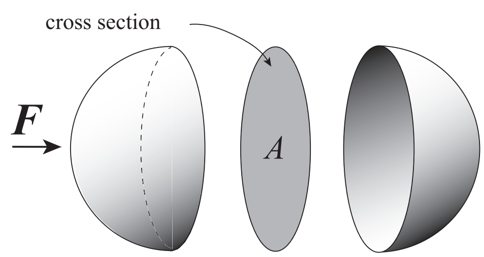


Figure 2.5: The Magdeburg hemispheres and the cross section with area A; $\boldsymbol{F}$ is the total on the left hemisphere due to atmosphere.

The total force on the left hemisphere $\boldsymbol{F}$ must be the same (in magnitude) as the force on one side of the cross section A due to the atmospheric pressure, because the hemisphere closed with the cross section A does not start to move due to the atmospheric pressure on it. Therefore, $F = PA = 10^5 \times \pi(1/4)^2 \approx 2 \times 10^4$ N. This is about equal to the force required to lift 2 tons of mass on the earth.

E1.3 [Phys 101 level question]
On a planet for the hydrogen molecule to escape from its surface (to infinity) it requires the surface temperature 320 K. What is the temperature required for methane to escape from the planet surface?

Solution.

[79] Wikipedia https://en.wikipedia.org/wiki/Magdeburg_hemispheres is nice. von Guerick was a successful statesman for his town Magdeburg: "He often would not explain scientifically how his shows worked leading people to believe in his wizardry, promoting his status as a great leader." (Wiki von Guericke).

To escape the planet surface means to get the gravitational potential energy of

$$U = GmM/R, \tag{2.26}$$

where M is the planet mass, R the planet radius, and m the mass of the hydrogen molecule. This must be provided by the kinetic energy $3k_BT_{H_2}/2$. For methane we need $U = Gm'M/R$, where m' is the methane mass, so $3k_BT_{H_2}/2 \times (m'/m)$ is the required kinetic energy. That is $T = T_{H_2}m'/m = 8T_{H_2} = 2560$ K.

E1.4 [Mean quare velocity].
There is a gas of mass 19 g in a container of 21 liters. In equilibrium, its pressure is 1.1 atm. What is the root mean-square velocity of the molecules in the gas?

Solution.
Our starting point is the formula due to Bernoulli

$$PV = (2/3)N\langle K\rangle = (1/3)M\langle \boldsymbol{v}^2\rangle, \tag{2.27}$$

where M is the total mass of the gas. You must convert all the units into the ones in SI. 1 atm $= 1.013 \times 10^5$ Pa. Therefore,

$$\langle \boldsymbol{v}^2\rangle = \frac{3PV}{M} = \frac{3 \times 1.013 \times 10^5 \times 1.1 \times 21 \times 10^{-3}}{19 \times 10^{-3}} = 3.60 \times 10^5. \tag{2.28}$$

That is, $\sqrt{3.6 \times 10^5} = 600$ m/s. This is a realistic value.

Notice that even if a gas consists of a single particle of mass 19 g, we get the same equation of state if we interpret the (time) average of the force acting on the wall as PA. Our calculation does not tell us anything about atoms.

E1.5 [Equipartition related].
In a mixture ideal gas maintained at temperature T are two molecules, 1 of mass m and 2 of mass M ($> m$). The ratio between the mean square relative velocity of these two molecules and the mean square velocity of molecule 1 is 1.2. What is the mass ratio M/m?

Solution.
Let the velocity of molecule i be $\boldsymbol{v}_i$. The relative velocity is $\boldsymbol{w} = \boldsymbol{v}_1 - \boldsymbol{v}_2$. We wish to compute

$$\langle \boldsymbol{w}^2\rangle = \langle \boldsymbol{v}_1^2\rangle + \langle \boldsymbol{v}_2^2\rangle - 2\langle \boldsymbol{v}_1 \cdot \boldsymbol{v}_2\rangle. \tag{2.29}$$

Since two molecules are statistically independent, and since their mean velocities must be zero ($\langle \boldsymbol{v}_1 \cdot \boldsymbol{v}_2\rangle = \langle \boldsymbol{v}_1\rangle \cdot \langle \boldsymbol{v}_2\rangle = \boldsymbol{0} \cdot \boldsymbol{0} = 0$),

$$\langle \boldsymbol{w}^2\rangle = \langle \boldsymbol{v}_1^2\rangle + \langle \boldsymbol{v}_2^2\rangle. \tag{2.30}$$

Now, we use the equipartition of the translational kinetic energy

$$\frac{1}{2}m\langle \boldsymbol{v}_1^2\rangle = \frac{1}{2}M\langle \boldsymbol{v}_2^2\rangle = \frac{3}{2}k_BT. \tag{2.31}$$

Therefore,

$$\langle \boldsymbol{w}^2 \rangle = \frac{3}{m} k_B T + \frac{3}{M} k_B T. \tag{2.32}$$

Thus, the ratio is

$$\frac{\langle \boldsymbol{w}^2 \rangle}{\langle \boldsymbol{v}_1^2 \rangle} = \frac{(3/m)k_B T + (3/M)k_B T}{(3/m)k_B T} = \frac{m+M}{M} = 1.2. \tag{2.33}$$

Therefore, $M/m = 5$.

3 Introduction to Probability

Summary
∗ Probability is essentially the 'volume' of our confidence measured on the 0-1 scale. Probability must satisfy additivity.
∗ Gamble called survival race forces our subjective probability to be consistent with empirical probability.
∗ Understand how to describe events in terms of sets.

Key words
Probability, elementary event, sample space, event, conditional probability, (statistical) independent event, stochastic (random) variable, expectation value, variance, standard deviation, indicator, statistical independence of random variables

What you should be able to do[80]
∗ Be able to calculate expectation values and variances for simple cases.
∗ Understand $P(A) = \langle \chi_A \rangle$.
∗ There is an appendix on the elementary combinatorics at the end of the lecture. Be familiar with its content (esp., the binomial theorem and the multinomial theorem).

To go beyond Daniel Bernoulli, we need the idea of probability. When Maxwell was 19 years old, he read an article introducing the continental statistical theory into British science (e.g., Gauss's theory), and was really fascinated by it. He wrote to his friend: "the true logic for this world is the Calculus of Probabilities $\cdots$."[81]

Following is an introduction to *measure-theoretical probability theory*, although no formal introduction of measures will be discussed.[82] You can simply understand that 'measure' is a precise concept corresponding to volumes and weights.

[80] This summarizes what you should be able to do in practice. Most things required in this course are practical.
[81] Brush p59
[82] An introductory exposition of measure may be found in YO, *The Nonlinear World* (Springer, 2012) p66. Its electronic version can be downloaded, free of charge, from our library.

3.1 Probability is a measure of confidence level

Suppose we have a jar containing 5 white balls and 2 black balls. What is the degree C_w on the 0-1 scale of your confidence for you to pick a white ball out of the jar? We expect that, on the average, 5 times out of 7 we will take a white ball out. Hence, it is sensible to say that our confidence in the above statement is 5/7 on the 0-1 scale; $C_w = 5/7$.

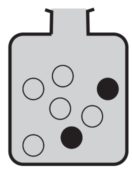


Figure 3.1: Take out one ball without looking in the jar with replacement. 'How much' are you sure you get a white ball?

Suppose you can obtain a dollar if you pick a white ball out, but otherwise must pay X dollars. Whether you wish to participate in this gamble or not depends on X. What is the wise choice? With our confidence C_w it is sensible to assume that we may estimate the expected gain (in the long run) as:

$$E_M = C_w - (1 - C_w)X. \tag{3.1}$$

If E_M is non-negative, i.e., if $X \le C_w/(1-C_w)$, then we may play this gamble. Since you are free to have any idea or belief, you may freely assume C_w to be any number between 0 and 1. However, there is no freedom of action, if you wish to stay happily in this world. C_w must be realistic. For our jar game $C_w = 5/7$ is demanded. We will soon learn why; we can check whether your confidence level is rational or not empirically by repeating the gamble.

3.2 What if events are not repeatable?

However, probability seems to show up even in cases where we cannot repeat events. How can we check our confidence level is rational or not? For example, the meaning of the statement that the precipitation probability tomorrow is 70 % is that we should have a confidence level of 0.7 in raining tomorrow (if you bet money on weather, you'd better use this confidence estimate). However, we cannot repeat 'tomorrow,' so how can we check that the choice is good? In practice, the extent of confidence is estimated relying on the past experiences of similar events.[83]

[83] Why does the estimated confidence level often match reality? It is thanks to the totality of our 4 billion year experiences (this is called phylogenetic learning that relies on the stability or even benevolence (recall **1.14**) of our world). Even if an event does not seem to be repeatable,

3.3 Events and sets

To make mathematical theory of probability, we must express events (= what can happen) as sets.

An event which cannot be analyzed further, or need not be analyzed further for our purpose, is called an *elementary event*. Elementary events need not be atomic events that cannot be dissected further into more basic events. For example, when we cast a dice, usually we regard a particular face, 1, 2, 3, 4, 5, or 6, to be up as an elementary event. However, if we pay attention only to the even-odd properties of the numbers, the elementary events could be even and odd only. On the other hand, if you wish to use the direction of the edges or locations of the dice as well as the faces, then 1, $\cdots$, 6 are no more elementary events. In statistical mechanics, elementary events are mechanical events that are not dissected further in mechanics.

Denote by Ω the totality of elementary events (called the *sample space*) allowed in the situation or to the system under study. Any (compound) *event* under consideration can be identified with a subset of Ω (Fig. 3.2).

When we say an event corresponding to a subset A of Ω *occurs*, we mean that one of the elements (= elementary events) in A actually occurs.

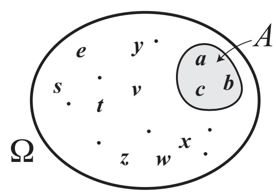


Figure 3.2: In this illustration the sample space is $\Omega = \{a, b, c, \cdots, x, y, z\}$, where letters denote elementary events; one of the elementary events is what actually happens (or what is actually sampled). Event $A = \{a, b, c\}$ is said to occur, if a, b or c actually happens.

3.4 Venn diagrams and events

Events are illustrated conveniently with the aid of the Venn diagrams (Fig. 3.3).[84]

3.5 Probability is in $[0, 1]$

sufficiently many very similar events happened in the past. "What has been is what will be, and what has been done is what will be done; there is nothing new under the sun." (Eccles. 1-9) We have been selected to be able to use the result of phylogenetic learning.

[84]due to John Venn (1834-1923) around 1860. who was a logician and a proponent of frequentist interpretation of probability.

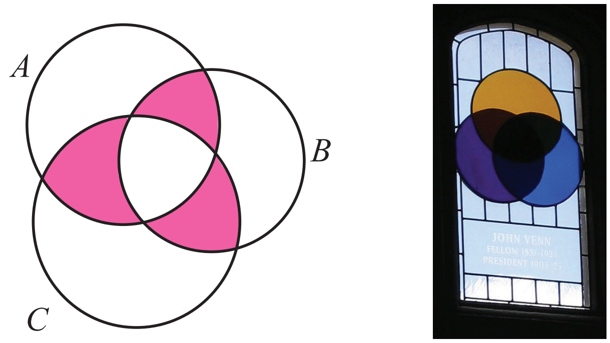


Figure 3.3: The Venn diagram conveniently illustrates compound events. **Left**: The colored portion denotes events in which only two events among A, B and C occur. **Right** Stained glass window at Gonville and Caius College, Cambridge, commemorating Venn and the Venn diagram. (From Wikipedia, 'John Venn.').

Let us denote the *probability* of $A \subset \Omega$ by $P(A)$. Since probability should measure the degree of our confidence on a 0-1 scale, we demand that

$$P(\Omega) = 1; \tag{3.2}$$

something must happen. Then, it is also sensible to assume

$$P(\emptyset) = 0; \tag{3.3}$$

the event that nothing happens never happens, because something surely happens.

3.6 Probability is additive for mutually exclusive events

Consider two *mutually exclusive events*, A and B. That is, when A occurs, B never occurs, and vice versa. Event A happens implies that one of the elementary events in A actually occurs (recall **3.3**). Since A and B never occur simultaneously, no elementary event in A should be in B (and vice versa). Hence, the mutual exclusiveness of events A and B means

$$A \cap B = \emptyset. \tag{3.4}$$

It is sensible to demand

$$P(A \cup B) = P(A) + P(B), \quad \text{if } A \cap B = \emptyset. \tag{3.5}$$

This is the *additivity* of probability.

For example, for a dice the probability (or your confidence) for face 1 is 0.15 and probability for face 2 or 3 is 0.4 (needless to say, this dice is not fair or you believe it is not fair), the probability to observe faces with values not more than 3 should be $0.15 + 0.4 + 0.4 = 0.95$.

As an example, let us consider a series of experiments tossing a coin three times.

There are eight possible outcomes corresponding to the combination of three H and T, so the sample space is

$$\Omega = \{\text{HHH, HHT, HTH, THH, HTT, THT, TTH, TTT}\}. \tag{3.6}$$

The word "fair" means that all elementary events are equally likely. Or, it means that we may live without any particular penalty even if we have the same confidence levels 1/8 for the occurrence of any elementary event. However, if one firmly believes that the world is created for H to continue, his confidence level in the occurrence of HHH may be 0.5, and HHT or THH may be 0.2, respectively. Even for such a person the totality of probability must be 1, and the probability for H not to continue must be $1 - 0.5 - 2 \times 0.2 = 0.1$.

The event A that at least two H appear is $A = \{\text{HHH, HHT, HTH, THH}\}$. Since all the elementary events are mutually exclusive, $P(A) = 1/2$ for a person who believes that the coin is fair, but it is obviously larger than 0.9 for the person with a peculiar H belief. The difference between these two confidence levels is so large that very quickly we can check (experimentally) which is realistic.

3.7 Probability is a measure with total measure unity

We know other quantities for which additivity (3.5) holds; length, area, volume, mass (if discrete, number), etc. Thus, we see that the probability measuring the amount of our confidence should be something like volume.

A function that assigns numbers to sets (or a map from sets to numbers) is called a *set function*.

Roughly speaking, an additive non-negative set function is called a measure. Above examples such as area, volume, etc., are mathematically refined as measures. If a measure whose value on the total set is normalized to unity, it is called a probability (or a probability measure)

Suppose a shape is drawn in a square of area 1 (a unit square) (Fig. 3.4). If we pepper it with points uniformly, then the probability = our confidence level of a point to land on the shape should be proportional to its area.[85] Thus, again it is intuitively plausible that probability and area or volume are closely related.

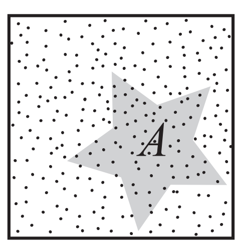


Figure 3.4: Peppering the unit square evenly with points, we can estimate the area of A.

[85] This has a practical consequence. See **4.9**.

3.8 What is probability theory?

If an event is given, a certain confidence level in the occurrence of this event may be expressed as a certain probability measure. Whether the confidence level is useful/rational or not is not a concern of probability theory.

Probability theory is interested in the conclusions we can deduce from the conditions any confidence belief encoded in P must satisfy:
(i) $P \in [0, 1]$,
(ii) P is additive in the sense of **3.6**.
In other words, P is a normalized measure (see **3.7**).

3.9 Relation to combinatorics

As can be seen from the example in **3.6** (especially from the calculation of the confidence levels for the one who believe the coin is fair), in many elementary cases, to count the number of cases satisfying a certain condition is the technical core of probability calculation. However, it is just a technical detail, and is not a crucial part of probability theory. Still, we should be able to do practical calculations, so elementary combinatorics is outlined in Appendix 3A.

3.10 Objectivity of subjective probability

Since probability is introduced as the confidence level, you might have thought that probability is only subjective. Indeed, in the sense that probability theory is indifferent to whether a particular probability (or confidence level) assignment is useful or not to live in this world, probability may be subjective and not objective. Then, such a subjective concept should not be relevant to objective science such as physics. However, our subjective feeling (emotion underlying decisions) has been molded by natural selection during the past 4 billion years, so our subjective probability estimates (confidence levels) are very often consistent with objective probability.[86]

Probabilities appearing in physics should be objective. If we say they are objective, there must be a means to measure them. To this end, we must learn elementary probability theory a bit further.

3.11 'Subadditivity' of probability

[86]Even other animals have considerable capability of estimating probabilities; they are free from strange religious beliefs, so their capability could be better than ours when our minds are clouded by strange beliefs.

From the additivity of probability (see **3.6**), we can get

$$P(A \cup B) = P(A) + P(B) - P(A \cap B). \tag{3.7}$$

This implies

$$P(A \cup B) \le P(A) + P(B). \tag{3.8}$$

This is the subadditivity of probabiulity.

If $A \subset B$, then $B = A \cap (B \setminus A)$,[87] so we conclude

$$A \subset B \Rightarrow P(A) \le P(B). \tag{3.9}$$

Denoting $\Omega \setminus A$ by A^c (complement), we get

$$P(A^c) = 1 - P(A). \tag{3.10}$$

Exercise. Show, if $P(A) = 1$, then $P(A \cap B) = P(B)$.
[Obvious! It is important to feel that this is obviously true, but you should be able to give a logical proof as well. Notice that $P(B) = P(A \cap B) + P(A^c \cap B)$. From (3.9) $P(A^c \cap B) \le P(A^c) = 0$, so $P(B) = P(A \cap B)$.]

3.12 Conditional probability

Suppose we know for sure that event B has occurred. Under this condition what is the probability of the occurrence of event A? Thus we need the concept of *conditional probability*. We write this conditional probability as $P(A|B)$, and define it as

$$P(A|B) = \frac{P(A \cap B)}{P(B)}, \tag{3.11}$$

so that $P(B \,|\, B) = 1$ should hold.

3.13 Statistical independence

When the occurrence of event A does not tell us anything about event B and vice versa, we say two events A and B are (statistically) independent. Do not confuse 'independent events' and 'mutually exclusive events.' Since knowing about event B does not help us to obtain more information about event A if A and B are independent, we should get

$$P(A|B) = P(A), \tag{3.12}$$

where $P(A \,|\, B)$ is the conditional probability just introduced in **3.12**. Therefore, the following formula must be an appropriate definition of *independence* of events A and B:

$$P(A \cap B) = P(A) \cdot P(B). \tag{3.13}$$

[87] ⟪**Setminus**⟫ 'Setminus' $\setminus$ denotes 'subtraction' as $A \setminus B = A \cap B^c$.

For example, when we use two fair dice 'a' and 'b' and ask the probability for 'a' to exhibit a number less than or equal to 2 (event A), and 'b' a number larger than 3 (event B), we have only to know the probability for each event $A = \{1_a, 2_a\}$ and $B = \{4_b, 5_b, 6_b\}$, where n_x denotes the elementary event that dice x gives face n. Thus, the answer is $P(A \cap B) = P(A) \cdot P(B) = 1/3 \cdot 1/2 = 1/6$ for fair dice.

3.14 Stochastic variables

You must have heard of 'stochastic processes.' A stochastic process is a process in which a 'stochastic variable' or 'random variable' takes various values as a function of time. Then, what is a 'stochastic variable' or 'random variable'?

Let Ω be a sample space and a probability P is given on it.[88] Then, a function (map) from Ω to some mathematical entity (real numbers, vectors, etc.) is called a *stochastic variable* or *random variable*.

Let $\Omega = \{\omega_i\}$. A real-valued stochastic variable F is a map $F : \Omega \to \mathbb{R}$. It is rational to write the probability for this stochastic variable to take a particular value f as

$$\mathrm{Prob}\,(F = f) = P(\{\omega \,|\, F(\omega) = f\}) = P(F^{-1}(f)). \tag{3.14}$$

Since $F^{-1}(f)$ is the totality of the elementary events ω such that $F(\omega) = f$, summing all the probabilities for these elementary events should be the probability of the set $F^{-1}(f)$ = 'event such that $F = f$' (see Fig. 3.5). Therefore, the above definition is very reasonable.

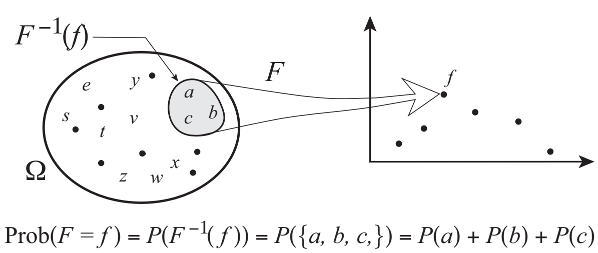


Figure 3.5: The probability for a stochastic variable F to assume a particular value f

For example, suppose you cast a dice ($\Omega = \{1, 2, 3, 4, 5, 6\}$), and you obtain \$1 if the face is odd; otherwise, you must pay \$1. Then, your gain F is a random variable $F : \Omega \to \{-1, +1\}$ such that $F^{-1}(-1) = \{2, 4, 6\}$ and $F^{-1}(+1) = \{1, 3, 5\}$. Therefore, $\mathrm{Prob}\,(F = +1) = P(\{1, 3, 5\})$ and $\mathrm{Prob}\,(F = -1) = P(\{2, 4, 6\})$.

[88] Here, that P is given on Ω implies that the value of P is given for all the elementary events in Ω (if Ω is discrete; if it is continuous, then P must be defined on an appropriate family of subsets of Ω). (Ω, P) is called a *probability space*. If you read a respectable probability book, you will encounter something like $(\Omega, \mathcal{B}, P)$, where $\mathcal{B}$ is a family of 'measurable sets.' We will not discuss this in these notes. (Not all the events should have probabilities to avoid something like $1 + 1 = 3$, so we must specify what events can have probabilities. This is the role of $\mathcal{B}$.)

In short, if we write the probability for a stochastic variable F to assume a value f as $P_F(f)$, then

$$P_F(f) = P(F^{-1}(f)). \tag{3.15}$$

3.15 Expectation values

The *expectation value* (= average) of F is written as (if one wishes to express the underlying probability P explicitly) $E_P(F)$ or $\langle F\rangle_P$ and is defined by

$$E_P(F) \equiv \langle F\rangle_P \equiv \sum_{\omega\in\Omega} P(\omega)F(\omega) = \sum_f P_F(f)f. \tag{3.16}$$

Often the suffix P is omitted. The last equality can be checked by a straightforward calculation (also see Fig. 3.5 above). Let us denote the event $F = f$ as $ev(F = f) = \{\omega \,|\, F(\omega) = f)\}$:

$$\begin{aligned}\sum_{\omega\in\Omega} P(\omega)F(\omega) &= \sum_f \left(\sum_{\omega\in ev(F=f)} P(\omega)F(\omega)\right) = \sum_f \left(\sum_{\omega\in ev(F=f)} P(\omega)f\right) \\ &= \sum_f \left(\sum_{\omega\in ev(F=f)} P(\omega)\right) f = \sum_f P(ev(F=f))f = \sum_f P_F(f)f.\end{aligned} \tag{3.17}$$

At the last step the definition of P_F was used.

The sum becomes integration when we study events which are specified by a continuous parameter. In this case,

$$E_P(F) \equiv \langle F\rangle_P \equiv \int_{\omega\in\Omega} F(\omega)P(d\omega) = \int_{\omega\in\Omega} F(\omega)dP(\omega), \tag{3.18}$$

where $P(d\omega)$ is the probability of the volume element $d\omega$; often $P(d\omega)$ is written as $dP(\omega)$. You may simply interpret this integral just as the Riemann integral.

3.16 Expectation value operator

E may be understood as an operator.[89] Let f and g be stochastic variables, and a and b real numbers. Then, we have the following equality

$$E(af + bg) = aE(f) + bE(g). \tag{3.19}$$

[89]'Operator' is a map that maps a function to another function or number. For example, the differential operator d/dx maps a differentiable function f to its derivative f' and is a linear operator.

That is, the expectation value of a linear combination is a linear combination of expectation values. An operator with this property is called a *linear operator*. The expectation value operator E is a linear operator.

3.17 Variance

We are also interested in the 'spread' of the variables. Its good measure is the *variance* of X defined as

$$V(X) = E([X - E(X)]^2) = E(X^2) - E(X)^2. \tag{3.20}$$

Its square root $\sigma(X) = \sqrt{V(X)}$ is called the *standard deviation* of X.

3.18 Indicator

The *indicator*s χ_A of a set (= event in our context) A is defined by

$$\chi_A(\omega) \equiv \begin{cases} 1 & \text{if } \omega \in A, \\ 0 & \text{if } \omega \notin A. \end{cases} \tag{3.21}$$

This indicates the answer 'yes' or 'no' to the question: is an elementary event ω in A? $\chi_A = 1$, if A happens.

Notice that (apply (3.16) straightforwardly)

$$\langle \chi_A \rangle_P = \sum_{\omega} \chi_A(\omega) P(\omega) = \sum_{\omega \in A} P(\omega) = P(A). \tag{3.22}$$

This is a very important relation for the computation of probabilities.

3.19 Random variable in terms of indicators

A random variable (= stochastic variable) is a function $X(\omega)$ ($\omega \in \Omega$) defined on Ω. If we denote the event $X = x$ as $ev(X = x) = \{\omega \,|\, X(\omega) = x\}$, then X defined on Ω may be written as

$$X(\omega) = \sum_x x \chi_{ev(X=x)}(\omega). \tag{3.23}$$

(3.16) follows from this and (3.22):

$$\langle X(\omega) \rangle = \sum_x x \langle \chi_{ev(X=x)}(\omega) \rangle = \sum_x x P_X(x), \tag{3.24}$$

where $P_X(x)$ is the probability for X to be x. Here, we have used the fact that the expectation value operator $\langle \; \rangle$ is a linear operator and a similar calculation as (3.17):

$$\langle \chi_{ev(X=x)}(\omega) \rangle = \sum_{\omega \in \Omega} \chi_{ev(X=x)}(\omega) P(\omega) = P(ev(X = x)) = P_X(x) \tag{3.25}$$

3.20 Independence of stochastic variables

How should we define 'independence' (*statistical independence*) of two stochastic variables X_1 and X_2? A reasonable answer is that

$$E(F(X_1)G(X_2)) = E(F(X_1))E(G(X_2)) \tag{3.26}$$

holds for any functions[90] F and G of the stochastic variables. In particular, if stochastic variables X_1 and X_2 are independent,

$$E(X_1X_2) = E(X_1)E(X_2). \tag{3.27}$$

If random variables X and Y are independent, then

$$V(X+Y) = V(X) + V(Y). \tag{3.28}$$

3.21 Covariance

If you have two random variables, you might wish to know their relations. For two stochastic variables X and Y

$$C(X,Y) = E([X - E(X)][Y - E(Y)]) = E(XY) - E(X)E(Y) \tag{3.29}$$

is called the *covariance* between X and Y, which shows up often when we wish to study fluctuations.

If X and Y are statistically independent variables, then $C(X,Y) = 0$, but the converse is not true. Let $Y = \pm X$, where $\pm$ is randomly chosen by coin-tossing. Then, $C(X,Y) = 0$, but we always have $X^2 = Y^2$, so they cannot be statistically independent; they violate the definition of statistical independence, and also intuitively we cannot say X and Y are unrelated.

[90]'Any functions' here means 'any (Lebesgue) integrable functions.'

Appendix 3A: Rudiments of combinatorics[91]

As noted above, often evaluation of elementary probabilities boils down to counting the number of ways to arrange objects. In statistical mechanics we must be able to count the number of elementary events (i.e., microscopic events) under various constraints. How to count is the main topic of combinatorics.

Sequential arrangement (without repetition) of r objects from n distinguishable objects: ${}_n P_r$

Suppose there is a set of n distinguishable objects. How many ways are there to make sequential arrangements of r objects taken from this set (without repetition)? This number is denoted by ${}_nP_r \equiv P(n,r)$.

There are two ways to get an explicit formula for this number:
(i) There are n ways in selecting the first object. To choose the second object, there are $(n-1)$ ways, because we have already taken out the first one. Here, the distinguishability of each object is crucial. In this way we arrive at

$$P(n,r) = n \cdot (n-1) \cdots (n-r+1) = \frac{n!}{(n-r)!}, \tag{3.30}$$

where $n! = 1 \cdot 2 \cdot 3 \cdots (n-1) \cdot n$; n factorial is the number of ways n distinguishable objects can be arranged in a sequence. The following symbol is also often used:

$$(n)_r \equiv n \cdot (n-1) \cdots (n-r+1). \tag{3.31}$$

(ii) The other derivation is an interpretation of the rightmost formula in (3.30). We can imagine distinguishable objects as monomers and try to make a polymer of length n from these monomers. There are total $n!$ different configurations (different polymers). Now, let us classify these polymers according to the first r monomer arrangements. How many different polymers with a given first r subpolymer? There are $(n-r)!$ ways to complete this subpolymer into a full length n polymer. Therefore, if we classify length n polymers according to the initial r monomer configuration, there are $n!/(n-r)!$ kinds.

Also from the logic in (i), we know that the number of ways to arrange r objects taken from n distinguishable objects with repetition allowed is n^r. We can show $(n)_r/n^r \to 1$, if n becomes large with fixed r. That is, asymptotically the samplings with and without replacement are the same (as intuitively expected).

Selection of r objects from n distinguishable objects: binomial coefficient, ${}_nC_r$

[91] W. Feller, *An Introduction to Probability Theory and Its Applications* (Wiley, 1957) volume 1, Chapter II is a useful reference.

Under the same distinguishability condition, we now disregard the order in the arrangement of r objects. That is, we wish to answer the question: how many different subsets can we make, if we choose r elements without repetition from a set consisting of n distinguishable elements?

Since we disregard the ordering in each arrangement of r distinguishable objects, the answer should be

$$ {}_nC_r \equiv \binom{n}{r} \equiv \frac{{}_nP_r}{r!} = \frac{n!}{(n-r)!r!}. \tag{3.32} $$

The number $\binom{n}{r}$ is called the *binomial coefficient* due to a reason clear from (3.35) below.

Exercise 1. Show the following equalities and give combinatorial explanations:

$$ {}_nP_r = \left(\begin{array}{c} n \\ r \end{array} \right) \cdot {}_rP_r, \tag{3.33} $$

$$ \left(\begin{array}{c} n \\ r \end{array} \right) = \left(\begin{array}{c} n-1 \\ r-1 \end{array} \right) + \left(\begin{array}{c} n-1 \\ r \end{array} \right). \tag{3.34} $$

$\square$

Binomial theorem

Consider the n-th power of $x + y$. There exists an expansion formula called the *binomial expansion*:

$$ (x+y)^n = \sum_{r=0}^{n} \binom{n}{r} x^{n-r} y^r. \tag{3.35} $$

This can be seen easily as follows: We wish to expand the product of n $(x + y)$:

$$ \overbrace{(x+y)(x+y)(x+y)\cdots(x+y)\cdots(x+y)}^{n}. \tag{3.36} $$

As an example take the term x^2y^{n-2}. To produce this term by expanding the above product, we must choose 2 x's from n $(x + y)$. There are $\binom{n}{2}$ ways to do this, so the coefficient must be $\binom{n}{2}$.

Multinomial coefficient

Suppose there are k species of particles. There are q_i particles for the i-th species. We assume that the particles of the same species are not distinguishable. The total number of particles is $n \equiv \sum_{i=1}^{k} q_i$. How many ways are there to arrange these particles in one dimensional array?

If we assume that all the particles are distinguishable, the answer is $n!$. However, the particles of the same species cannot be distinguished, so we need not worry which i-th particle is chosen first. Hence, we have over-counted the number of ways by the factor $q_i!$ for the i-th species. The same should hold for all species. Thus we arrive at

$$\frac{n!}{q_1!q_2!\cdots q_{k-1}!q_k!}. \tag{3.37}$$

This is called the *multinomial coefficient*.

Multinomial theorem

There is a generalization of (3.35) to the case of more than two variables and is called the *multinomial expansion*:

$$(x_1 + x_2 + x_3 + \cdots + x_m)^n = \sum_{q_1+q_2+\cdots+q_m=n,\, q_i\geq 0} \frac{n!}{q_1!q_2!\cdots q_m!} x_1^{q_1} x_2^{q_2} \cdots x_m^{q_m}, \tag{3.38}$$

whose demonstration is very similar to that explained around (3.36).

Arrangement of indistinguishable objects into distinguishable boxes

Consider n indistinguishable objects. We wish to distribute them into r distinguishable boxes. How many distinguishable arrangements can we make?

Since the boxes are distinguishable, we arrange them in a fixed sequence, and then distribute the indistinguishable objects (Fig. 3.6).

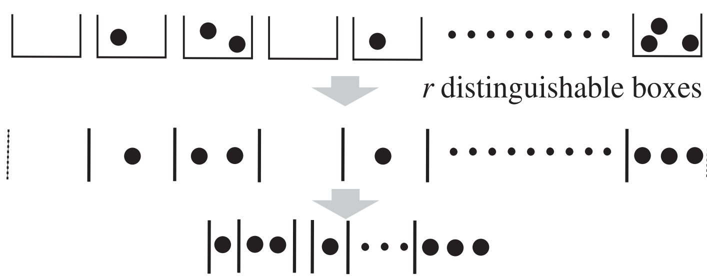


Figure 3.6: Indistinguishable objects

Hence, the problem is equivalent to counting the number of arrangements of n indistinguishable balls and $r-1$ indistinguishable bars on a line (Fig. 3.6 bottom). Apply (3.37) to obtain the answer:

$$\frac{(n+r-1)!}{n!(r-1)!} = \binom{n+r-1}{n}. \tag{3.39}$$

How about the arrangement of the distinguishable n into r distinguishable boxes? The first particle can be put into one of r boxes. Then, the second, etc. Thus, there are r^n ways.

There are two more conceivable cases:

(i) How about the arrangement of n distinguishable particles into r indistinguishable boxes?
(ii) How about the arrangement of n indistinguishable particles into r indistinguishable boxes? [This is not easy. This is related to the decomposition of n into r positive integers = *integer partition problem*. http://en.wikipedia.org/wiki/Partition_(number_theory)]
Exercise 2. How many ways are there to distribute n distinguishable balls into n distinguishable boxes?
Exercise 3. How many ways to distribute n distinguishable balls into n distinguishable boxes with exactly one box left empty? [$\binom{n}{2}n!$]
Exercise 4. There are 4 workers who produced total 4 defective products. What is the probability of a particular person produced 3 defective products? Assume all the workers are equally skilled.

Derangement
A *derangement* is a permutation of the elements of a set such that none of the elements appear in their original position [http://en.wikipedia.org/wiki/Derangement]. Let D_n be the number of derangements of n (distinguishable) objects. Then,

$$D_n = (n-1)D_{n-1} + (n-1)D_{n-2} \tag{3.40}$$

for $n \geq 3$. Note that $D_1 = 0$, $D_2 = 1$. This gives

$$\frac{1}{n!}D_n = \sum_{k=2}^{n}(-1)^k \frac{1}{k!} = \frac{1}{2!} - \frac{1}{3!} + \frac{1}{4!} - \cdots + (-1)^n \frac{1}{n!}. \tag{3.41}$$

This converges to $1/e$ in the large n limit.

Q3-1. [Fun problems]
(1) Which probability is larger, (a) or (b), assuming the 6-sided dice are fair?
(a) At least one '1' face appears in one throw of 4 dice.
(b) Two '1' faces appear simultaneously at least once in 25 throws of two dice.

(2) There are two kittens. You are told that at least one of them is a male. What is the probability that the two kittens are both males? What is the probability that one kitten is a female? (Assume that the sex ratio of kittens is 1 to 1.)

(3) There are 5 boxes A-E of which one contains a prize of \$1000. You are asked to choose one box. After you choose one of the five boxes, the 'coordinator' of the gamble opens 3 of the remaining boxes which are all empty. Then, he tells you that if you pay \$250 you may switch your choice. What is a good choice for you (assuming that you wish to get more money), and your expected gain?
Soln.
(1)
(a) The complement of the event 'at least one' is 'none.' That is, if we compute the probability p for the event that no '1' face appears in one throw of 4 dice, $1-p$ must be the answer ($P(A) = 1 - P(A^c)$). This is $1 - (5/6)^4 = 0.5177$.

(b) This is very similar to (a). The probability p of the complement (no simultaneous '1' is $(35/36)^{25}$). Therefore, $1 - (35/36)^{25} = 0.5055$. Thus, (a) is slightly more likely.

The French nobleman and gambler Chevalier de Méré suspected (purely empirically, of course) that (a) was higher than (b) with 24 throws (in this case the probability is 0.4914; about 5% difference) instead of 25, but his mathematical skill was not great enough to demonstrate why this should be so. He posed the question to Pascal, who solved the problem and proved de Méré correct.[92] We did better: even if we throw 25 times, still (a) is more likely.

(2) For two kittens (you must recognize kittens can be distinguished), there are 4 different sex combinations: mm, mf, fm, ff. You know one of three occurred: mm, mf or fm, since one is male. These three cases occur with equal probability. Therefore, with 1/3 of the probability the other is male.

(3) If you do not switch your choice, obviously your expected gain will be $\$200 = 1000 \times (1/5)$.
The remaining 4 boxes contain the prize with probability 4/5. After the coordinator opens 3 empty boxes, this probability is 'concentrated in' the remaining box. Therefore, if you switch your choice, then your expected gain would be \$800. Thus, definitely you should pay \$250 and switch!

In this case, the new information changes the condition, under which you should reconsider your 'confidence level.'

The above solution assumes (as usual in this type of questions) that the coordi-

[92] basically from Wikipedia.

nator knows where the prize is. What if the coordinator does not know where the prize is? Or you can imagine a wind opens three boxes, and they happen to be all empty. In this case, what is your choice? An elementary answer is as follows: (1) If you choose the prize-containing boxes, there are $\binom{4}{3}$ ways to open three boxes. (2) If you choose the empty box, then there is only one way to choose three empty boxes from the remaining 4 boxes. There are 4 ways for you to choose an empty box. That is, both are equally probable. Thus, you should not switch the box.

Suppose you are told that your choice does not contain the prize, but then told that if you pay \$300, you may choose a new box. Will you pay this price?

It may be fun to read: J. Rosenhouse, *The Monty Hall Problem* (Oxford, 2009).

Q3-2. There were 400 students in an exam. A professor was interested in who were cheating in the exam, so he watched out for rare agreements of wrong solutions. He found a pair whose errors agreed exactly, and he could calculate that the probability of this agreement was at most 10^{-5}. Therefore, he accused the pair of cheating. Is his decision rational?

Soln.
The number of pairs is $\binom{400}{2} = 200 \times 399 = 79800 \simeq 80000$, so on the average we always find at least 0.8 rare-agreement pair. What does this mean? Without any ill intention, on the average almost one pair will be accused! Therefore, his decision is irrational.

When there are numerous (statistically independent) samples simultaneously as in most problems of bioinformatics (say, ca. 20,000 genes for us), we must be very careful about false positives. There are many ways to cope with this problem, but the simplest is the Bonferroni correction. Look this up.

4 Law of large numbers

Summary
∗ The law of large numbers allows us to measure probability.
∗ We can use the law of large numbers to estimate integrals. Recognize the power of randomness.

Key words
Chebyshev's inequality, law of large numbers

What you should be able to do
∗ You must be able to use the law of large numbers to estimate how many samples you need to determine the empirical average with a prescribed error tolerance level.

4.1 How can we measure probability?

Let us return to the problem in Fig. 3.4. Suppose χ_A is the indicator of the area A in the unit square. We pepper dots on it evenly. If the ith dot (location x_i) is on A, $\chi_A(x_i) = 1$, otherwise, 0. If we count the number N_1 of points for which $\chi_A = 1$ in the total trial with N dots, N_1/N should be close to the area, which is the probability P for the dot to land on A. We expect

$$\frac{1}{N}\sum_{i=1}^{N}\chi_A(x_i) \to E(\chi_A) = P(A) \tag{4.1}$$

in the large N limit. This can be verified by the most important theorem of probability theory: the *law of large numbers*.

The most important message above is that probabilities of events may be observed experimentally. Although we introduced probability $P(A)$ as a measure of our (subjective) confidence in the occurrence of event A, whether the probability is realistic or not can be determined empirically in many cases. Do not forget that our intuition/emotional judgement is based on our nervous systems, which have been subjected to rigorous selection processes in the past 1 billion years. Thus, inevitably, our subjective judgements tend to be consistent with the objective world.

4.2 Bernoulli recognized the law of large numbers for coin tossing

For a fair coin let X_n be the indicator of head (i.e., $X_n = 1$ if the outcome of the nth tossing is a head, otherwise, 0) for the n-th tossing of the coin. Then, we expect

$$\frac{1}{N}\sum_{n=1}^{N} X_n \to \frac{1}{2}. \tag{4.2}$$

Jakob Bernoulli (1654-1705) proved this (Fig. 4.1).[93]

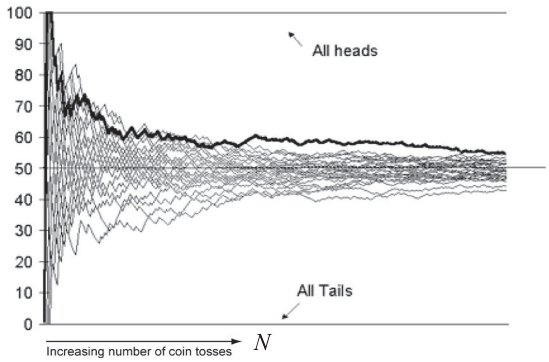


Figure 4.1: Left: The law of large numbers illustrated: the percentage of H in N trials [from http://www.mathaholic.com/?tag=law-of-large-numbers. This article, 'Why casinos don't lose money," is recommended.]. Right: Jacob Bernoulli (1654-1705) proved the law of large numbers (published posthumously in 1713) [Swiss stamp in 1994, courtesy of Professor M. Börgens of Technische Hochschule Mittelhessen].

The following URL illustrates the law of large numbers:
http://demonstrations.wolfram.com/IllustratingTheLawOfLargeNumbers/
You will realize that convergence is not very fast.

4.3 Precise statement of law of large numbers

A precise statement of the law of large numbers (LLN) is as follows:
Let $\{X_i\}$ be a collection of independently and identically distributed (often abbreviated as *iid*) stochastic variables. For any $\varepsilon > 0$,

$$\lim_{N\to\infty} P\left(\left|\frac{1}{N}\sum_{n=1}^{N} X_n - E(X_1)\right| > \varepsilon\right) = 0 \tag{4.3}$$

holds under the condition that the distribution of X_i is not too broad: $E(|X_1|) < \infty$. If $V(X_1) < +\infty$, the condition is satisfied.[94] In the following, the law of large numbers is demonstrated under this assumption.

The interpretation of (4.3) is as follows: We make a single run consisting of N

[93]published posthumously in *Art Conjectandi* (1713). e was introduced by him as well.

[94]Since all X_n are distributed identically, we use X_1 as a representative, so $E(|X_1|)$, etc., show up in the statement.

repetitions of sampling or trials. We can make the empirical average from this run $\{x_i\}_{i=1}^N$ as $\sum_{i=1}^N x_i/N$. The probability for this empirical expectation value to be more than ε away from the true expectation value is given by the probability in (4.3) before taking the $N \to \infty$ limit. If this probability is 0.01 for a certain finite N, it means that if you make numerous runs each consisting of N trials, you will encounter the empirical expectation value deviating larger than ε from the true expectation once in 100 runs on the average.

4.4 Another expression of law of large numbers

The following is also a precise expression:[95]

$$\sum_{n=1}^{N} X_n = NE(X_1) + o[N]. \tag{4.4}$$

The interpretation of (4.3) is as follows: we perform a series of N experiments to produce the *empirical expectation value*)$(1/N)\sum_{n=1}^N x_n$. This set of N experiments is understood as a single 'run,' and we imagine many such runs. Then, (4.3) tells us that the probability that these runs produce empirical averages S_N/N deviating from the true mean $E(X_1)$ by more than (any positive number) ε goes to zero in the limit of the infinite run length.

Remark: Suppose you find an empirical average S_N/N larger than $E(X_1)$. Then, you might expect more outcomes smaller than $E(X_1)$ in the near future. This is the famous *gambler's fallacy* (or fallacy of the maturity of chances). See `http://en.wikipedia.org/wiki/Gambler's_fallacy`, especially, psychology behind the fallacy. □

4.5 Why is the law of large numbers plausible?

Before going to a rigorous demonstration of LLN, let us understand why it is plausible. We could expect that the average of S_N/N (the empirical average) should fluctuate around $E(X_1)$. Its width of fluctuation must be evaluated by the variance: (notice that $V(cX) = c^2V(X)$ and 'additivity' (3.28) in the following calculation)

$$V\left(\frac{1}{N}\sum_{n=1}^{N} X_n\right) = \frac{1}{N^2}V\left(\sum_{n=1}^{N} X_n\right) = \frac{1}{N^2}\sum_{n=1}^{N} V(X_n) = \frac{1}{N}V(X_1). \tag{4.5}$$

Thus, the width of the distribution shrinks as N is increased. That is why S_N/N clusters tightly around $E(X_1)$ as $N \to \infty$. This is the essence of LLN. This is illus-

[95] Note for the instructor: (4.3) and this (if properly stated as an almost sure convergence) are different; the former is called the weak law of large numbers and the latter the strong law of large numbers. However, in many realistic situations we encounter in statistical mechanics, whenever the weak law holds, so does the strong law.

trated in:
http://demonstrations.wolfram.com/ChebyshevsInequalityAndTheWeakLawOfLargeNumbersForIidTwoVect/

4.6 Chebyshev's inequality

The key to an honest proof of LLN is *Chebyshev's inequality*[96]

$$a^2 P(|X - E(X)| \geq a) \leq V(X). \tag{4.6}$$

This can be shown as follows (let us redefine X by shifting as $X - E(X)$ to get rid of $E(X)$ from the calculation).[97] Fig. 4.2 illustrates the demonstration.
:

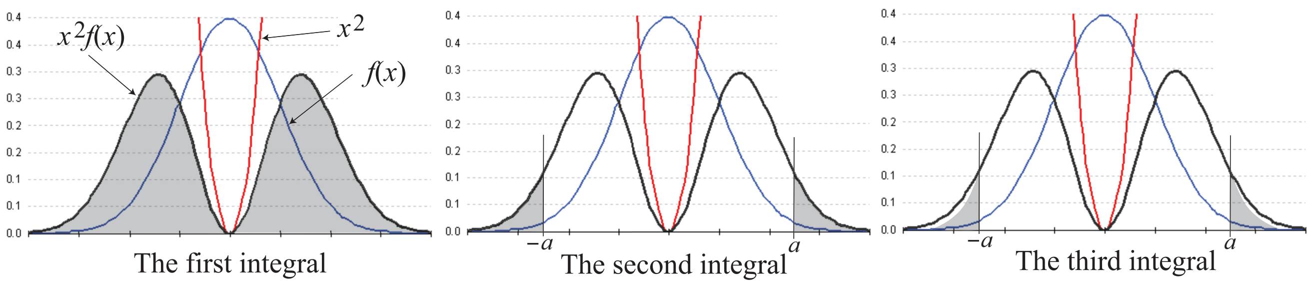


Figure 4.2: (4.9) illustrated. If we introduce the density distribution function f, (4.9) reads $V(X) = \int X^2 f(X)\,dX \geq \int_{|X|\geq a} X^2 f(X)\,dX \geq a^2 \int_{|X|\geq a} f(X)\,dX = a^2 P(|X| \geq a)$. The integrals appearing in this formula are shaded areas. The inequalities are apparent from the figures.

We start from the definition of the variance:

$$V(X) = \int X^2 dP(\omega). \tag{4.7}$$

Here, the integration range is over all values of X. Now, let us remove the range $|X| < a$ from this integration range. The contribution of the removed portion to the original integrand is positive, so obviously

$$V(X) = \int X^2 dP(\omega) \geq \int_{|X|\geq a} X^2 dP(\omega). \tag{4.8}$$

On the integration range $|X| \geq a$, $X^2 \geq a^2$, so

$$\int_{|X|\geq a} X^2 dP(\omega) \geq \int_{|X|\geq a} a^2 dP(\omega) = a^2 \int_{|X|\geq a} dP(\omega). \tag{4.9}$$

[96]In the following the assertion is proved under a stronger condition that $V(X)$ is finite. To prove the law under the condition $E(|X_1|) < \infty$ requires some tricks.

[97]Or, you can use $V(X) = V(X - a)$ for any number a; the width does not change wherever the distribution is placed.

This implies

$$V(X) \geq a^2 P(|X| \geq a). \tag{4.10}$$

Since we have shifted X by $E(X)$, this implies Chebyshev's inequality (4.6).

4.7 Proof of the law of large numbers

We wish to apply Chebyshev's inequality (4.6) to the sample average $(1/N)\sum X_n$. Replacing corresponding quantities in (4.6) ($X \to (1/N)\sum X_n$, $a \to \varepsilon$), and using (4.5), we get

$$P\left(\left|\frac{1}{N}\sum_{n=1}^{N} X_n - E(X_1)\right| \geq \varepsilon\right) \leq \frac{V(X_1)}{\varepsilon^2 N}. \tag{4.11}$$

Taking $N \to \infty$, we arrive at LLN.

4.8 Detecting unfair coins

We have shown that indeed (4.1) can be used to observe the probability of an event.

How many times should we throw a coin to check its fairness? The empirical probability for Head is given by N_H/N, where N is the total number of trials and N_H the number of trials resulting in Head. The expectation value of N_H/N is the probability of Head p_H. Let X_i be the indicator of the Head event for the i-th trial. Its expectation value is also p_H and $N_H = \sum_i X_i$. Let V ($\leq 1/4$) be its variance. Then, the Chebyshev inequality (4.11) implies

$$P\left(\left|\frac{N_H}{N} - p_H\right| \geq \varepsilon\right) \leq \frac{V}{\varepsilon^2 N}. \tag{4.12}$$

Therefore, the more unfair the easier to estimate p_H accurately (because $V = p_H - p_H^2$), but, for example, 10% unfairness is not very easy to detect.

Perhaps it is fun to simulate the experiments described above computationally.

4.9 Monte Carlo integration

Let us consider the problem of numerically evaluating a high-dimensional integral (the *Monte-Carlo integration* method):

$$I = \int_0^1 dx_1 \cdots \int_0^1 dx_{1000} f(x_1, \cdots, x_{1000}). \tag{4.13}$$

If we wish to sample (only) two values for each variable, we need to evaluate the function at $2^{1000} \sim 10^{300}$ points (you should remember $2^{10} \simeq 10^3$). Such sampling is of course impossible.

This integral can be interpreted as the average of f over a 1000 dimensional unit hypercube:

$$I = \frac{\int_0^1 dx_1 \cdots \int_0^1 dx_{1000} f(x_1, \cdots, x_{1000})}{\int_0^1 dx_1 \cdots \int_0^1 dx_{1000}}. \tag{4.14}$$

Therefore, randomly sampling the points $\boldsymbol{r}_n$ in the hypercube, we can obtain

$$I = \lim_{N\to\infty} \frac{1}{N} \sum_{n=1}^{N} f(\boldsymbol{r}_n). \tag{4.15}$$

How many points should we sample to estimate the integral within 10^{-2} error, if we allow larger errors at most once out of 1000 such calculations? We can readily know the answer from (4.11): $V(f(X_1))10^7$.[98] The variance of the value of f is of order $\max|f|^2$, a constant. Compare this number with 10^{300} above and appreciate the power of randomness. This is the principle of the Monte Carlo integration. Notice that the computational cost does *not* depend on the dimension of the integral.

How fast or slow the convergence of this method is may be felt from the estimation of π by peppering a disk:
http://demonstrations.wolfram.com/MonteCarloEstimateForPi/

4.10 Why LLN is important: no fluctuation of internal energy[99]

As we will learn the totality of mechanical energy of a macroscopic system is called the internal energy. The law of large numbers and the equipartition of energy (Section 2) imply that for an ideal gas the internal energy does not fluctuate macroscopically. Let us see why.

Let us take an ideal gas consisting of N particles in an isolated volume. We have demonstrated that all the particles have the same average kinetic energy $3k_BT/2$ (equipartition of kinetic energy). Hence. the law of large numbers tells us

$$P\left(\left|\frac{1}{N}\sum_{n=1}^{N}\frac{1}{2}m\boldsymbol{v}_n^2 - \frac{3}{2}k_BT\right| > \varepsilon\right) < \frac{V(e)}{\varepsilon^2 N}, \tag{4.16}$$

where $V(e)$ is the variance of the kinetic energy of each particle. Or, since $E = \sum(1/2)m\boldsymbol{v}_n^2$ is the internal energy for the (monatomic) ideal gas,

$$P\left(\left|\frac{E}{N} - \frac{3}{2}k_BT\right| > \varepsilon\right) < \frac{V(e)}{\varepsilon^2 N}. \tag{4.17}$$

---

[98]Here, the inequality gives a sufficiently safe estimate. In practice, a smaller number of samples might be OK.

[99]Very strictly speaking, we do not know yet how big N is, although we have already discussed this informally in **1.7**. Empirically at this point, perhaps we could measure the temperature fluctuation of the system and guess how many 'statistically independent parts' make up the system.

This implies that the probability that the internal energy lies in the following range

$$N(3k_BT/2 - \varepsilon) < E < N(3k_BT/2 + \varepsilon) \tag{4.18}$$

is larger than $1 - V(e)/\varepsilon^2 N$. Here, in practice, $N\varepsilon$ need not be microscopic. We are dealing with a macroscopic body with $N \sim 10^{20}$. Practically, we may need E within a 1% error ($\varepsilon = 0.01(3k_BT/2)$). Notice that $V(e)$ is of the same order of $(k_BT)^2$. This implies that the probability to observe E in the range of (4.18) is larger than $1 - c/(0.01)^2N$, where $c = V(e)/(3k_BT/2)^2$ and is a constant of order unity. Thus, we have realized that 'surely' E is constant within 1%. Actually, even if we increase the observation accuracy to 10^{-5}% still the situation does not change very much for a 1 liter air around us.

Discussion 2

D2.1. [Elementary combinatorics questions]
Although combinatorics is a side issue of probability theory, if all the elementary events are equally probable, counting becomes the main problem of evaluation of probabilities, so let us look at its rudiments. **You must have read** Appendix 3A up to the multinomial theorem.

(1) How many ways
   (i) to put 3 distinguishable balls into three distinguishable boxes? More generally, how about n balls and M boxes?
   (ii) to put 3 indistinguishable balls into three distinguishable boxes? General case? This is to distribute energy quanta to three different molecules.
   (iii) to put 3 distinguishable balls into three indistinguishable boxes? General case? This is a grouping problem.[100]
   (iv) to put 3 indistinguishable balls into three indistinguishable boxes? This is related to a partition question of integers.[101]

Solution.
(i) Let us call distinguishable balls a, b and c, and distinguishable boxes A, B, and C. Each ball has three choices A, B, and C irrespective of the choices of the other two balls. Thus, there are $3 \times 3 \times 3 = 3^3 = 27$ ways. The general case is M^n.
(ii) This is the problem of arranging two indistinguishable spacers and three indistinguishable balls: the case of Fig. 3.6 in the notes. Therefore,

$$\binom{5}{3} = \frac{5!}{2!\,3!} = 10 \tag{4.19}$$

ways. The general case is just discussed in the notes (see (3.39)):

$$\frac{(n+M-1)!}{n!(M-1)!}. \tag{4.20}$$

If $n \ll M$ (i) and (ii) are not very different. Take log of the general formulas

$$\log n^M = n \log M, \tag{4.21}$$

$$\log \frac{(n+M-1)!}{n!(M-1)!} = (n+M)\log(n+M) - n\log n - M\log M$$
$$\simeq n\log M - n - n\log n \simeq n\log M. \tag{4.22}$$

[100] This is related to the partition of sets: https://en.wikipedia.org/wiki/Bell_number [thanks to J A Claes].
[101] This is related to the number partition problem: https://en.wikipedia.org/wiki/Partition_(number_theory)

Here, we have used an easily obtained approximation $\log N! = N\log N - N$ (see Section 13) and assumed $\log M \gg 1$. If $n \gg M$, then

$$\log\frac{(n+M-1)!}{n!(M-1)!} = (n+M)\log(n+M) - n\log n - M\log M \simeq M\log n - M - M\log M \simeq M\log n. \tag{4.23}$$

Thus, its growth rate as a function of n is far smaller than (i); since n particles are indistinguishable, this is natural.

(iii) Actually, this problem should be solved after (iv). We wish to group a, b, and c into three subgroups that may be empty. Therefore, there are three kinds of grouping: $3+0+0$, $2+1+0$, and $1+1+1$. For the first and the third cases, there are only one case each, (abc) and (a)(b)(c). For 2+1+0, there are three cases (ab)(c), (bc)(a) and (ca)(b). Thus, there are 5 ways. The general case is difficult.
(iv) If both are indistinguishable, what matters is to divide '3' into the sum of three non-negative integers. Thus, 3 is equal to $3+0+0 = 2+1+0 = 1+1+1$. There are three ways. In this case no clean general result exists.

(2) All the elementary particles of the same kind [and all the molecules of the same chemical species with the same internal state] are indistinguishable.

If the number density is extremely low, then whether these particles are distinguishable or not is virtually irrelevant, so we may handle them just as 'marbles.'

However, the number density is not too small, their indistinguishability manifests itself. For example, suppose you have two particles and two distinguishable boxes (= one-particle states). There is only one way to put one particle each in each box (not two as the case of two marbles) (see Fig. 21.6).

Empirically, we know there are only two kinds of elementary particles from the combinatorial point of view:

bosons: indefinitely many particles can assume a single identical one-particle state (examples: α-particle, hydrogen atom, ^{4}He atom);

fermions: all the indistinguishable particles must assume distinct one-particle states [Pauli's exclusion principle] (examples: electron, proton, ^{3}He atom).

There are M distinguishable one-particle states and $n \le M$ particles. Any particle can assume any one-particle state in M, if left alone. How many different combinations of one-particle states[102] are possible, if particles are
(i) marbles,
(ii) α-particles,
(iii) electrons?

Solution.
(i) This is the distinguishable case, so it is just as (i) in (1); each particle can choose

[102]We later call such combinations specified microscopically microstates; **do not confuse microstates and one-particle states**.

any microstate without paying any attention to the choices of other particles: M^n ways.
(ii) This is the boson case, so it is just as (ii) in (1). Therefore, as illustrated in Fig. 3.6, the answer must be

$$\binom{M+n-1}{n} = \frac{(M+n-1)}{n!\,(M-1)!}. \tag{4.24}$$

(iii) This is the fermion case, so if we can mark the one-particle states that will become states of individual electrons, we can describe one possible microstate. There are $\binom{M}{n}$ ways to mark the distinguishable one-particle state. That is, there are $\binom{M}{n}$ distinct microstates for the system.

D2.2 [Events and sets]
(1) Let $\Omega = \{\omega_i\}$ be the sample space (= the totality of possible elementary events). Let A ($\subset \Omega$) $= \{\omega_1, \omega_3, \omega_4\}$. What is the meaning of the statement that event A actually occurs?
(2) Let $A \subset \Omega$. Is event A and event Ω statistically independent?

Perhaps, it is convenient to refurbish your knowledge of de Morgan's law and the distributive law about $\cap$ and $\cup$ (see algebra of sets) before proceeding further.

(3) Find simple expressions for
(i) $(A \cup B) \cap (A \cup B^c)$ (here $B^c = \Omega \setminus B$, the complement of B in Ω).
(ii) $(A \cup B) \cap (B \cup C)$.
(4) Is $(A \cup B \cup C)^c = A^c \cap B^c \cap C^c$ true?
(5) There are three events A, B and C in the common Ω. Illustrate the following events, using Venn diagrams:
(i) No more than two events occur.
(ii) At least two events occur.

Solution.
(1) That an event A occurs means that actually an elementary event in A occurs, so ω_1 or ω_3 or ω_4 actually occurs.
(2) The definition of statistical independence of two events A and B is $P(A \cap B) = P(A)P(B)$. Since $A \cap \Omega = A$ and $P(\Omega) = 1$, indeed $P(A \cap \Omega) = P(A)P(\Omega)$. Thus, these two events are statistically independent. This is intuitively obvious, because even if you know about Ω (that is, something happens), you cannot tell anything about A. If A happens, of course something happens, so we cannot know anything new about Ω (worse, even if you know A does not occur, you cannot know whether anything happens or not).
(3) The distributive law tells us (if you wish, draw Venn diagrams)

$$A \cap (B \cup C) = (A \cap B) \cup (A \cap C), \tag{4.25}$$

$$A \cup (B \cap C) = (A \cup B) \cap (A \cup C). \tag{4.26}$$

(i)

$$(A \cup B) \cap (A \cup B^c) = A \cup (B \cap B^c) = A \cup \emptyset = A. \tag{4.27}$$

(ii)

$$(A \cup B) \cap (B \cup C) = (B \cup A) \cap (B \cup C) = B \cup (A \cap C). \tag{4.28}$$

(4) Recall de Morgan's law.

$$(A \cup B \cup C)^c = (A \cup B)^c \cap C^c = (A^c \cap B^c) \cap C^c = A^c \cap B^c \cap C^c. \tag{4.29}$$

Yes.
(5)

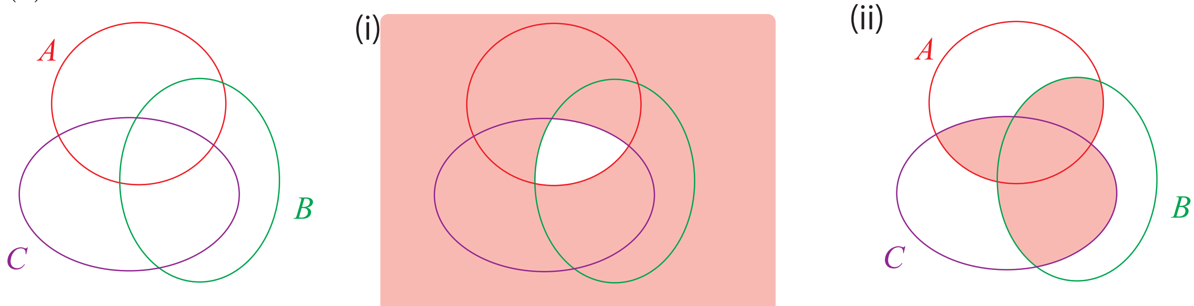


Figure 4.3: Solution to **D2.2** (5).

D2.3 [Elementary probability questions]
(1) Try to understand **Q3-1** thoroughly (i.e., try to solve it first by yourself with sparingly consulting the solutions).
(2) Two fair coins are thrown but you cannot see them. You are told at least one coin exhibits a Head (H) and that if there is a coin exhibiting a Tail (T), you will be awarded \$1,000. However, to participate in this game, you must pay a participation fee of \$500. Will you still play the game, expecting some monetary gain?[103]

Solution.
(2) The possible cases are (H, T), (T, H) and (H, H) just as the kitten problem. Thus, with probability 2/3, you will win. The expected gain must be $1000 \times 2/3 > 500$. Go ahead (if you wish to increase your income).

D2.4 [Law of large numbers]
Throwing a coin 1,000 times, you get 611 heads, so you suspect the coin is not fair. How rational is this conclusion from the point of view of the law of large numbers?

Solution.

[103]Perhaps a discussion problem: there are two electrons and their spins, up or down, are measured. Let us consider the gambling problem with the coins H/T replaced with electrons U/D. What will you decide?

Let us assume that the coin is fair (the null hypothesis). If you use the law of large numbers, we wish to estimate

$$P\left(\left|\frac{1}{1000}\sum_{k=1}^{1000} X_i - 0.5\right| > 0.111\right). \tag{4.30}$$

We know $V(X_1) = 1/4$, so the Chebyshev estimate is

$$P\left(\left|\frac{1}{1000}\sum_{k=1}^{1000} X_i - 0.5\right| > 0.111\right) < \frac{0.25}{0.111^2 \times 1000} = 0.021. \tag{4.31}$$

That is, even if the coin is fair, the obtained result can happen twice in 100 such trials. Well, the judgement is up to you, depending on what you stake on the outcome.

You may have the following comment: we actually know the average is larger than 0.5, so we should estimate the probability of

$$P\left(\frac{1}{1000}\sum_{k=1}^{1000} X_i - 0.5 > 0.111\right). \tag{4.32}$$

Notice that

$$P\left(\left|\frac{1}{1000}\sum_{k=1}^{1000} X_i - 0.5\right| > 0.111\right) > P\left(\frac{1}{1000}\sum_{k=1}^{1000} X_i - 0.5 > 0.111\right). \tag{4.33}$$

Therefore, our estimate of the probability is a conservative one.

D2.5 [Monte-Carlo estimate]
Design a 'dart-throwing experiment' to estimate $\sqrt{2}$. To obtain two digits for $\sqrt{2}$ with the failing rate of once in 100 trials, how many darts do you have to throw? An order of 100, 1000, or? Give a reasonable guess.

Solution.
Look at Fig. 4.4. The red rectangle has an area $\sqrt{2}$ and the green one 1. Therefore, we can estimate $1/\sqrt{2} = \sqrt{2}/2$ probabilistically.

The failing probability is according to Chebyshev

$$\frac{V}{\varepsilon^2 N}, \tag{4.34}$$

where V is product of the probability of a dart landing on the target area and the probability otherwise, so it is about $1/4$. ε in our case is about 0.1, so

$$0.25 \times 100/N < 1/100. \tag{4.35}$$

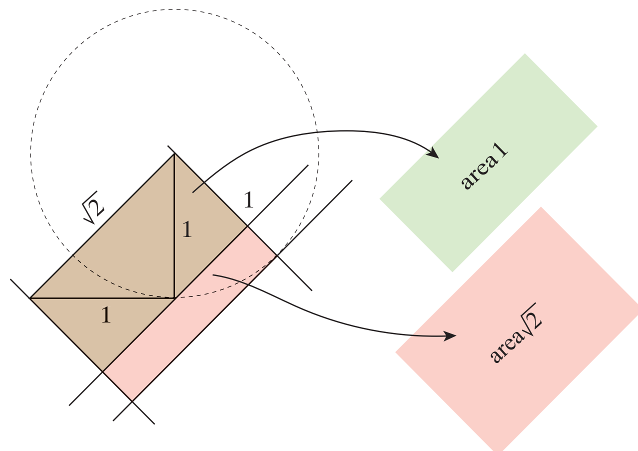


Figure 4.4: How to get $\sqrt{2}/2$ by peppering points on the red rectangle uniformly

That is, $N > 4000$. Roughly a few thousands are required.

D2.6 [Borel-Cantelli lemma related] [Discussion problem]
Let us repeat coin-tossing infinitely many times. Then, irrespective of the fairness of the coin (as long as both H and T are possible at all), we intuitively expect that we will observe infinitely many heads. In other words, we expect that with probability one we will not see only finitely many heads.

The relevance of this statement to statistical thermodynamics is: for macrosystems what we actually observe with positive probability is determined by a set of macroscopically many microstates.[104]

This should be intuitively obvious, but can you prove it from the 'axioms' of the probability: P is an additive set function whose range is $[0, 1]$?
(1) Let A_k be the event that the k-th trial (throwing) gives a head. What is the meaning of $B_N = \cap_{k=N}^{\infty} A_k^c$?
(2) In terms of B_N express the event F that only finitely many heads occur.
(3) Do you see $B_N \subset B_{N+1}$? This means

$$P(F) = \lim_{N\to\infty} P(B_N). \tag{4.36}$$

(4) Show

$$P(B_N) = \prod_{k=N}^{\infty} (1 - P(A_k)). \tag{4.37}$$

This implies $P(F) = 0$.

Solution.

[104]As noted above, 'microstate' is a microscopically described state of the system. For example, 'half the spins in a magnetic lattice are up' does not describe a microstate, since the spins of the atoms sitting at lattice points are not individually described; 'the spins of the atoms sitting at lattice points $\{x_i\}$ are up' specifies a single microstate.

(1) A_k^c means that the k-th trial is not H. Therefore, $B_N = \cap_{k=N}^{\infty} A_k^c$ implies the event that H never appears beyond the Nth trial.
(2) F means at least one of B_N occurs for $N \geq 1$:

$$F = \cup_{N=1}^{\infty} B_N = \cup_{N=1}^{\infty} (\cap_{k=N}^{\infty} A_k^c). \tag{4.38}$$

(3) Notice that $\{B_N\}$ is a monotone expanding sequence of sets: $B_N \subset B_{N+1} \to F$, because B_{N+1} is less constrained than B_N (one condition less). Therefore, $\{P(B_N)\}$ is a monotone increasing sequence converging to $P(F)$:

$$P(F) = \lim_{N \to \infty} P(B_N) \tag{4.39}$$

(4) Due to the statistical independence of A_k's

$$P(B_N) = P(\cap_{k=N}^{\infty} A_k^c) = \prod_{k=N}^{\infty} P(A_k^c) = \prod_{k=N}^{\infty} (1 - P(A_k)). \tag{4.40}$$

There are infinitely may 1/2 factors in this product, $P(F) = 0$.[105]

[105]This is almost a trivial use of Borel-Cantelli lemma: If events A_k are statistically independent, and $\sum P(A_k) = \infty$, then infinitely many A_k's occur.

Exercise 2

E2.1 [Elementary combinatorics]
There are 5 distinguishable containers[106] and 5 particles.

(1) Obtain the numbers of ways to distribute these particles for the cases:
(i) protons,
(ii) candies,
(iii) hydrogen atoms.

(2) How many ways to put 3 ^{3}He atoms and ^{4}He atoms atoms in 5 distinguishable boxes? Ignore any energetic interactions among them.

Solution.
(1)
(i) This is a fermion case, so there is only 1 possibility: each proton is in each one-particle state.
(ii) This is a distinguishable (classic) case, so $5^5 = 3125$ ways.
(iii) This is a boson case, so $\binom{9}{5} = 9 \cdot 8 \cdot 7 \cdot 6/4 \cdot 3 \cdot 2 = 126$ ways.

(2) Since the distinct particles do not interfere statistically, and since we assume there is no physical interaction among the particles, we can simply superpose the results for distinct particles.

^{3}He are fermions and ^{4}He are bosons. Therefore,

$$\binom{5}{3} \times \binom{7}{3} = 10 \times 35 = 350 \tag{4.41}$$

ways.

E2.2 [Sets and events]
Show the following statements:
(1) If two events A and B are statistically independent, then A^c and B^c are independent as well.
(2) Any event A and $\emptyset$ are statistically independent.

Solution.
(1) We wish to show $P(A^c \cap B^c) = P(A^c)P(B^c)$.

$$P(A^c \cap B^c) = P((A \cup B)^c) = 1 - P(A \cup B) = 1 - [P(A) + P(B) - P(A \cap B)] \tag{4.42}$$

$$= 1 - P(A \cup B) = 1 - [P(A) + P(B) - P(A)P(B)] = (1 - P(A))(1 - P(B)). \tag{4.43}$$

(2) $P(A \cap \emptyset) = P(\emptyset) = 0 = P(A)P(\emptyset)$. Or any event and Ω are statistically independent as we have shown in **D2.2**, so, in particular, A^c and Ω are statistically

[106] For particles, interpret the containers as one-particle states as in Discussion.

independent, so (1) gives what we want.

E2.3 [Law of large numbers]
We wish to compute the following integral

$$I = \int_0^1 dx\,(1 - x^2) \tag{4.44}$$

by the Monte-Carlo method. That is, we draw the graph of $(1-x^2)$ and consider the area below it (between the graph and the x-axis in $[0,1]$) in the square $[0,1] \times [0,1]$ by peppering points uniformly on the square. To get I within 1% relative error and with a failing rate of once in 500 trials, how many points N do you need?

Solution.
Let χ be the indicator of the set sandwiched between the x-axis and the graph of $y = 1 - x^2$ in the square $[0,1] \times [0,1]$ (the red region in Fig. 4.5). Then. $I = \langle \chi \rangle$.

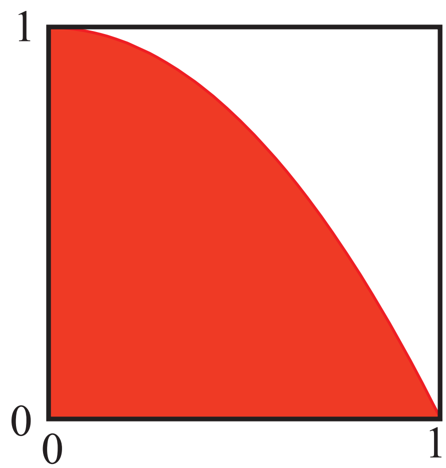


Figure 4.5: The curve is $1 - x^2$ and I is the area of the red portion, If you pepper points evenly on the black-edged square, I is exactly the probability for a point to land on the red portion.

Since Chebyshev's inequality reads

$$P\left(\left|\frac{1}{N}\sum_{i=1}^{N} \chi(x_i) - I\right| > \varepsilon\right) < \frac{V}{\varepsilon^2 N}, \tag{4.45}$$

where x_i is the location of the ith point landing on the unit square and V the variance of $\chi(x_i)$. In our case, $\varepsilon = 0.01I$ and the failure probability is $1/500$, so

$$\frac{V}{10^{-4} I^2 N} \le \frac{1}{500}. \tag{4.46}$$

We know $V = I(1 - I)$, so

$$N \ge 500 \times 10^4 (1 - I)/I. \tag{4.47}$$

We know $I = 2/3$, so $N \geq 2.5 \times 10^6$.

E2.4 [Apparent aftereffect]
Shooter A hits the target with probability 0.8 and B with probability 0.4. They shoot simultaneously and one bullet hits the target. What is the probability that the bullet is due to B?

Solution.
We need the conditional probability under the condition that one bullet hits the target. We may assume that the performance of the shooters is mutually statistically independent, so the expected probabilities of the relevant events are

a: only A hits $0.8(1 - 0.4) = 0.48$,
b: only B hits $(1 - 0.8)0.4 = 0.08$,
ab: both hit $0.8 \times 0.4 = 0.32$
e: none hits $(1 - 0.8)(1 - 0.4) = 0.12$.

Therefore, event b under one bullet hitting the target must be the conditional probability of event b under the condition that a or b occurs: Thus, $P = 0.08/(0.48 + 0.08) = 0.143$. Notice that this is much smaller than 0.4.

5 Maxwell's distribution

Summary
∗ Maxwell's distribution of the particle velocity is derived.
∗ How to calculate Gaussian integral and averages is explained.
∗ Boltzmann factor $e^{-\beta U}$ is derived and used to obtain Maxwell's distribution (again).
∗ Although slightly advanced, try to understand how to use the δ-function (how to use practically: Appendix 5A).

Key words
Density distribution function, Maxwell's distribution, Boltzmann factor, Gaussian integral, δ-function

What you should be able to do
∗ Be able to use distribution functions (to estimate expectation values). Recall the use of indicators (see Appendix 5A).
∗ Recognize that the molecular speed in a gas is of the same order of the sound speed in it.
∗ Be able to explain intuitively what the δ-function is. Also you would better be able to use it systematically to compute various distribution functions (say, the distribution of the kinetic energy).

In this lecture, some computational techniques (not mere tricks but the ones practically useful) will be explained. Even if these explanations are not understood, the physics of the topics would be understandable, so the technical explanations are all in fine letters. If you do not read them, you would not encounter big difficulties (but you'd better browse through them at least).

5.1 Density distribution function

To make the kinetic theory quantitative, we must know the probability of a particle to assume various velocities. For the velocity of a particle to be $\boldsymbol{v}$ exactly is obviously with probability zero.

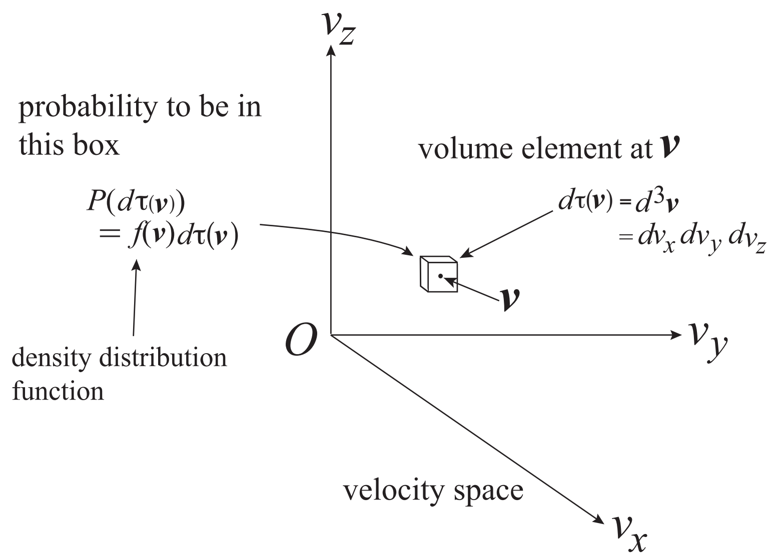


Figure 5.1: Volume element of the velocity space and the density distribution function

In the present case, the sample space is $\Omega = \{\boldsymbol{v} \mid v_x, v_y, v_z \in \mathbb{R}\} = \mathbb{R}^3$.[107] Thus, we need a probability measure[108] P defined on Ω. In the present case, for a set $A \subset \Omega$, $P(A) \to 0$ as volume[109] of $A \to 0$,[110] so we may define the probability density; symbolically (see Fig. 5.1),[111]

$$f(\boldsymbol{v}) = \frac{P(d\tau(\boldsymbol{v}))}{d\tau(\boldsymbol{v})}, \tag{5.1}$$

where $d\tau(\boldsymbol{v})$ is the volume element (of the 3-space) around $\boldsymbol{v}$, which may be written as $d^3\boldsymbol{v} = dv_x dv_y dv_z$. Here, its volume is also denoted by the same symbol $d\tau(\boldsymbol{v})$. The probability $P(A)$ of event $A \subset \Omega$ may be expressed as

$$P(A) = \int_A d^3\boldsymbol{v}\, f(\boldsymbol{v}). \tag{5.2}$$

5.2 Maxwell's derivation of Maxwell's distribution function: set up

In his "Illustrations of the dynamical theory of gases" (1860) Maxwell introduced the

[107]⟪***n*-object**⟫ Generally, 'n-object' implies n-dimensional object. Thus, $\mathbb{R}^3$ is the 3-space consisting of 3-vectors

[108]'Probability measure': You may interpret this as the correct use of the math terminology, if you know what measure is. Here, however, you may simply understand it informally as the usual probability, noting that the concept of probability is just the 'volume of our confidence' as we discussed in Lect 3, esp., around **3.1** and **3.5**.

[109]This is the actual volume of A as a subset of 3-space, which mathematicians call the Lebesgue measure of A.

[110]Mathematicians say that the probability measure P is absolutely continuous.

[111]Actually, this notation is mathematically justified as the Radon-Nikodym derivative.

density distribution function $f(\boldsymbol{v})$ of the velocity of gas particles, which is usually called Maxwell's distribution.

Let us follow Maxwell's logic. He assumed that in equilibrium[112] orthogonal components of the velocity of particles are statistically independent. This implies (why? recall **3.13**) that we may write

$$f(\boldsymbol{v}) = \phi_x(v_x)\phi_y(v_y)\phi_z(v_z), \tag{5.3}$$

where ϕ_x, etc., are density distribution functions for individual components. Maxwell also assumed the isotropy, so f is a function of $v^2 \equiv |\boldsymbol{v}|^2$, $f(\boldsymbol{v}) \equiv F(v^2)$ and ϕ_x, etc., do not depend on the suffixes specifying the coordinates: $\psi(s^2) \equiv \phi_x(s) = \cdots$. Therefore,

$$F(x+y+z) = \psi(x)\psi(y)\psi(z). \tag{5.4}$$

5.3 Maxwell's distribution: solving the functional equation

Maxwell originally assumed the differentiability of the functions, but here we only assume that the density distribution function is continuous. Since we are interested in the functional form of the density distribution function, and the normalization constant can be determined later, let us assume $\psi(0) = 1$.[113] Then, we get from (5.4)

$$F(x+y) = \psi(x)\psi(y) = F(x)F(y). \tag{5.5}$$

Let $G(x) = \log F(x)$. Then, (5.5) reads

$$G(x+y) = G(x) + G(y), \tag{5.6}$$

which is called the *Cauchy functional equation*, whose general solution is $G(x) = cx$, where c is a constant, if we assume G is continuous (or monotone) (as we see just below **5.4**).

This implies $F(x) \propto e^{cx}$; remember that normalization constant must be determined. That is, we may write with a new constant c (> 0)

$$f(\boldsymbol{v}) \propto e^{-c\boldsymbol{v}^2}. \tag{5.7}$$

We should not forget, however, that Maxwell actually did not like the above derivation that assumed statistical independence of three orthogonal directions. He

[112] What is *equilibrium*? It is a state reached by a gas isolated in a box sufficiently long after its preparation. There is no macroscopic flow in it and the gas is spatially uniform and time-independent (if observed on the macroscale).

[113] If you do not like this, simply set $\psi(0) = a > 0$, a constant. Then, instead of (5.6) you get $G(x+y) = G(x) + G(y) - b$, where $b = 3\log a$. Defining $g = G - b$, we get $g(x+y) = g(x) + g(y)$, from which we obtain $F(x) \propto e^{cx}$.

rederived it later with a different logic. Note that the above logic cannot work in 1-dimensional space.

5.4 Cauchy's functional equation

$G(2x) = 2G(x)$ is immediately obtained from (5.6). Repeating this, we get $G(nx) = nG(x)$ for positive integer n. This implies $nG(1/n) = G(1)$ or $G(1/n) = G(1)/n$. Therefore, $G(m/n) = mG(1/n) = (m/n)G(1)$ for positive integers m and n. Also, $G(0) = 2G(0)$, so $G(0) = 0$. This implies $G(x) = -G(x)$. Thus, we have demonstrated that for $q \in \mathbb{Q}$ (rational numbers) $G(q) = cq$, where $c = G(1)$ is a constant. Since we assume G to be continuous (because F is positive and continuous), $G(x) = cx$ must hold for any real x.

5.5 Gaussian integral

We must compute the normalization constant and c in (5.7). An easy way (the easiest way?) to compute the normalization constant is the following elegant method.

Since the integral is positive, let us compute the square of what we want:

$$\left[\int_{-\infty}^{\infty} dx\, e^{-x^2/2\sigma^2}\right]^2 = \int_{-\infty}^{\infty} dx\, e^{-x^2/2\sigma^2} \int_{-\infty}^{\infty} dy\, e^{-y^2/2\sigma^2} = \int_{\mathbb{R}^2} dxdy\, e^{-(x^2+y^2)/2\sigma^2}. \tag{5.8}$$

Now, we go to the polar coordinates $(x, y) \to (r, \theta)$:

$$\int_{\mathbb{R}^2} dxdy\, e^{-(x^2+y^2)/2\sigma^2} = 2\pi \int_0^{\infty} e^{-r^2/2\sigma^2} r dr = 2\pi \int_0^{\infty} dz\, e^{-z/\sigma^2} = 2\pi\sigma^2. \tag{5.9}$$

Hence,

$$\int_{-\infty}^{\infty} dx\, e^{-x^2/2\sigma^2} = \sqrt{2\pi}\sigma. \tag{5.10}$$

5.6 Gaussian density distribution function

The *Gaussian density distribution function* $g(x)$ generally has the following form:

$$g(x) = \frac{1}{\sqrt{2\pi}\sigma} e^{-(x-m)^2/2\sigma^2}, \tag{5.11}$$

where $E(x) = m$ and $V(x) = \sigma^2$ (recall the notations: **3.15**, **3.17**). Thus, we can know a Gaussian (density) distribution function, if we know its expectation value and variance.[114]

When the density distribution function for a quantity x is given by the Gaussian

[114] We will discuss the general multivariate Gaussian distribution in Lecture 19. We will learn that if we know the expectation value and the covariance matrix, we can determine the multivariate Gaussian distribution.

form (5.11), we say the quantity obeys a Gaussian distribution or, simply, is Gaussian.

5.7 Maxwell's distribution

Since $\langle v_x \rangle = 0$ and $V(v_x) = (2/m)(k_BT/2) = k_BT/m$ (thanks to the equipartition of kinetic energy, **2.15**), and since our distribution is Gaussian, we have

$$\phi(v_x) = \sqrt{\frac{m}{2\pi k_B T}} e^{-mv_x^2/2k_BT}. \tag{5.12}$$

That is,

$$f(\boldsymbol{v}) = \left(\frac{m}{2\pi k_B T}\right)^{3/2} e^{-m\boldsymbol{v}^2/2k_BT}. \tag{5.13}$$

This is *Maxwell's distribution* function. You must be able to compute various probabilities and expectation values with the aid of Maxwell's distribution function (see Appendix 5A also).

Up to this point we discussed in 3-space, but the general $\mathfrak{d}$-Maxwell distribution should be obtained easily.

Exercise. The *mode speed* v_M of the particles is the value of $v = |\boldsymbol{v}|$ for which the probability for the particles to have the speed between v and $v + dv$ becomes the largest. What can you expect for $\langle v \rangle / v_M$ in the $\mathfrak{d} \to \infty$ limit, where $\langle v \rangle$ is the average speed (the average of $|\boldsymbol{v}|$)? [See Appendix 5A]

5.8 Generating function

At this juncture, let us practice a basic trick. You must be able to compute the expectation value of $e^{\alpha x}$ for a Gaussian distribution, where α is generally a complex number:

$$\langle e^{\alpha x} \rangle = \frac{1}{\sqrt{2\pi}\sigma} \int_{-\infty}^{\infty} dx\, e^{\alpha x - (x-m)^2/2\sigma^2}. \tag{5.14}$$

If $\alpha = -s$, it is the Laplace transform of the distribution function; if $\alpha = ik$, where k is real, $\langle e^{ikx} \rangle$ is the Fourier transform of the density distribution, and is called the *generating function*.[115]

The standard trick to compute this integral is to complete the square as follows (to make the form $A(x-B)^2 + C$):

$$\alpha x - \frac{1}{2\sigma^2}(x-m)^2 = \alpha(x-m) + \alpha m - \frac{1}{2\sigma^2}(x-m)^2 = -\frac{1}{2\sigma^2}(x-m-\sigma^2\alpha)^2 + \frac{\sigma^2\alpha^2}{2} + \alpha m. \tag{5.15}$$

Therefore, (5.14) can be rewritten as

$$\langle e^{\alpha x} \rangle = \frac{1}{\sqrt{2\pi}\sigma} \int_{-\infty}^{\infty} dx\, e^{-(x-m-\sigma^2\alpha)^2/2\sigma^2 + \sigma^2\alpha^2/2\ + \alpha m}. \tag{5.16}$$

[115] http://www.yoono.org/ApplicableMath/ApplicableMath.html, Chapters 32 and 33 give a practical summary.

We shift the integration range by $m + \sigma^2\alpha$ (or you introduce a new integration variable $x' = x - m - \sigma^2\alpha$ and rewrite the integral). Then, the integration just gives the normalization factor, so

$$\langle e^{\alpha x}\rangle = e^{\sigma^2\alpha^2/2\ +\alpha m}. \tag{5.17}$$

Notice that

$$\frac{d}{d\alpha}\langle e^{\alpha x}\rangle\bigg|_{\alpha=0} = E(x) = m, \tag{5.18}$$

and

$$\frac{d^2}{d\alpha^2}\langle e^{\alpha(x-m)}\rangle\bigg|_{\alpha=0} = V(x) = \sigma^2. \tag{5.19}$$

5.9 Daniel Bernoulli revisited

Using Maxwell's distribution function, let us review Bernoulli's kinetic interpretation of pressure **2.14**.

The (kinetic interpretation of) pressure on the wall is the average momentum (impulse) given to the wall per unit time and area. Consider the wall perpendicular to the x-axis (just as was in the elementary discussion in Lecture 2). Then, the number of particles with its x-component of the velocity being between v_x and $v_x + dv_x$ that can impinge on the unit area on the wall per unit time is given by

$$nv_x dv_x \int_{-\infty}^{\infty} dv_y \int_{-\infty}^{\infty} dv_z f(\boldsymbol{v}), \tag{5.20}$$

where n is the number density (= number of particles in unit volume) of the gas molecules. Each particle gives the momentum $2mv_x$ upon hitting the wall, so

$$P = \int_{v_x\geq 0} d\boldsymbol{v}\, 2mnv_x^2 f(\boldsymbol{v}) = \int d\boldsymbol{v}\, mnv_x^2 f(\boldsymbol{v}) = \frac{1}{3}mn\langle \boldsymbol{v}^2\rangle, \tag{5.21}$$

where we have used the symmetry $f(\boldsymbol{v}) = f(-\boldsymbol{v})$, and the isotropy, $\langle v_x^2\rangle = \langle v_y^2\rangle = \langle v_x^2\rangle = (1/3)\langle v_x^2 + v_y^2 + v_x^2\rangle$. Or,

$$PV = \frac{2}{3}N\langle K\rangle, \tag{5.22}$$

where K is the kinetic energy of the single gas particle, and N is the number of particles in the volume V. Thus, Bernoulli's equation has been derived once more (but rather mechanically).

5.10 Important Remark: N was not known

Although the Boyle-Charles law is obtained, this does not tell us anything about molecules, because we do not know N. We cannot tell the mass of the particle, either. Remember that k_B was not known when the kinetic theory of gases was being developed.

A notable point is that with empirical results that can be obtained from strictly equilibrium studies of uniform systems, we cannot tell anything about molecules, even about their existence. We may interpret Bernoulli's theory as a means to study a continuum gas with a particulate approximation approach (you could take $N \to \infty$ limit at the end, keeping the total energy constant).

Remember that the law of combining volumes for chemical reactions (**2.11** (iii)) crucial to demonstrate the particular nature of chemical substances is about (often violent) irreversible processes from the reactants to the products. If we make a tiny hole on the wall of the container, we could make a molecular beam, so in principle, we can measure $\langle K \rangle$. However, this is a study of a system far away from equilibrium.

The (root-mean-square) speed of the molecules can be computed correctly, however, because we only need PV/Nm. Thus, in 1857 Clausius calculated the speed of molecules at 0°C: oxygen 461m/s, nitrogen 492m/s, and hydrogen 1,844m/s.[116] Notice, that these speeds are not very different from the sound speeds in respective gases.[117]

5.11 Sedimentation equilibrium

Take a vertical column of gas with cross-section A in the gravitational field just around us.

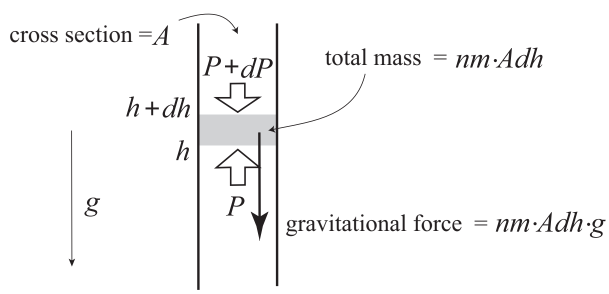


Figure 5.2: Force balance along a gas column in gravity (5.23)

Consider the force balance on the slice between heights h and $h+dh$ of a cylinder. If n is the number density and m the mass of the molecule, we have as a force balance equation with the aid of $P = nk_BT$

$$n \times Adh \times mg = -A(P + dP) + AP = -AdP = -Ak_BTdn \tag{5.23}$$

or

$$\frac{dn}{dh} = -\beta nmg, \tag{5.24}$$

[116]This is in his paper, "The Nature of the Motion which we call Heat" (Annalen der Physik, **100**, 353 (1857); English translation in Phil Mag **14**,108 (1857)). Millet's *The Gleaners* is this year.

[117]Sound speeds (in the standard state): oxygen 317 m/s, nitrogen 337 m/s, hydrogen 1270 m/s. As you see, this is about 2/3 of the molecular speed. For ideal gases, this ratio is exact.

where $\beta = 1/k_B T$ (a standard abbreviation we will use often). That is,

$$n = n_0 e^{-\beta mgh}. \tag{5.25}$$

This can describe the *sedimentation equilibrium* of colloidal particles.

Remark. In the above derivation, it is assumed that the temperature in equilibrium is not dependent on the height. Is this correct? A particle going upward must lose its kinetic energy, so aren't particles with lower temperatures at higher locations? This is not the case. We saw this already in **D1.2**.

5.12 The Boltzmann factor

The equation (5.25) suggests how the (relative) number of molecules depends on the potential energy difference. More generally, the same logic derives for conserved forces with potential U

$$n(\boldsymbol{r}) = n(\mathbf{0})e^{-\beta[U(\boldsymbol{r})-U(\mathbf{0})]}. \tag{5.26}$$

That is, the factor $e^{-\beta U}$ called the *Boltzmann factor* tells us the ratio of particle densities (or the probabilities to find particles) at different locations, when there is a position-dependent potential energy U.[118]

You can find the following elementary derivation of Maxwell's distribution with the aid of the Boltzmann factor in the Feynman lectures. The derivation may require some maturity of the reader; elementary approaches need not be very simple, so do not worry to much even if you do not understand this derivation of Maxwell's distribution when you read it for the first time.

5.13 Elementary derivation of Maxwell's distribution

Consider a column of an ideal gas which is in equilibrium with gravity. Let $n_{>u}(z)$ be the number of particles with $v_z > u > 0$ passing through height z upward per second (Fig. 5.3).

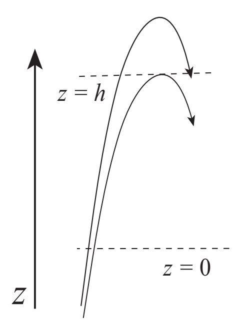


Figure 5.3: If $mu^2/2 = mgh$, then $n_{>u}(0) = n_{>0}(h)$.

[118]This is true even if U is extremely complicated. Thus, even if U is not due to an external effect but due to other molecules in the system, this relation holds. This is also explained in the Feynman lectures. If you do not take the interactions with other molecules into account, then you cannot use the ideal gas law, but the actual equation of state for the fluid.

Since stationarity of the distribution implies $n_{>u}(0) = n_{>0}(h)$, if $mgh = (1/2)mu^2$,

$$\frac{n_{>0}(h)}{n_{>0}(0)} = \frac{n_{>u}(0)}{n_{>0}(0)}. \tag{5.27}$$

Since $n_{>0}(h)/n_{>0}(0) = n(h)/n(0)$, we can use the Boltzmann factor just obtained:

$$\frac{n_{>u}(0)}{n_{>0}(0)} = e^{-\beta mgh} = e^{-\beta mu^2/2}. \tag{5.28}$$

The derivation is for the case without collisions, but since we have only to track energies that are conserved, collisions do not change the situation at all.

Let $n(0, u)$ be the number density of particles at height 0 with the z-component of the velocity being u. Notice that more numerous faster particles pass height 0 than slower ones, so we must take care of the speed in the z-direction:

$$n_{>u}(0) = \int_u^\infty u\, n(0, u)\, du \propto e^{-\beta mu^2/2}. \tag{5.29}$$

Thus, differentiating this equation, we obtain $n(0, u) \propto e^{-\beta mu^2/2}$.

Now, we wish to go to a technical topic that will be crucial in more advanced physics, and also make many calculations about distributions quite mechanical (no special wisdom or insight is needed!).

How to read the rest of this lecture: You must clearly understand **5.14**-**??**: what the δ-function is, and how it is related to the density distribution function. The rest may be skipped for the first time reading.

5.14 What average gives the density distribution?

We have learned in **3.18** that the probability $P(A)$ is given by the expectation value of the indicator χ_A of event A:

$$P(A) = \langle \chi_A \rangle_P. \tag{5.30}$$

Therefore, we may write (5.1) formally as (suffix P is omitted)

$$f(\boldsymbol{u}) = \left\langle \frac{\chi_{d\tau(\boldsymbol{u})}(\boldsymbol{v})}{d\tau(\boldsymbol{u})} \right\rangle, \tag{5.31}$$

where the average is over $\boldsymbol{v}$, and $\chi_{d\tau(\boldsymbol{u})}$ the indicator of the volume element $d\tau(\boldsymbol{u})$ located at $\boldsymbol{u}$.

5.15 Let us introduce $\boldsymbol{\delta}$-function

How does the quantity $\chi_{d\tau(\boldsymbol{u})}(\boldsymbol{v})/d\tau(\boldsymbol{u})$ we formally obtained look like as a function of $\boldsymbol{v}$? Here, $\boldsymbol{u}$ is a fixed parameter and the variable $\boldsymbol{v}$ denotes the 'event.' See Fig. 5.4 for the two-dimensional case. In the figure the actually infinitesimal volume element $d\tau(\boldsymbol{u})$ is assumed to be a tiny finite square for the illustration sake.

Informally,

$$\frac{\chi_{d\tau(\boldsymbol{u})}(\boldsymbol{v})}{d\tau} = \begin{cases} 1/d\tau = \infty, & \text{if } \boldsymbol{v} \in d\tau(\boldsymbol{u}). \\ 0, & \text{otherwise.} \end{cases} \tag{5.32}$$

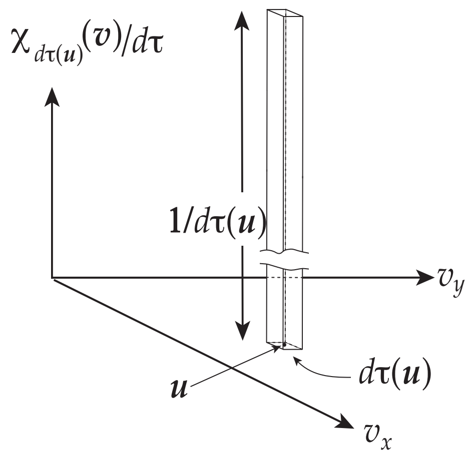


Figure 5.4: $\chi_{d\tau(\boldsymbol{u})}/d\tau(\boldsymbol{v})$, where the indicator of the volume element is concentrated around $\boldsymbol{u}$. Its value is $1/d\tau(\boldsymbol{u})$ on the volume element around $\boldsymbol{u}$, but other wise zero.

Here, ∞ appears because $d\tau$ is infinitesimally small. Then, following Dirac, let us introduce the δ-function (delta function) (in the $\mathfrak{d}$-dimensional space) concentrated at $\boldsymbol{u}$ (here $\boldsymbol{v}$ is assumed to be the running variable, and $\boldsymbol{u}$ is a fixed constant vector. See Fig. 5.4.) to denote $\chi_{d\tau(\boldsymbol{u})}(\boldsymbol{v})/d\tau(\boldsymbol{u})$ as $\delta(\boldsymbol{v}-\boldsymbol{u})$:

$$\delta(\boldsymbol{v}-\boldsymbol{u})\, d^{\mathfrak{d}}\boldsymbol{v} = \begin{cases} 0, & \text{if } \boldsymbol{v} \neq \boldsymbol{u}, \\ 1, & \text{if } \boldsymbol{v} = \boldsymbol{u}. \end{cases} \tag{5.33}$$

This implies that for any continuous function φ of $\boldsymbol{v}$

$$\int \varphi(\boldsymbol{v})\delta(\boldsymbol{v}-\boldsymbol{u})\, d^{\mathfrak{d}}\boldsymbol{v} = \varphi(\boldsymbol{u}). \tag{5.34}$$

Intuitively, as a function of $\boldsymbol{v}$ you can imagine $\delta(\boldsymbol{v}-\boldsymbol{u})$ as an infinitely thin but infinitely long needle at $\boldsymbol{v}=\boldsymbol{u}$ whose total volume is unity.

5.16 Formal expression of density distribution

Suppose we know the probability measure P for a vector $\boldsymbol{v}$. Then the density distribution function $f(x)$ of $x = F(\boldsymbol{v})$ can be written as

$$f(x) = \langle \delta(x - F(\boldsymbol{v})) \rangle_P, \tag{5.35}$$

because

$$f(x) = \left\langle \frac{\chi_{dx}(F(\boldsymbol{v}))}{dx} \right\rangle_P . \tag{5.36}$$

The δ-function in (5.35) is the 1-space δ-function. Notice that 'δ-function' may be regarded as an even function (see Fig. 5.5). You must keep in mind with respect to what variable you are taking the expectation value; in the above case with respect to $\boldsymbol{v}$, not x.

As we will see soon, for example you can compute the distribution of the kinetic energy easily with the aid of (5.35). To this end we would be better familiar with the properties of the 1-space δ-function.

5.17 1D δ-function and its integral

Since 1D δ-function is a needle located at $x = 0$ with the 'area' unity

$$\delta(x)\,dx = \begin{cases} 0, & \text{if } x \neq 0, \\ 1, & \text{if } x = 0, \end{cases} \tag{5.37}$$

if we integrate it, we get a (Heaviside) step function $\Theta(x)$

$$\int_{-\infty}^{x} dy\,\delta(y) = \Theta(x), \tag{5.38}$$

where

$$\Theta(x) = \begin{cases} 1, & \text{for } x \geq 0, \\ 0, & \text{for } x < 0. \end{cases} \tag{5.39}$$

5.18 Derivative of step function

The step function $\Theta(x)$ is constant except at $x = 0$, so its 'derivative' $\Theta'(x)$ is zero, if $x \neq 0$. However, it cannot be 0 everywhere. Although it is impossible to 'differentiate a vertical wall,' we intuitively see it to be $\Theta'(0) = +\infty$ (infinitely steep uphill). The area between $\Theta'(x)$ and the x-axis must be unity, because $\Theta(x)$ jumps exactly by 1 at $x = 0$. You may intuitively imagine an infinitely long needle at $x = 0$ whose 'area' is $0 \times \infty =$ unity as noted in (5.37); $\Theta'(x)$ should be identical to $\delta(x)$. Thus, we wish to conclude

$$\frac{d}{dx}\Theta(x) = \delta(x). \tag{5.40}$$

Our intuition just explained may be illustrated as Fig. 5.5.[119] Therefore, for any

[119]This is total nonsense! This cannot be mathematics! However, we can almost completely rationalize our 'intuitive picture' with the aid of the theory of distributions due to Schwartz. Fig. 5.5 Right tells us that $0 \times \infty = 1$ is not so absurd.

continuous function $\varphi(x)$ on the real line (see (5.34))

$$\int_{-\infty}^{+\infty} \varphi(x)\delta(x-a)dx = \varphi(a). \tag{5.41}$$

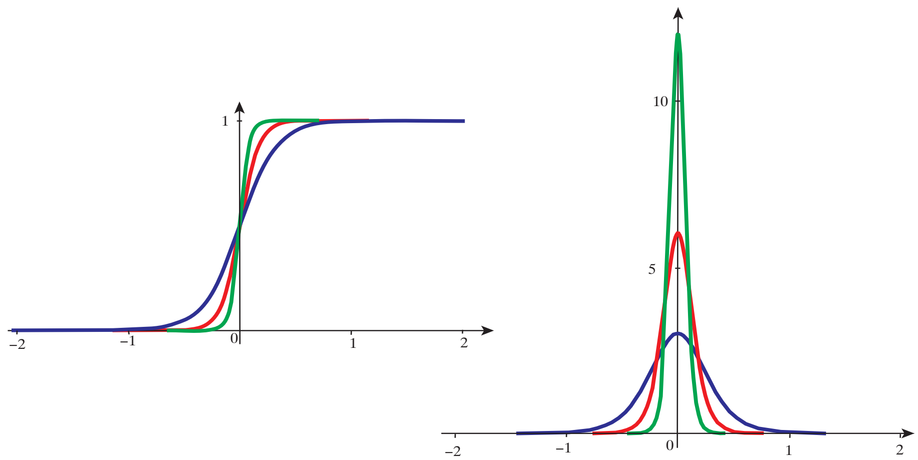


Figure 5.5: The derivatives (Right) of increasingly steep cliffs (Left). Colors are correspondent. Imagining such a limiting process, we can understand the δ-function as the derivative of the step function. Notice that the areas below the graphs in Right are always unity.

5.19 The most useful formula for theoretical physicists

Thus, the Fourier transformation of $\delta(x)$ is

$$\int_{-\infty}^{+\infty} e^{ikx}\delta(x)dx = 1. \tag{5.42}$$

Inverse Fourier transforming this, we get[120]

$$\delta(x) = \frac{1}{2\pi}\int_{-\infty}^{+\infty} e^{-ikx}dk. \tag{5.43}$$

This is perhaps the most useful identity in theoretical physics.

The delta function is quite important in (theoretical) physics. A practical summary (as well as a short introduction to the general theory of such 'hyperfunctions' may be found in

http://www.yoono.org/ApplicableMath/ApplicableMath_files/AMI-14.pdf

In the following, a 'practical minimum' is outlined.

[120]All these formal calculations are justified by the theory of distribution. An elementary summary of this theory may be found here: http://www.yoono.org/ApplicableMath/ApplicableMath_files/AMI-14.pdf.

5.20 Key formula 1 to utilize the δ-function

Let α ($\neq 0$) be a real number. We have the following important identity:

$$\delta(\alpha(x-a)) = \frac{1}{|\alpha|}\delta(x-a). \tag{5.44}$$

This may be shown as

$$\int_{-\infty}^{\infty} dx\, \delta(\alpha x - \alpha a)\varphi(x) = \int_{-\infty}^{\infty} d(y/|\alpha|)\, \delta(y-\alpha a)\varphi(y/\alpha) = \frac{1}{|\alpha|}\varphi(a), \tag{5.45}$$

5.21 Key formula 2 to utilize the δ-function

How about $\delta(g(x))$ for a differentiable function g? Suppose x_0 is a simple real zero of $g(x)$. That is, assume $g(x) \simeq g'(x_0)(x-x_0)$ near x_0. Then, (5.44) suggests that near $x = x_0$, $\delta(g(x))$ must be

$$\delta(g(x)) = \frac{1}{|g'(x_0)|}\delta(x-x_0). \tag{5.46}$$

There might be more than one simple real zeros of $g(x)$ (i.e., $g(r_1) = g(r_2) = \cdots = 0$). Thus, we obtain

$$\delta(g(x)) = \sum_i \frac{1}{|g'(r_i)|}\delta(x-r_i) = \frac{1}{|g'(x)|}\sum_i \delta(x-r_i), \tag{5.47}$$

where the summation is over all the simple real zeros of g. For example, assuming $a > 0$

$$\delta(x^2-a^2) = \frac{1}{|2x|}[\delta(x-a)+\delta(x+a)] = \frac{1}{2a}[\delta(x-a)+\delta(x+a)]. \tag{5.48}$$

5.22 Some practice

Let's have some practice:

$$\int_0^{10} dx\, \delta(x-\pi/6)\sin x = \frac{1}{2}, \tag{5.49}$$

$$\int_{-1}^{1} dx\, \delta(3x)\cos x = \frac{1}{3}, \tag{5.50}$$

$$\int_{-1}^{1} dx\,\delta(\pi - 6x)\cos x = \frac{1}{6}\cos\frac{\pi}{6} = \frac{\sqrt{3}}{12}, \tag{5.51}$$

$$\int_{3}^{4} dx\,\delta(\pi - 6x)\cos x = 0, \tag{5.52}$$

$$\int_{-\infty}^{\infty} dx\,\delta(x^2 - 3x - 10)x^3 = \frac{1}{7}(125 - 8) = \frac{117}{7}. \tag{5.53}$$

We will have more in **D3.1**.

5.23 Kinetic energy density distribution of 2D ideal gas

Since we have seen the energy distribution of a 2D gas in a demo simulation, let us obtain its formula, and demonstrate that it is independent of the particle mass. Our starting point is a formal expression of the density distribution:

$$f(K) = \langle \delta(m\boldsymbol{v}^2/2 - K)\rangle, \tag{5.54}$$

where the average is over the 2D Maxwell distribution. Therefore, we must cook

$$f(K) = \int dv_x dv_y \left(\frac{m}{2\pi k_B T}\right) e^{-m\boldsymbol{v}^2/2k_BT}\delta((m/2)(v_x^2 + v_y^2) - K). \tag{5.55}$$

Rewrite this into a 1D integral with the aid of the polar coordinates (v, θ). We know the distribution must be isotropic, we can integrate over the direction θ to get 2π, so

$$\begin{aligned} f(K) &= 2\pi\left(\frac{m}{2\pi k_B T}\right)\int_0^\infty vdv\,\delta(mv^2/2 - K)e^{-mv^2/2k_BT} && (5.56)\\ &= 2\pi\left(\frac{m}{2\pi k_B T}\right)\int_0^\infty vdv\,\frac{1}{mv}\delta(v - \sqrt{2K/m})e^{-mv^2/2k_BT} && (5.57)\\ &= \left(\frac{1}{k_BT}\right)e^{-K/k_BT}. && (5.58)\end{aligned}$$

This is just what we guessed from the simulation in http://falstad.com/gas/.

Appendix 5A: More calculations related to the Maxwell distribution

These days you may say no analytical muscle is needed thanks to Matlab, Mathematica, Maple, etc. However, wise use of these softwares requires good pattern recognition capability and strategic thinking. Such skills may be largely innate (genetic) but still can be nurtured considerably by practice.

The density distribution function of the particle velocity $\boldsymbol{v}$ of mass m at temperature T is given by the following Maxwell distribution function:

$$f(\boldsymbol{v}) = \left(\frac{m}{2\pi k_B T}\right)^{3/2} e^{-m\boldsymbol{v}^2/2k_BT}. \tag{5.59}$$

In this Appendix various expectation values and related distribution functions are studied.

(1) The (density) distribution function $F(u)$ of $u = |\boldsymbol{v}|$. As noted in (**??**), we have

$$F(u) = \langle \delta(u - |\boldsymbol{v}|)\rangle \tag{5.60}$$

or

$$\begin{aligned} F(u) &= \langle \delta(u - |\boldsymbol{v}|)\rangle = \int_{\boldsymbol{v}\in\mathbb{R}^3} d^3\boldsymbol{v}\,\delta(u - |\boldsymbol{v}|)\,\left(\frac{m}{2\pi k_B T}\right)^{3/2} e^{-m\boldsymbol{v}^2/2k_BT} && (5.61)\\ &= \int_0^\infty 4\pi|\boldsymbol{v}|^2 d|\boldsymbol{v}|\,\delta(u - |\boldsymbol{v}|)\,\left(\frac{m}{2\pi k_B T}\right)^{3/2} e^{-m|\boldsymbol{v}|^2/2k_BT} && (5.62)\\ &= \int_0^\infty 4\pi v^2 dv\,\delta(u - v)\,\left(\frac{m}{2\pi k_B T}\right)^{3/2} e^{-mv^2/2k_BT} && (5.63)\\ &= 4\pi u^2 \left(\frac{m}{2\pi k_B T}\right)^{3/2} e^{-mu^2/2k_BT} = \sqrt{\frac{2}{\pi}}\left(\frac{m}{k_B T}\right)^{3/2} u^2 e^{-mu^2/2k_BT}. && (5.64)\end{aligned}$$

From this we can compute the mode (= the most probable value) of v = 'u that maximizes $F(u)$' (use the logarithmic derivative for simplicity):

$$\frac{d}{du}(2\log u - mu^2/2k_BT) = 0, \tag{5.65}$$

so $\sqrt{2k_BT/m}$ is the mode speed (typical speed).

The average speed $\langle v\rangle$ is

$$\begin{aligned} \langle v\rangle &= \int_0^\infty dv\,F(v)v = \int_0^\infty \sqrt{\frac{2}{\pi}}\left(\frac{m}{k_B T}\right)^{3/2} v^2 e^{-mv^2/2k_BT} v\,dv && (5.66)\\ &= 2\int_0^\infty \sqrt{\frac{2}{\pi}}\left(\frac{m}{k_B T}\right)^{3/2} x e^{-mx/k_BT} dx \quad (\text{here } x = v^2/2). && (5.67)\end{aligned}$$

To compute this integral, we can use the following relations:

$$\int_0^\infty xe^{-\alpha x}dx = -\frac{d}{d\alpha}\int_0^\infty e^{-\alpha x}dx = -\frac{d}{d\alpha}\frac{1}{\alpha} = \frac{1}{\alpha^2}. \tag{5.68}$$

Thus,

$$\langle v\rangle = 2\sqrt{\frac{2}{\pi}}\left(\frac{m}{k_BT}\right)^{3/2}\left(\frac{k_BT}{m}\right)^2 = \sqrt{\frac{8k_BT}{\pi m}}. \tag{5.69}$$

(2) Energy distribution: for $E = mv^2/2$ find its density distribution function $F(E)$. Just as above,

$$F(E) = \langle\delta(E - mv^2/2)\rangle = \int_0^\infty 4\pi v^2 dv\,\delta(E - mv^2/2)\left(\frac{m}{2\pi k_BT}\right)^{3/2} e^{-mv^2/2k_BT}. \tag{5.70}$$

Then, we use (5.47) to cook the delta function with a nontrivial variable:

$$\delta(g(x) - E) = \delta(x - x_E)\frac{1}{|g'(x_E)|}, \tag{5.71}$$

where $g(x_E) = E$. Applying this to our case, we have

$$\delta(E - mv^2/2) = \delta(v - \sqrt{2E/m})\frac{1}{\sqrt{2mE}}. \tag{5.72}$$

Therefore, (you can use the result of (1) as well)

$$\begin{aligned}
F(E) &= \int_0^\infty 4\pi v^2 dv\,\delta(v - \sqrt{2E/m})\frac{1}{\sqrt{2mE}}\left(\frac{m}{2\pi k_BT}\right)^{3/2} e^{-mv^2/2k_BT} && (5.73)\\
&= 4\pi\frac{2E}{m}\frac{1}{\sqrt{2mE}}\left(\frac{m}{2\pi k_BT}\right)^{3/2} e^{-E/k_BT} && (5.74)\\
&= 2\sqrt{\frac{E}{\pi}}\left(\frac{1}{k_BT}\right)^{3/2} e^{-E/k_BT}. && (5.75)
\end{aligned}$$

(3) Relative velocity distribution

Let us obtain the root-mean square relative velocity $\boldsymbol{w}$ of two particles 1 and 2 with mass m in an ideal gas at T.

Using the delta function technique, we can write the density distribution function $F(\boldsymbol{w})$ for the relative velocity $\boldsymbol{w} = \boldsymbol{v}_1 - \boldsymbol{v}_2$ as

$$\begin{aligned}
F(\boldsymbol{w}) &= \langle\delta(\boldsymbol{w} - (\boldsymbol{v}_1 - \boldsymbol{v}_2))\rangle_{\boldsymbol{v}_1,\boldsymbol{v}_2} && (5.76)\\
&= \left(\frac{m}{2\pi k_BT}\right)^3\int d^3\boldsymbol{v}_1\int d^3\boldsymbol{v}_2\,\delta(\boldsymbol{w} - (\boldsymbol{v}_1 - \boldsymbol{v}_2))e^{-m\boldsymbol{v}_1^2/2k_BT - m\boldsymbol{v}_2^2/2k_BT} && (5.77)\\
&= \left(\frac{m}{2\pi k_BT}\right)^3\int d^3\boldsymbol{v}_1 e^{-m\boldsymbol{v}_1^2/2k_BT - m(\boldsymbol{w}-\boldsymbol{v}_1)^2/2k_BT}. && (5.78)
\end{aligned}$$

The integration over $\boldsymbol{v}_1$ is performed with the aid of completion of square (as explained in the lecture):

$$\begin{aligned} m\boldsymbol{v}_1^2 + m(\boldsymbol{w} - \boldsymbol{v}_1)^2 &= 2m\boldsymbol{v}_1^2 + m\boldsymbol{w}^2 - 2m\boldsymbol{w}\cdot\boldsymbol{v}_1 &(5.79)\\ &= 2m\left(\boldsymbol{v}_1 - \boldsymbol{w}/2\right)^2 + m\boldsymbol{w}^2 - (m/2)\boldsymbol{w}^2 &(5.80)\\ &= 2m\left(\boldsymbol{v}_1 - \boldsymbol{w}/2\right)^2 + (m/2)\boldsymbol{w}^2. &(5.81)\end{aligned}$$

Thus, we obtain

$$F(\boldsymbol{w}) = \left(\frac{m}{4\pi k_B T}\right)^{3/2} e^{-m\boldsymbol{w}^2/4k_BT}. \tag{5.82}$$

This means

$$\langle \boldsymbol{w}^2\rangle = \frac{6k_BT}{m}. \tag{5.83}$$

Check that the answer agrees with the result obtained by the equipartition of energy (and statistical independence of two particles).

(4) Root mean square velocity: we know an easy way, but here let us compute $\langle \boldsymbol{v}^2\rangle$ honestly as

$$\langle \boldsymbol{v}^2\rangle = \int_{\boldsymbol{v}\in\mathbb{R}^3} d^3\boldsymbol{v}\, \boldsymbol{v}^2 \left(\frac{m}{2\pi k_B T}\right)^{3/2} e^{-m\boldsymbol{v}^2/2k_BT}. \tag{5.84}$$

It is convenient to use the polar coordinate system with $v = |\boldsymbol{v}|$. Then,

$$\langle \boldsymbol{v}^2\rangle = \int_0^\infty 4\pi v^2 dv\, v^2 \left(\frac{m}{2\pi k_B T}\right)^{3/2} e^{-mv^2/2k_BT}. \tag{5.85}$$

Thus, the following integral is needed:

$$I(s,\alpha) = \int_0^\infty dv\, v^s e^{-\alpha v^2}, \tag{5.86}$$

which can be written with the aid of the Γ-function, but we do not go into it. For example,

$$I(4,\alpha) = \frac{d^2}{d\alpha^2}\int_0^\infty dv\, e^{-\alpha v^2} = \frac{d^2}{d\alpha^2} I(0,\alpha) = \frac{d^2}{d\alpha^2}\frac{1}{2}\sqrt{\frac{\pi}{\alpha}} = \frac{3}{8}\frac{\sqrt{\pi}}{\alpha^{5/2}}. \tag{5.87}$$

We know

$$\langle \boldsymbol{v}^2\rangle = I(4,\alpha)/I(2,\alpha) = \frac{3}{2}\frac{1}{\alpha} = \frac{3k_BT}{m}. \tag{5.88}$$

Q5-1. Consider D-dimensional ideal gas ($D > 1$). That is, the velocity is a D-vector $\boldsymbol{v} = (v_1, v_2, \cdots, v_D)$, and the kinetic energy of a single particle is given by $(m/2)\boldsymbol{v}^2 = (m/2)(v_1^2 + v_2^2 + \cdots + v_D^2)$, where m is the mass of the particle. [Here, our approach is elementary, but you can use the δ-function technique already explained in Appendix 4B. If the problem becomes more complicated as the next problem, the δ-function is much easier than the elementary approach.]
(1) Write down the D-dimensional Maxwell distribution function (i.e., find the density distribution function of the velocity in D-space).
(2) What is the most probable speed v_D in D-space? That is, what is the mode speed (the speed for which the density distribution function for the speed is maximal)?
(3) What is the ratio of v_D obtained in (2) and the root-mean-square velocity in the $D \to \infty$ limit?
(4) Is your result in (3) consistent with the law of large numbers?

Solution.
(1) As you can guess from the 3D result, we have only to multiply D 1D results as (If you do not like mere guessing, you can go back to Maxwell's proof. You will realize that the proof boils down to $F(x+y) = F(x)F(y)$ just as in 3D.)

$$f(\boldsymbol{v}) = \left(\frac{m}{2\pi k_B T}\right)^{D/2} e^{-m|\boldsymbol{v}|^2/2k_BT}.$$

(2) We need the density distribution function $F(v)$ of the speed $v = |\boldsymbol{v}|$.

$$F(u) = \langle \delta(u - |\boldsymbol{v}|)\rangle = \int d^D\boldsymbol{v}\, \delta(u - |\boldsymbol{v}|) \left(\frac{m}{2\pi k_B T}\right)^{D/2} e^{-m|\boldsymbol{v}|^2/2k_BT}$$

Notice that to use the rule of the computation of the integral containing a δ-function, the independent variable in the δ-function (in our case $|\boldsymbol{v}|$) must be the integration variable. Thus we must convert the δ-function or convert the integration variable (in our case, we convert the integration variable from $\boldsymbol{v}$ to $|\boldsymbol{v}|$).

Now we should go to the polar coordinate system in D-space:

$$d^D\boldsymbol{v} = S_{D-1} v^{D-1} dv,$$

where S_{D-1} is the volume of the $D-1$-unit sphere (corresponding to 4π in 3D). This actual form may be found in my grad course lecture notes (there is a clever way to compute it as explained there), but we do not need its explicit form. Integrating over the velocity, we get

$$F(u) = S_{D-1} \left(\frac{m}{2\pi k_B T}\right)^{D/2} u^{D-1} e^{-mu^2/2k_BT}.$$

This is the density distribution function for the speed. To find its peak, we have only to maximize $mu^2/2k_BT - (D-1)\log u$:

$$\frac{mu}{k_BT} - (D-1)\frac{1}{u} = 0,$$

Or $u^2 = (D-1)k_BT/m$. That is,

$$v_D = \sqrt{\frac{(D-1)k_BT}{m}}.$$

(3) The equipartition of kinetic energy tells us that

$$\left\langle \frac{1}{2}m\boldsymbol{v}^2 \right\rangle = \frac{mD}{2}\langle v_x^2 \rangle = \frac{D}{2}k_BT.$$

That is, the root-mean-square velocity is $\sqrt{Dk_BT/m}$. The ratio obviously converges to unity.
(4) The LLN tells us that for any positive ε

$$P\left(\left| \frac{\boldsymbol{v}^2}{D} - \frac{k_BT}{m} \right| > \varepsilon \right) < \frac{V(v_1^2)}{\varepsilon^2 D}.$$

That is, the probability for

$$D\left(\frac{k_BT}{m} - \varepsilon\right) < \boldsymbol{v}^2 < D\left(\frac{k_BT}{m} + \varepsilon\right)$$

is asymptotically unity as $D \to \infty$ for any $\varepsilon > 0$. Since $F(u)$ has peak(s) in this range, the most probable value should be within this range as well. That is, the mode speed is forced to agree with the root-mean square average.

Q5-2 [Density distribution of relative velocity]
(1) There are two particles 1 and 2 in an equilibrium pure ideal gas. Write down the simultaneous density distribution function $f(\boldsymbol{v}_1, \boldsymbol{v}_2)$ of their velocities $\boldsymbol{v}_1$ and $\boldsymbol{v}_2$. You may assume the temperature of the gas is T, and the mass of the individual particles is m.
(2) Now, introduce the velocity $\boldsymbol{V}$ of the center of mass of these two particles and the relative velocity $\boldsymbol{w} = \boldsymbol{v}_1 - \boldsymbol{v}_2$. Write down the simultaneous density distribution function $g(\boldsymbol{w}, \boldsymbol{V})$ of $\boldsymbol{w}$ and $\boldsymbol{V}$.
(3) Find the density distribution function of $\boldsymbol{w}$. Compute $\langle |\boldsymbol{w}| \rangle$ and compare it with the root-mean square of $\boldsymbol{w}$ (i.e., $\sqrt{\langle \boldsymbol{w}^2 \rangle}$).

Solution.
(1) Maxwell's (density) distribution function $f(\boldsymbol{v})$ implies

$$P(d\boldsymbol{v}) = f(\boldsymbol{v})d\boldsymbol{v}, \tag{5.89}$$

where $d\boldsymbol{v}$ is the volume element of the velocity space. Since we know two particles are statistically independent,

$$P(d\boldsymbol{v}_1, d\boldsymbol{v}_2) = P(d\boldsymbol{v}_1)P(d\boldsymbol{v}_2), \tag{5.90}$$

the density $f(\boldsymbol{v}_1, \boldsymbol{v}_2)$ must be a product of two Maxwellian distributions. Therefore,

$$f(\boldsymbol{v}_1, \boldsymbol{v}_2) = \left(\frac{m}{2\pi k_B T}\right)^3 e^{-m(\boldsymbol{v}_1^2+\boldsymbol{v}_2^2)/2k_B T}. \tag{5.91}$$

(2) $\boldsymbol{v}_1 = \boldsymbol{V} + \boldsymbol{w}/2$ and $\boldsymbol{v}_2 = \boldsymbol{V} - \boldsymbol{w}/2$, so

$$\boldsymbol{v}_1^2 + \boldsymbol{v}_2^2 = 2\boldsymbol{V}^2 + \frac{1}{2}\boldsymbol{w}^2. \tag{5.92}$$

Since we are computing the density distribution, we must demand

$$f(\boldsymbol{v}_1, \boldsymbol{v}_2) d\boldsymbol{v}_1 d\boldsymbol{v}_2 = g(\boldsymbol{V}, \boldsymbol{w}) d\boldsymbol{V} d\boldsymbol{w}, \tag{5.93}$$

or

$$f(\boldsymbol{v}_1, \boldsymbol{v}_2)\frac{\partial(\boldsymbol{v}_1, \boldsymbol{v}_2)}{\partial(\boldsymbol{V}, \boldsymbol{w})} = g(\boldsymbol{V}, \boldsymbol{w}). \tag{5.94}$$

The Jacobian appearing in the above formula is unity, so

$$g(\boldsymbol{V}, \boldsymbol{w}) = \left(\frac{m}{2\pi k_B T}\right)^3 e^{-(2m\boldsymbol{V}^2+(m/2)\boldsymbol{w}^2)/2k_B T}. \tag{5.95}$$

Notice that the center of mass kinetic energy is $(1/2)(2m)\boldsymbol{V}^2$, and the kinetic energy of the relative motion is $(1/2)(m/2)\boldsymbol{w}^2$, where $m/2$ is the reduced mass. You can read them off from the above formula.

(3) The marginal distribution $g(\boldsymbol{w})$ is obtained by integrating $\boldsymbol{V}$ out, or simply splitting $g(\boldsymbol{V}, \boldsymbol{w})$ using statistical independence of $\boldsymbol{V}$ and $\boldsymbol{w}$:

$$g(\boldsymbol{w}) = \left(\frac{m}{4\pi k_B T}\right)^{3/2} e^{-m\boldsymbol{w}^2/4k_B T} \tag{5.96}$$

$$\langle|\boldsymbol{w}|\rangle = \left(\frac{m}{4\pi k_B T}\right)^{3/2} \int d\boldsymbol{w}|\boldsymbol{w}|e^{-m\boldsymbol{w}^2/4k_B T} = \left(\frac{m}{4\pi k_B T}\right)^{3/2} 4\pi \int_0^\infty w^3 e^{-mw^2/4k_B T} dw \tag{5.97}$$

The integral can be calculated analytically:

$$4\pi \int_0^\infty w^3 e^{-mw^2/4k_B T} dw = 2\pi \left(\frac{4k_B T}{m}\right)^2. \tag{5.98}$$

Therefore,

$$\langle|\boldsymbol{w}|\rangle = 2\pi \left(\frac{4k_B T}{m}\right)^2 \left(\frac{m}{4\pi k_B T}\right)^{3/2} = \frac{4}{\sqrt{\pi}} \left(\frac{k_B T}{m}\right)^{1/2}. \tag{5.99}$$

On the other hand

$$\langle\boldsymbol{w}^2\rangle = \left(\frac{m}{4\pi k_B T}\right)^{3/2} 4\pi \int_0^\infty w^4 e^{-mw^2/4k_B T} dw = \left(\frac{m}{4\pi k_B T}\right)^{3/2} 48\pi^{3/2} \left(\frac{k_B T}{m}\right)^{5/2} = \frac{6k_B T}{m}, \tag{5.100}$$

or $\sqrt{\langle \boldsymbol{w}^2\rangle} = 3\sqrt{2}\sqrt{k_BT/m}$, which we will use in the next Lecture to estimate the mean free path. This must be larger than $\langle w\rangle$, because the variance of $w = |\boldsymbol{w}|$ (i.e, $\langle w^2\rangle - \langle w\rangle^2$) must be positive.

Q5-3. Let us obtain the root-mean square relative velocity of two molecules with different masses m and M in an equilibrium gas at temperature T.
(1) Using the delta function trick, we can write the density distribution function $F(\boldsymbol{w})$ for the relative velocity $\boldsymbol{w}$ as

$$F(\boldsymbol{w}) = \left(\frac{m}{2\pi k_BT}\right)^{3/2}\left(\frac{M}{2\pi k_BT}\right)^{3/2}\int d^3\boldsymbol{v}_1\int d^3\boldsymbol{v}_2\,\delta(\boldsymbol{w}-(\boldsymbol{v}_1-\boldsymbol{v}_2))e^{-m\boldsymbol{v}_1^2/2k_BT-M\boldsymbol{v}_2^2/2k_BT}. \tag{5.101}$$

Perform the integration over $\boldsymbol{v}_2$.
(2) Then, perform the integration over $\boldsymbol{v}_1$ to obtain $F(\boldsymbol{w})$.
(3) Find $\langle \boldsymbol{w}^2\rangle$ and check that the answer agrees with the result obtained by the equipartition of energy.

Solution.
(1) This is straightforward. By inspection, we get

$$F(\boldsymbol{w}) = \left(\frac{m}{2\pi k_BT}\right)^{3/2}\left(\frac{M}{2\pi k_BT}\right)^{3/2}\int d^3\boldsymbol{v}_1 e^{-m\boldsymbol{v}_1^2/2k_BT-M(\boldsymbol{w}-\boldsymbol{v}_1)^2/2k_BT}.$$

(2) To perform the Gaussian integral we use the trick to complete the square:

$$\begin{aligned} m\boldsymbol{v}_1^2 + M(\boldsymbol{w}-\boldsymbol{v}_1)^2 &= (m+M)\boldsymbol{v}_1^2 + M\boldsymbol{w}^2 - 2M\boldsymbol{w}\boldsymbol{v}_1 && (5.102)\\ &= (m+M)\left(\boldsymbol{v}_1 - \frac{M}{m+M}\boldsymbol{w}\right)^2 + M\boldsymbol{w}^2 - \frac{M^2}{m+M}\boldsymbol{w}^2 && (5.103)\\ &= (m+M)\left(\boldsymbol{v}_1 - \frac{M}{m+M}\boldsymbol{w}\right)^2 + \frac{mM}{m+M}\boldsymbol{w}^2. && (5.104)\end{aligned}$$

Thus, we obtain

$$F(\boldsymbol{w}) = \left(\frac{mM}{2(m+M)\pi k_BT}\right)^{3/2} e^{-\frac{mM}{m+M}\boldsymbol{w}^2/2k_BT}. \tag{5.105}$$

Notice that the appearance of the reduced mass is quite natural.
(3) The expectation value can be read off from the formula as

$$\langle \boldsymbol{w}^2\rangle = 3\frac{m+M}{mM}k_BT.$$

The result is of course consistent with the elementary results as follows:

$$\langle \boldsymbol{w}^2\rangle = \langle \boldsymbol{v}_1^2\rangle + \langle \boldsymbol{v}_2^2\rangle = \frac{3k_BT}{m} + \frac{3k_BT}{M} = 3\frac{m+M}{mM}k_BT.$$

Q5-4. We know, in equilibrium, the mean kinetic energy E is given by the equipartition of energy. What is the probability of a particle to have the kinetic energy more than the average kinetic energy $3k_BT/2$ (in equilibrium)?

Solution.
We know the density distribution of E in Appendix 4B, so we can use it, but here we proceed step by step.

$$P \equiv P(E \geq 3k_BT/2) = \langle \chi_{\{\boldsymbol{v}:v^2 \geq 3k_BT/m\}} \rangle = \int_{\{\boldsymbol{v}:v^2 \geq 3k_BT/m\}} f(\boldsymbol{v})d\boldsymbol{v}, \tag{5.106}$$

where f is Maxwell's distribution. Therefore,

$$\begin{aligned} P &= 4\pi \int_{\sqrt{3k_BT/m}}^{\infty} \left(\frac{m}{2\pi k_BT}\right)^{3/2} e^{-mv^2/2k_BT} v^2 dv \qquad (5.107) \\ &= \frac{4}{\sqrt{\pi}} \int_{\sqrt{3/2}}^{\infty} e^{-x^2} x^2 dx \simeq 0.39. \qquad (5.108) \end{aligned}$$

This should be less than 1/2 because we can expect very high energy but rare particles.

Q5-5. There are N particles which can be in one of the two states A and B. State A has a potential energy about $U = 0.2k_BT$ higher than B. How many particles N do you need to estimate U within 1% (relative) error from a single measurement of the occupation probability of state A (i.e., N_A/N) in equilibrium at temperature T (according to the usual law of large numbers estimate)? [In this question, you must assume your 'failure tolerance level', e.g., a larger than ε error once in 100 observations, or once in 500 observations, etc. Choose your tolerance level.]

Solution.
This is a LLN problem. $p_A = N_A/N$ is the empirical probability you can measure. We know $N_A/N_B = e^{-U/k_BT} \simeq e^{-0.2} = 0.8187$, and $N = N_A + N_B$

$$p_A = 1/(1 + e^{\beta U}) \simeq 0.45 \tag{5.109}$$

LLN tells us for any ε (> 0), if P_A is the true probability of state A (from which we may compute accurate U)

$$P(|p_A - P_A| > \varepsilon) < \frac{V(p_A)}{\varepsilon^2 N}, \tag{5.110}$$

where $V(p_A)$ is the variance of p_A: $V(p_A) = P_A(1 - P_A) \simeq p_A(1 - p_A) = 0.248$. We tolerate the relative error of 1% in U (i.e., $\Delta U/U \sim 0.01$). The tolerated error is estimated as

$$|\Delta p_A| = p_A^2 e^{\beta U} \beta U(\Delta U/U) = 0.45^2 \times e^{0.2} \times 0.2 \times 0.01 = 0.000494. \tag{5.111}$$

Therefore, $\varepsilon = 0.0005$. Thus, the error bound in the above formula reads

$$\frac{V(p_A)}{\varepsilon^2 N} = \frac{0.248}{(0.0005)^2 N}, \tag{5.112}$$

If we allow one failure in 1000 observations, this must be less than 1/1000. Therefore,

$$N > 248/(0.0005)^2 = 1. \times 10^9. \tag{5.113}$$

Discussion 3

We discuss the Maxwell distribution, the Boltzmann factor and the use of δ-function.

D3.1 [Use of δ-function]
Suppose we know how to compute the average $\langle\ \rangle_u$ over a random variable u. Then, the density distribution function f for $x = \varphi(u)$ is given by (see **5.16**)

$$f(x) = \langle \delta(x - \varphi(u)) \rangle_u. \tag{5.114}$$

This is the most important formula for density distribution functions.

(1) You must be able to explain why this is so.
(2) Next, you should be able to use δ-functions. Compute the following integrals.

$$\text{(i)} \qquad \int_0^2 dx\, \delta(x-1)(x^2+2x-3). \tag{5.115}$$

$$\text{(ii)} \qquad \int_0^1 dx\, \delta(x-\pi/3)\cos x. \tag{5.116}$$

$$\text{(iii)} \qquad \int_0^2 dx\, \delta(3x-\pi)\cos x. \tag{5.117}$$

$$\text{(iv)} \qquad \int_0^\infty dx\, \delta(x^2-3x-4)x^3. \tag{5.118}$$

$$\text{(v)} \qquad \int_{-\infty}^\infty dx\, \delta(x^3+2x^2-x-2)e^x. \tag{5.119}$$

Solution.
(1) The density distribution function is defined by the following 'derivative'[121] in terms of the indicator χ_{dx} of the volume element dx:

$$f(x) = \frac{P(dx)}{dx}. \tag{5.120}$$

Therefore, we may perform the following formal calculation

$$f(x) = \frac{\langle \chi_{dx}(\varphi(u)) \rangle_u}{dx} = \langle \delta(x - \varphi(u)) \rangle_u, \tag{5.121}$$

where δ may be intuitively understood as

$$\delta(x-y)dx = \begin{cases} 0, & \text{if } x \neq y, \\ 1, & \text{if } x = y. \end{cases} \tag{5.122}$$

[121] Actually, the Radon-Nikodym derivative.

(2)
(i)

$$\int_0^2 dx\,\delta(x-1)(x^2+2x-3) = (x^2+2x-3)_{x=1} = 0. \tag{5.123}$$

(ii)

$$\int_0^1 dx\,\delta(x-\pi/3)\cos x = 0, \tag{5.124}$$

because $\pi/3 \notin [0,1]$.

(iii) We use $|a|\delta(ax) = \delta(x)$, so $3\delta(3x-\pi) = \delta(x-\pi/3)$:

$$\int_0^2 dx\,\delta(3x-\pi)\cos x = \int_0^2 dx\,\frac{1}{3}\delta(x-\pi/3)\cos x = \frac{1}{3}\cos\frac{\pi}{3} = \frac{1}{6}. \tag{5.125}$$

(iv) Since $x^2-3x-4 = (x-4)(x+1)$, $x=4$ is only zero that matters in $[0,\infty)$, so on this interval

$$\delta(x^2-3x-4) = \frac{1}{|2x-3|}\delta(x-4) = \frac{1}{5}\delta(x-4). \tag{5.126}$$

Therefore,

$$\int_0^\infty dx\,\delta(x^2-3x-4)x^3 = \frac{1}{5}\int_0^\infty dx\,\delta(x-4)x^3 = \frac{64}{5}. \tag{5.127}$$

(v) Since $x^3+2x^2-x-2 = (x-1)(x^2+3x+2) = (x-1)(x+1)(x+2)$,

$$\delta(x^3+2x^2-x-2) = \frac{1}{|3x^2+4x-1|}[\delta(x-1)+\delta(x+1)+\delta(x+2)] \tag{5.128}$$

$$= \frac{1}{6}\delta(x-1)+\frac{1}{2}\delta(x+1)+\frac{1}{3}\delta(x+2). \tag{5.129}$$

Therefore,

$$\int_{-\infty}^\infty dx\,\delta(x^3+2x^2-x-2)e^x = \int_{-\infty}^\infty dx\,\left[\frac{1}{6}\delta(x-1)+\frac{1}{2}\delta(x+1)+\frac{1}{3}\delta(x+2)\right]e^x \tag{5.130}$$

$$= \frac{e}{6}+\frac{e^{-1}}{2}+\frac{e^{-2}}{3} = \frac{1}{3}\cosh(1)+\frac{2e^{-3/2}}{3}\cosh(1/2). \tag{5.131}$$

D3.2 [2D ideal gas][122]

There is a 2D ideal gas in equilibrium at temperature T.
Let us introduce the following notations:

$\overline{v}$: the root mean square velocity[123] of the particles.
v_p: the mode (= the most probable) speed[124] of the particles.
v_m: the median speed[125] of the particles.
$\overline{v}_s$: the average speed[126] of the particles.

(1) Calculate all the quantities. [Calculate the density distribution for the speed; using the δ-function is handy.]
(2) Show that generally $\overline{v} \geq \overline{v}_s$ (even if the gas is not in equilibrium).
(3) Is there any general inequality between v_p and v_m irrespective of the actual distribution?

Remark. You may use some software to perform integrals, BUT I strongly recommend you not to do so blindly. Use it sparingly. My solution will not use it.

Solution.
(1) Since all are wrt the speed (even $\overline{v} = \sqrt{\langle \boldsymbol{v}^2 \rangle} = \sqrt{\langle |\boldsymbol{v}|^2 \rangle} = \sqrt{\langle v^2 \rangle}$), let us determine the density distribution function $f(v)$ for the speed $v = |\boldsymbol{v}|$.

$$f(v) = \langle \delta(v - |\boldsymbol{v}|) \rangle = \int_{\boldsymbol{v} \in \mathbb{R}^2} d^2\boldsymbol{v}\, \delta(v - |\boldsymbol{v}|) \left(\frac{m}{2\pi k_B T} \right) e^{-m\boldsymbol{v}^2/2k_BT} \tag{5.132}$$

$$= \int_0^\infty 2\pi |\boldsymbol{v}| d|\boldsymbol{v}|\, \delta(v - |\boldsymbol{v}|) \left(\frac{m}{2\pi k_B T} \right) e^{-m|\boldsymbol{v}|^2/2k_BT} \tag{5.133}$$

$$= \int_0^\infty 2\pi u du\, \delta(v - u) \left(\frac{m}{2\pi k_B T} \right) e^{-mu^2/2k_BT} \tag{5.134}$$

$$= 2\pi v \left(\frac{m}{2\pi k_B T} \right) e^{-mv^2/2k_BT} = \frac{m}{k_B T} v e^{-mv^2/2k_BT}. \tag{5.135}$$

This can also be obtained easily with an elementary change of variables. Confirm that this is indeed normalized.

Let us calculate a general formula:

$$\langle v^\alpha \rangle = \int_0^\infty dv\, \frac{m}{k_B T} v^{1+\alpha} e^{-mv^2/2k_BT} \tag{5.136}$$

$$= \int_0^\infty \sqrt{\frac{k_B T}{2mx}} dx\, \frac{m}{k_B T} \left(\sqrt{\frac{2k_B T}{m}} \sqrt{x} \right)^{1+\alpha} e^{-x} \tag{5.137}$$

---

[122] This is related to **Q5-1**.
[123] $\sqrt{\langle \boldsymbol{v}^2 \rangle}$.
[124] the most frequent speed.
[125] the speed such that the probability of a particle to have the speed less than that is 1/2.
[126] $\langle |\boldsymbol{v}| \rangle$.

$$= \int_0^\infty \frac{1}{\sqrt{2k_BTx/m}} dx \left(\sqrt{\frac{2k_BT}{m}}\sqrt{x}\right)^{1+\alpha} e^{-x} \tag{5.138}$$

$$= \int_0^\infty dx \left(\sqrt{\frac{2k_BT}{m}}\sqrt{x}\right)^{\alpha} e^{-x} \tag{5.139}$$

$$= \left(\frac{2k_BT}{m}\right)^{\alpha/2} \Gamma(1+\alpha/2), \tag{5.140}$$

where Γ is the Gamma function defined by

$$\Gamma(x) = \int_0^\infty t^{x-1}e^{-t}dt \tag{5.141}$$

for x whose real part is positive.[127] $\Gamma(1/2) = \sqrt{\pi}$ (just a disguised Gaussian integral), $\Gamma(1) = 1$, and note that

$$\Gamma(x+1) = x\Gamma(x), \tag{5.142}$$

because

$$\Gamma(x+1) = \int_0^\infty dt\, t^x e^{-t} = -\int_0^\infty dt\, t^x \frac{d}{dt}e^{-t} = t^x e^{-t}\big|_{t=0}^\infty + x\int_0^\infty dt\, t^{x-1}e^{-t} = x\Gamma(x). \tag{5.143}$$

Therefore, for example, $\Gamma(5/2) = (3/2)\Gamma(3/2) = (3/4)\sqrt{\pi}$, and $\Gamma(N+1) = N!$ for positive integer N.

As you see from the formula (5.139), if α is an even positive integer, we can perform the integral in an elementary fashion. Otherwise, I do not believe you can do it easily; you need an integral table (obsolete now) or some software. However, you should understand why the result is rather aesthetic with $\sqrt{\pi}$ instead of an ugly number. See

`http://www.yoono.org/ApplicableMath/ApplicableMath_files/AMI-9.pdf`

for a fairly quick study of the Gamma function, or the real reference `http://dlmf.nist.gov/5`. The latter is a NIST applied math site, useful for practitioners.

Thus,

$$\overline{v}^2 = \frac{2k_BT}{m}\Gamma(2) = \frac{2k_BT}{m}. \tag{5.144}$$

That is,

$$\overline{v} = \sqrt{\frac{2k_BT}{m}}. \tag{5.145}$$

[127]and then is analytically continued to the complex plane except for non-positive integers. Since Phys 427 is a course taken by those who are graduating from physics, I take it for granted that you know elementary analysis (with multivariate functions), linear algebra, complex analysis and differential equations.

This can be obtained immediately from the equipartition of kinetic energy **2.15** $m\overline{v}^2/2 = k_BT$ (in 2D!).

$$\overline{v}_s = \left(\frac{2k_BT}{m}\right)^{1/2}\Gamma(3/2) = \sqrt{\frac{\pi k_BT}{2m}} \simeq \sqrt{\frac{1.57k_BT}{m}} \tag{5.146}$$

The mode speed is obtained from the peak position of $f(v)$. It is wise to use the logarithmic derivative to obtain

$$\frac{d}{dv}\left(\log v - \frac{mv^2}{2k_BT}\right) = \frac{1}{v} - \frac{mv}{k_BT} = 0. \tag{5.147}$$

Therefore,

$$v_p = \sqrt{\frac{k_BT}{m}}. \tag{5.148}$$

The median speed v_m is obtained by

$$\frac{1}{2} = \int_0^{v_m} dv\, f(v) = \int_0^{v_m} dv\, \frac{mv}{k_BT}e^{-mv^2/2k_BT} = \int_0^{mv_m^2/2k_BT} dx\, e^{-x} = 1 - e^{-mv_m^2/2k_BT}. \tag{5.149}$$

That is, $mv_m^2/2k_BT = \log 2$ or

$$v_m = \sqrt{\frac{(2\log 2)k_BT}{m}} \simeq \sqrt{\frac{1.386k_BT}{m}}. \tag{5.150}$$

Thus, we have realized in equilibrium in 2-space

$$\overline{v} > \overline{v}_s > v_m > v_p \tag{5.151}$$

as illustrated in Fig. 5.6A.

In our case, because of the density distribution tail, $\overline{v}_s$ is larger than v_m. If the system is not in equilibrium, then $\overline{v}_s$ can be smaller than v_m.

(2) $\overline{v}^2 = \langle v^2\rangle$. We know the variance of the speed $\langle v^2\rangle - \langle v\rangle^2 = \overline{v}^2 - \overline{v}_s^2$ is non-negative, so irrespective of the state of the gas, $\overline{v} \geq \overline{v}_s$.

(3) Anything goes, since for a given density distribution you can place the peak anywhere you wish without changing the median at all (anything is possible as demonstrated by Fig. 5.6B).

D3.3 [Boltzmann factor]

We need the Boltzmann constant k_B although we will discuss how to determine its value later. Here is a summary:

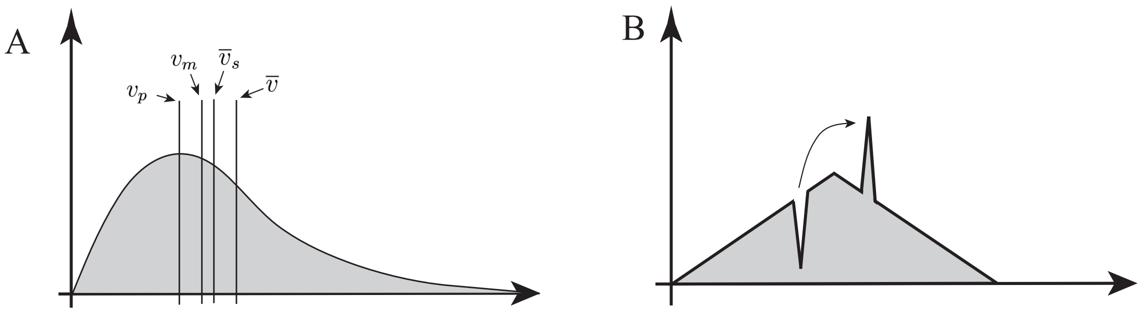


Figure 5.6: A: Illustration of (5.151). $f(v)$ is the shaded figure. B shows that you can place v_p 'anywhere' you wish without changing v_m at all. The 'spike' is dug up from the left hand side and 'grafted' to the right.

Summary of the Boltzmann constant $\boldsymbol{k_B}$[128]
It would be practical to have some sense of the magnitude of the Boltzmann constant.

$$
\begin{aligned}
k_B &= 1.3806503 \times 10^{-23} \text{ J/K} \\
&= 1.3806503 \times 10^{-2} \text{ pN·nm/K} \\
&= 8.617343 \times 10^{-5} \text{ eV/K.}
\end{aligned}
$$

The *gas constant* R is defined by

$$
R \equiv N_A k_B = 8.314462 \text{ J/mol·K} = 1.986 \text{ cal/mol·K.} \tag{5.152}
$$

Here, $N_A = 6.02214078(18) \times 10^{23}$/mol is *Avogadro's constant* and 1 cal = 4.18605 J.

It is convenient to remember that at room temperature (300 K):[129]

$$
\begin{aligned}
k_B T &= 4.14 \text{ pN·nm} \\
&= 0.026 \text{ eV,} \\
RT &= 2.49 \text{ kJ/mol} = 0.6 \text{ kcal/mol.}
\end{aligned}
$$

(1) There is a potential step of height 4.2 pN·nm as shown in Fig. 5.7. The system is assumed to be uniform (within the walls parallel to the sheet of paper). The particles in the box barely interact with each other (i.e., as an ideal gas). What is the ratio of the number densities in A and in B: n_B/n_A at 300 K? [See the summary of the Boltzmann constant at the end.]

[128] ⟪**Representative energy scales**⟫ 5∼10 pN is a typical force felt or exerted by molecular machines; a few nm is a typical displacement of molecular motors. Cf., the diameter of DNA is 2 nm (its pitch is 3.4 nm); the α-helix pitch is 3.6 amino acid residues = 0.54 nm. To ionize an atom, a few electron volts are needed, so, if T is the room temperature (300 K), it is about 100 k_BT. Note that even on the surface of the sun (with the temperature corresponding to the black body radiation of about 6000 K; see **23.5**), hydrogen atoms are not significantly ionized.

[129] Under physiological condition, hydrolysis of a single ATP molecule provides about $20k_BT$.

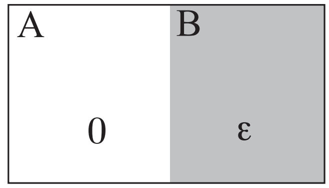


Figure 5.7: A box with a potential step of height $\varepsilon = 4.2$ pN·nm. The gray portion is with potential energy ε higher relative to the white portion in the container.

(2) There are two one-particle states the energy gap between which is $150k_B$ (in K). We have two particles that do not energetically interact. What is the probability to find only one particle in the higher energy one-particle state at $T = 300$ K (Recall **D2.1**(2)),

(i) if the particles are identical fermions?
(ii) if the particles are identical bosons?
(iii) if the particles are not identical?

(3) A typical intermolecular force (in 3-space) is described by the Lenard-Jones potential $\varphi(r)$:

$$\varphi(r) = 4\varepsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6} \right], \tag{5.153}$$

which is illustrate in Fig. 5.8.

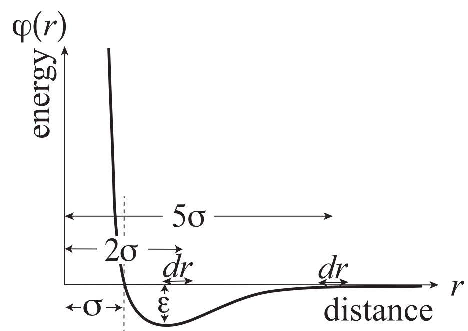


Figure 5.8: Lenard-Jones potential

Let us assume realistic values[130] $\varepsilon/k_B = 150$ (in K) and $\sigma = 3.5 \times 10^{-10}$ m. Estimate the ratio of probabilities to find another particle (of the same chemical species) around 2σ and around 5σ from the origin. Here, 'around' means the shells of thickness dr. Do not forget that the particles are in 3-space.

Solution.
(1) This is a trivial question $n_B = n_A e^{-\varepsilon/k_B T}$. $\varepsilon/k_B T = 4.2/4.12 \simeq 1.014$, so $n_B/n_A = e^{-1.014} = 0.36$.

(2) Let us illustrate the possible microstates:

[130]e.g., cf. E. Wilhelm and R. Battino, Estimation of Lennard-Jones (6,12) Pair Potential Parameters from Gas Solubility Data, J. Chem. Phys., **55**, 4012 (1971).

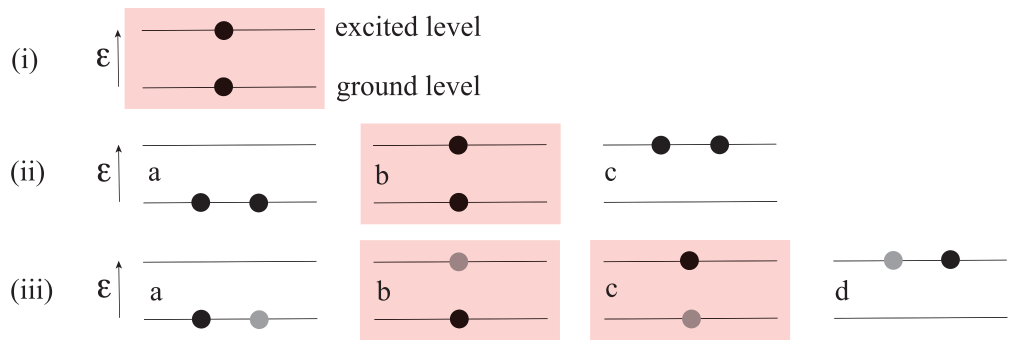


Figure 5.9: Two-level system; (i) fermions, (ii) bosons, (iii) distinguishable case. Red shaded microstates meet the required condition.

All the possible cases are illustrated in Fig. 5.9.
(i) For fermions there is only one microstate, so with probability 1 (i.e., for sure) we find one particle in the higher energy level (higher-energy one-particle state).
(ii) For bosons there are three states. To place a particle in the 'excited state' costs you energy (or potential energy) $\varepsilon = 150k_B$, so for $T = 300$ K the probability to find it relative to the ground level is $e^{-\varepsilon/k_BT} = e^{-0.5} = 0.607$. If you wish to put two particles we need another Boltzmann factor $e^{-\varepsilon/k_BT}$. This means that exp(−total energy needed/k_BT) is the ratio we need. Thus we, see in Fig. 5.9 (ii): (a) is the lowest energy microstate. Relative to the probability of this state, the probability of (b) is $e^{-\beta\varepsilon}$, and (c) $e^{-2\beta\varepsilon}$. (b) is the only state satisfying our requirement; the probability of (b) is given by

$$\frac{e^{-\beta\varepsilon}}{1+e^{-\beta\varepsilon}+e^{-2\beta\varepsilon}} = \frac{0.607}{1+0.607+0.607^2} = \frac{0.607}{1.975} = 0.31. \tag{5.154}$$

(iii) From the calculation in (ii) you should have concluded that the answer should be

$$\frac{2e^{-\beta\varepsilon}}{1+2e^{-\beta\varepsilon}+e^{-2\beta\varepsilon}} = \frac{2\times 0.607}{1+2\times 0.607+0.607^2} = \frac{1.214}{2.585} = 0.47. \tag{5.155}$$

(3) The Boltzmann factor gives us the ratio of the number density of the center of the molecules around these locations. However, since the world is 3D, we must take the difference in shell surface areas (actually the volume ratio of the thin shells of thickness dr) into account. The ratio is $(5/2)^2 = 6.25$. The needed Boltzmann factor is

$$e^{-\beta\varphi(5\sigma)}/e^{-\beta\varphi(2\sigma)}, \tag{5.156}$$

so the ratio of probabilities to find particle centers at distance 5σ and at 2σ from the origin is

$$6.25\times e^{-\beta\varphi(5\sigma)+\beta\varphi(2\sigma)}. \tag{5.157}$$

Since the repulsive part (with the power 12) should not be effective, we have

$$\beta\varphi(5\sigma) = -2\left(\frac{1}{5}\right)^6 = -0.0001,\ \ \beta\varphi(2\sigma) = -2\left(\frac{1}{2}\right)^6 = -0.0312. \tag{5.158}$$

Thus we get $6.25e^{-0.0311} \simeq 6.25 \times 0.97 = 6.06$.

D3.4 [Harmonic potential]
A point mass of mass $m = 1.2$ pg is tethered at the origin with a harmonic spring with the spring constant $k = 3.2$ pN/nm.[131]
(1) Find the (correctly normalized) density distribution function $f(\boldsymbol{r})$ of its location $\boldsymbol{r}$ in 3-space.
(2) What is the density distribution function $g(\ell)$ of the length ℓ of the spring?
(3) What is the mean-square displacement of the point mass from the origin?
(4) What is the most probable ℓ?

Solution.
Notice that (3) may be answered without calculation, if you refer to (or mimic the calculation of) the equipartition of the kinetic energy.
(1) The Boltzmann factor tells us the probability ratio for volume elements (of the same volume) is

$$e^{-\beta k\boldsymbol{r}^2/2}, \tag{5.159}$$

which is a product of three independent Gaussian distributions just as 3-Maxwell **5.7**: for $\boldsymbol{r} = (x, y, z)^T$

$$e^{-\beta kx^2/2}e^{-\beta ky^2/2}e^{-\beta kz^2/2}. \tag{5.160}$$

If you look at the expression for the Maxwell distribution **5.7** or **5.6**, we get the normalization constant easily without any new calculation: for x

$$\sqrt{\frac{k}{2\pi k_BT}}e^{-\beta kx^2/2}. \tag{5.161}$$

Hence,

$$f(\boldsymbol{r}) = \left(\frac{k}{2\pi k_BT}\right)^{3/2} e^{-\beta k\boldsymbol{r}^2/2}. \tag{5.162}$$

(2) By definition, since $\ell = |\boldsymbol{r}|$

$$g(\ell) = \langle\delta(\ell - |\boldsymbol{r}|)\rangle_{\boldsymbol{r}}. \tag{5.163}$$

There are many ways to compute this, but let us use the most mechanical way (trivial way; the way you need not use your brain too much):

$$g(\ell) \;\; = \;\; \left(\frac{k}{2\pi k_BT}\right)^{3/2} \int_{\mathbb{R}^3} d^3\boldsymbol{r}\, e^{-\beta k\boldsymbol{r}^2/2}\delta(\ell - |\boldsymbol{r}|) \tag{5.164}$$

[131] These units are convenient ones for biomacromolecules.

$$
\begin{aligned}
&= 4\pi\left(\frac{k}{2\pi k_B T}\right)^{3/2}\int_0^\infty L^2 dL\, e^{-\beta k L^2/2}\delta(\ell - L) && (5.165)\\
&= 4\pi\left(\frac{k}{2\pi k_B T}\right)^{3/2}\ell^2 e^{-\beta k\ell^2/2}. && (5.166)
\end{aligned}
$$

(3) Comparing with the equipartition law, we can guess

$$
\left\langle \frac{1}{2}kx^2\right\rangle = \frac{1}{2}k_B T, \tag{5.167}
$$

so we have

$$
\sqrt{\langle \boldsymbol{r}^2\rangle} = \sqrt{3\frac{k_B T}{k}} = \sqrt{\langle \ell^2\rangle}. \tag{5.168}
$$

Let us check. Using $g(\ell)$ (5.166), we have (I did all the calculations here)

$$
\begin{aligned}
\langle \ell^2\rangle &= 4\pi\left(\frac{k}{2\pi k_B T}\right)^{3/2}\int_0^\infty d\ell\,\ell^4 e^{-\beta k\ell^2/2} && (5.169)\\
&= 4\pi\left(\frac{k}{2\pi k_B T}\right)^{3/2}\int_0^\infty dz\, 2^{3/2} z^{3/2} e^{-\beta k z} && (5.170)\\
&= 4\pi\left(\frac{k}{2\pi k_B T}\right)^{3/2}(\beta k/2)^{-5/2}\frac{1}{2}\int_0^\infty dx x^{3/2}e^{-x} && (5.171)\\
&= 4\pi\left(\frac{k}{2\pi k_B T}\right)^{3/2}(\beta k/2)^{-5/2}\frac{1}{2}\Gamma(5/2) && (5.172)\\
&= \frac{4\pi}{\pi^{3/2}}(\beta k/2)^{-1}\frac{3}{8}\sqrt{\pi} = 3k_B T/k. && (5.173)
\end{aligned}
$$

(4) Let us find the max for $\log g(\ell)$: its derivative is

$$
\frac{2}{\ell} - \beta k\ell = 0. \tag{5.174}
$$

Therefore,

$$
\ell_{\text{mode}} = \sqrt{\frac{2k_B T}{k}}. \tag{5.175}
$$

This can be guessed from the 3-Maxwell result [just below (5.70)].

Exercise 3

E3.1 [δ-function exercise]
Evaluate the following expressions

$$(1) \qquad \int_{\pi/10}^{19\pi/10} d\theta\, \delta(\sin\theta)\cos\theta. \tag{5.176}$$

$$(2) \qquad \int_{-1/2}^{\infty} dx\, e^{-x}\delta(\sin(\pi x)). \tag{5.177}$$

$$(3) \qquad \int_{-\infty}^{\infty} dx\, |x|\, \delta(2x^2 - 5x - 3). \tag{5.178}$$

Solution.
(1) $\sin\theta$ vanishes only at $\theta = \pi$ in $[\pi/10, 19\pi/10]$, so

$$\delta(\sin\theta) = \frac{1}{|\cos\theta|}\delta(\theta - \pi), \tag{5.179}$$

$$\int_{\pi/10}^{19\pi/10} d\theta\, \delta(\sin\theta)\cos\theta = \int_{\pi/10}^{19\pi/10} d\theta\, \frac{\cos\theta}{|\cos\theta|}\delta(\theta - \pi) = -1. \tag{5.180}$$

(2) $\sin\pi x = 0$ for any $x = n \in \mathbb{N}$. Therefore, in $[-1/2, \infty)$

$$\delta(\sin\pi x) = \frac{1}{\pi|\cos\pi x|}\sum_{n=0}^{\infty}\delta(x - n) = \frac{1}{\pi}\sum_{n=0}^{\infty}\delta(x - n). \tag{5.181}$$

Hence,

$$\int_{-1/2}^{\infty} dx\, e^{-x}\delta(\sin(\pi x)) = \int_{-1/2}^{\infty} dx\, \frac{1}{\pi}\sum_{n=0}^{\infty}\delta(x-n)e^{-x} = \frac{1}{\pi}\sum_{n=0}^{\infty} e^{-n} = \frac{1}{\pi}\frac{e}{e-1}. \tag{5.182}$$

(3) $2x^2 - 5x - 3 = (2x+1)(x-3)$, so

$$\delta(2x^2 - 5x - 3) = \frac{1}{|4x - 5|}[\delta(x-3) + \delta(x+1/2)] = \frac{1}{7}[\delta(x-3) + \delta(x+1/2)]. \tag{5.183}$$

Therefore,

$$\int_{-\infty}^{\infty} dx\, |x|\, \delta(2x^2 - 5x - 3) = \int_{-\infty}^{\infty} dx\, |x| \times \frac{1}{7}[\delta(x-3) + \delta(x+1/2)] = \frac{1}{7}(3 + 0.5) = \frac{1}{2}. \tag{5.184}$$

E3.2 [3-Harmonic potential energy]
Find the potential energy distribution $F(U)$ for the 3-harmonic oscillator already

described in **D3.4**. Here, $U = k\boldsymbol{r}^2/2$.

Solution.
We have only to evaluate

$$F(U) = \langle \delta(U - k\boldsymbol{r}^2/2)\rangle_{\boldsymbol{r}}. \tag{5.185}$$

We know the density distribution function f for $\boldsymbol{r}$ (see (5.162)). Thus

$$F(U) = \int_{\mathbb{R}} d^3\boldsymbol{r} \left(\frac{k}{2\pi k_B T}\right)^{3/2} e^{-\beta k\boldsymbol{r}^2/2}\delta(U - k\boldsymbol{r}^2/2). \tag{5.186}$$

You can simply mimic the Maxwell case, but here, let us proceed step by step.

It is convenient to convert the integral to a 1D integral. We use the spherical symmetry of the system, so we may introduce the spherical coordinates and integrate over the solid angle (obtaining 4π):

$$F(U) = 4\pi \left(\frac{k}{2\pi k_B T}\right)^{3/2} \int_0^\infty d\ell\, \ell^2 e^{-\beta k\ell^2/2}\delta(U - k\ell^2/2). \tag{5.187}$$

We know (note that $\ell \geq 0$)

$$\delta(U - k\ell^2/2) = \frac{1}{k\ell}\delta(\ell - \sqrt{2U/k}). \tag{5.188}$$

Thus,

$$\begin{aligned} F(U) &= \frac{4\pi}{k}\left(\frac{k}{2\pi k_B T}\right)^{3/2} \int_0^\infty d\ell\, \ell e^{-\beta k\ell^2/2}\delta(\ell - \sqrt{2U/k}) && (5.189)\\ &= \frac{4\pi}{k}\left(\frac{k}{2\pi k_B T}\right)^{3/2} \sqrt{\frac{2U}{k}} e^{-\beta U} && (5.190)\\ &= \frac{2^{5/2}}{2^{3/2}\pi^{1/2}}\left(\frac{1}{k_B T}\right)^{3/2} \sqrt{U} e^{-\beta U} && (5.191)\\ &= \frac{2}{k_B T}\sqrt{\frac{U}{\pi k_B T}} e^{-\beta U}. && (5.192)\end{aligned}$$

This you should have guessed.

E3.3 [Three level system][132]
There are three one-particle states with energies 0, ε and 2ε, where $\varepsilon = 150 k_B$ (in K). We have three particles that do not energetically interact. Assume $T = 300$ K.

(1) What is the probability to find only one particle in the energy 2ε one-particle

[132]Some questions are really trivial, or you may well say stupid.

state,

(i) if the particles are identical fermions?

(ii) if the particles are identical bosons?

(2) What is the probability to find no particle in the one-particle ground state,

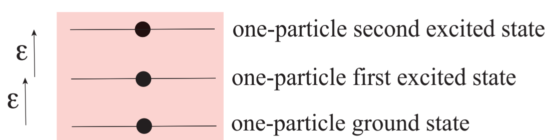
(i) if the particles are identical fermions?

(ii) if the particles are identical bosons?

Solution

It should be convenient to illustrate all the possible situations (or tabulate all the possible situations). For the fermion case there is only one microstate. For the boson case $\binom{3+3-1}{3} = 10$ distinguishable microstates.

(i)



(ii)

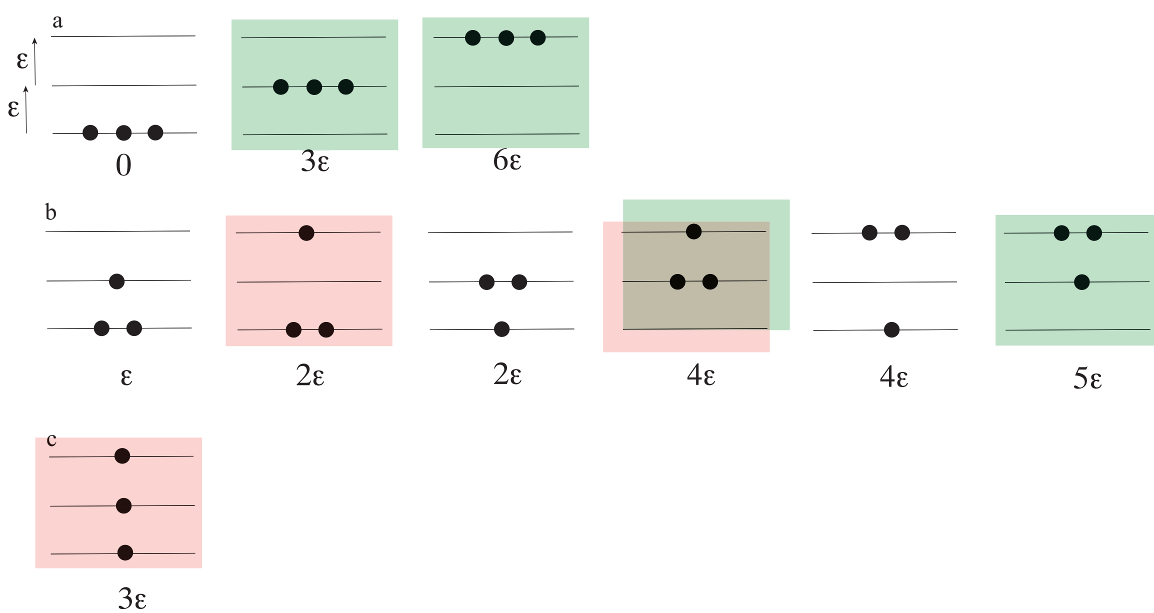


Figure 5.10: All the possible microstates: (i) is for fermions and (ii) for bosons. The energies of the microstates relative to the lowest energy microstate are denoted below each microstate.

The red shaded microstates meet the condition in (1) and the green the condition in (2).

(1)

(i) For the fermion case the possible microstate is unique: with probability one the

first excited level is occupied by one particle.
(ii) There are three red-shaded states. We must pay attention to the Boltzmann factors. The total sum Z of the Boltzmann factors is given by

$$Z = 1 + e^{-\beta\varepsilon} + 2e^{-2\beta\varepsilon} + 2e^{-3\beta\varepsilon} + 2e^{-4\beta\varepsilon} + e^{-5\beta\varepsilon} + e^{-6\beta\varepsilon}. \tag{5.193}$$

Since $\varepsilon = 150k_B$, $\beta\varepsilon = 1/2$, $e^{-\beta\varepsilon} \simeq 0.6$. Therefore,

$$\begin{aligned} Z &= 1 + 0.6 + 2(0.6)^2 + 2(0.6)^3 + 2(0.6)^4 + (0.6)^5 + (0.6)^6 && (5.194) \\ &= 1 + 0.6(1 + 0.6(2 + 0.6(2 + 0.6(2 + 0.6(1 + 0.6))))) && (5.195) \\ &= 3.14. && (5.196) \end{aligned}$$

Thus, the probability we want is given by

$$\begin{aligned} P((1)) &= \frac{1}{Z}(e^{-2\beta\varepsilon} + e^{-3\beta\varepsilon} + e^{-4\beta\varepsilon}) = (0.6^2 + 0.6^3 + 0.6^4)/3.14 && (5.197) \\ &= \frac{0.71}{3.14} \simeq 0.23. && (5.198) \end{aligned}$$

(2)
(i) 0, of course.
(ii) Now, we collect the green microstates: Thus, the probability we want is given by

$$\begin{aligned} P((2)) &= \frac{1}{Z}(e^{-3\beta\varepsilon} + e^{-4\beta\varepsilon} + e^{-5\beta\varepsilon} + e^{-6\beta\varepsilon}) && (5.199) \\ &= 0.6^3(1 + 0.6 + 0.6^2 + 0.6^3)/3.14 && (5.200) \\ &= 0.6^3\frac{1 - 0.6^4}{1 - 0.6}\frac{1}{3.14} = \frac{0.47}{3.14} \simeq 0.15. && (5.201) \end{aligned}$$

6 Mean free path and transport phenomena

Summary
∗ Clausius introduced the concept of mean free path.
∗ Linear transport phenomena are outlined. Fluxes are proportional to $(-)$gradients of the density fields.
∗ Transport coefficients in the gas phase can be estimated with the aid of elementary kinetic theory.
∗ Elementary transport theories and approximate equations of state allow us to estimate Avogadro's constant and the molecular size (as Loschmidt and Maxwell did for the first time).

Key words
Mean free path, linear transport phenomena, density, flux, gradient, divergence, conservation law, Laplacian, transport coefficient, diffusion, diffusion coefficient, shear viscosity, heat conductivity

What you should be able to do
This lecture is a bit complicated for those who have never encountered partial differential equations such as the diffusion equation. Those who feel this Lecture a bit too much (with, e.g., partial differential equations) should understand the concepts such as the mean-free path, density, flux, gradient and divergence at least intuitively, and try to understand the flow of Maxwell's logic.

Those who have without much trouble with partial differential equations should pay attention to the following:

∗ Rudimentary vector analysis should be reviewed (gradient, divergence, Laplacian; you must be able to explain their intuitive meanings).
∗ Understand how to handle the averages of vector components.
∗ You should be able to understand how to derive the partial differential equation describing the conservation law.
∗ Recognize that the law of large numbers is essential to describe the transport phenomena.
∗ Recognize that there are some relations among transport coefficients; dimensional analysis is useful.

6.1 Gas mixing is slow compared with molecular speed

Dutch meteorologist C. H. D. Buys-Ballot (1817-1890)[133] noticed that if the molecules

[133] who noticed the Buys-Ballot law: In the Northern Hemisphere, if a person stands with his

of gases really moved that fast as Clausius estimated (see **5.10**), the mixing of gases by diffusion should have been much faster than we observed it to be.

The (first half of the) following YouTube video about diffusion demonstrates the point (too elementary for most of you):

`http://www.youtube.com/watch?v=H7QsDs8ZRMI`.[134]

6.2 Molecular collisions and mean free path

Upon this criticism, Clausius (1858[135]) realized that the gas molecules have large enough diameters so a molecule cannot move very far without colliding with another one. In this way Clausius defined a new parameter called the *mean free path* ℓ of gas that describes the average distance a molecule can run between two consecutive collisions. We can obtain it with the idea of 'swept volume' by a particle (see Fig. 6.1). The moving molecule sweeps a cylinder ('swept volume') of radius d (= the diameter of the molecule).

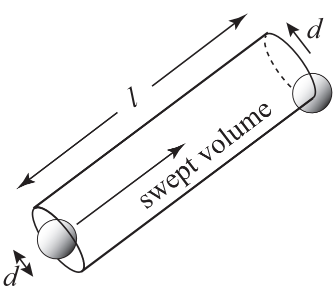


Figure 6.1: Intuitive explanation of (6.1). The swept volume is illustrated.

If this volume does not contain any center of mass of other molecules, no intermolecular collision occurs. If it contains one, there is a collision. Therefore, if the swept volume $\times n \sim 1$, where n is the number density, the height of the cylinder must be the 'mean free path' length. Hence, we guess

$$\ell = 1/n\pi d^2, \tag{6.1}$$

if all other particles are fixed in space, where πd^2 is the cross-section of the swept volume.

Actually, all the molecules are moving. When they collide, the average relative

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back to the wind, the low pressure area will be on his left (published in 1857).

[134]However, you must take into account that the demo is affected by gravity, because Br_2 is far heavier than air.

[135][1858: the Lincoln-Douglas debate, the Government of India Act. Planck ($\sim$1947) was born. However, the most important event was that the idea of natural selection was officially published by Darwin and Wallace. Physicists should recognize that Boltzmann called the 19th century the century of Darwin (not of Maxwell) (see E. Broda, *Ludwig Boltzmann, Mensch·Physiker·Philosoph* (F Deuticke, 1955) Part III).]

speed must be the relevant velocity, which is $\sqrt{2}$ times the mean velocity. That is, the molecule collides $\sqrt{2}$ times more often than the case where all other molecules are fixed in space. Therefore,

$$\ell = \frac{1}{\sqrt{2}\pi n d^2} \tag{6.2}$$

must be the true mean free path length.[136]

6.3 Why transport phenomena matter

Clausius did not have any method to estimate ℓ. However, as we can expect from the criticism by Buys-Ballot, if we could study the so-called transport phenomena, there is a hope to determine ℓ. This is a step toward estimating N. This was exactly the approach Loschmidt and Maxwell took to obtain the first realistic value of Avogadro's number **6.16**. To understand what they accomplished, we must know a bit about transport phenomena.

6.4 What is a (linear) transport phenomenon?

Suppose a macroscopic system is not far away from equilibrium. The system may be spatially nonuniform, but is macroscopically only gently so. For example, the number density of the molecules in the system may not be spatially constant and may be described as a number-density field $n(t, \boldsymbol{r})$, where t is time and $\boldsymbol{r}$ is the spatial position vector.

If there is a gentle spatial nonuniformity in some physical quantity X,[137] there is a field of its density $\hat{x}(t, \boldsymbol{r})$. We can expect a flow of this physical quantity to reduce the nonuniformity. Thus, X must be transported from one point to another. This is generally called the *transport phenomenon*. If $\partial\hat{x}/\partial t$ is a linear functional of $\hat{x}$,[138] we say the transport phenomenon is linear.

6.5 Density

Let X be a physical quantity carried by molecules. Its density around space-time

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[136] If you sit on one particle and observe other particles, their mean speed is, on the average, $\sqrt{2}$ times the actual mean speed of the particles (relative to the coordinates fixed to the ground). Thus, collisions become $\sqrt{2}$ times more frequent than when other particles are still.

[137] In transport phenomena, we are interested in 'extensive quantities.' We will learn what they are later **8.6**.

[138] F being a 'linear functional' implies the following: $F(aX_1 + bX_2) = aF(X_1) + bF(X_2)$

point $(t, \boldsymbol{r})$ may be expressed as

$$\hat{x}(t, \boldsymbol{r}) = \frac{\sum_{\boldsymbol{r}_i \in d\tau(\boldsymbol{r})} x_i}{d\tau(\boldsymbol{r})}, \tag{6.3}$$

where x_i is the amount of X carried by the ith molecule whose spatial location is $\boldsymbol{r}_i$ at time t. Here, $d\tau(\boldsymbol{r})$ indicates the volume element around $\boldsymbol{r}$, which is very small[139] from the macroscopic point of view, but it is huge from the microscopic molecular point of view. Its volume is also denoted by the same symbol $d\tau(\boldsymbol{r})$. The summation on the numerator means that we calculate the summation over particles whose centers of mass are in $d\tau(\boldsymbol{r})$. The law of large numbers tells us that $\hat{x}(t, \boldsymbol{r})$ thus defined is not appreciably fluctuating, so we identify it with the density of X at (around) $\boldsymbol{r}$ at time t.

6.6 Flux

To describe the flow of X, we need the concept of *flux*. A *flux* $\boldsymbol{J}_X$ of X is a vector pointing in the direction of the flow, whose magnitude is the amount of the quantity going through the unit cross section per unit time (see Fig. 6.2). If the system is quite uniform, then we may write $\boldsymbol{J}_X$ to be the product of the density of X and the velocity of the underlying flow carrying it: $\boldsymbol{J}_X = \hat{x}\boldsymbol{v}$.

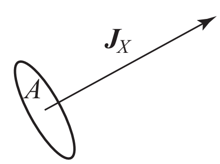

Figure 6.2: The flux vector $\boldsymbol{J}_X$ for the quantity X (here, its density is denoted by $\hat{x}$): its direction is the transport direction, and its magnitude is the flow rate: the quantity of X through the area A perpendicular to $\boldsymbol{J}_X$ (converted to the amount per unit area) per unit time.

This expression may be microscopically written as

$$\boldsymbol{J}_X = \frac{\sum_{\boldsymbol{r}_i \in d\tau(\boldsymbol{r})} x_i \boldsymbol{v}_i}{d\tau(\boldsymbol{r})}. \tag{6.4}$$

6.7 Gradient and nabla ∇

If the transport phenomenon is linear, the flux $\boldsymbol{J}_X$ of X is proportional to the

[139]But *still* macroscopic in the sense that the number of particles in it is, say, 10^{10}. For an ordinary gas in the so-called standard state (at 1 atm-273K), its volume is about 200×10^{-6} mm^3 $\simeq$ a cube with 60 μm edge. It may be a bit larger than our cells.

gradient of its density, grad $\hat{x}(\boldsymbol{r})$ (its direction is opposite; cf. Fig. 6.3; here time t is suppressed):

$$\boldsymbol{J}_X = -L\,\mathrm{grad}\,\hat{x}(\boldsymbol{r}), \tag{6.5}$$

where L is a positive constant called the *transport coefficient*.

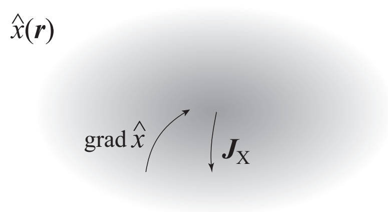

Figure 6.3: Gentle nonuniformity causes linear transport phenomena. The gradient vector *grad* $\hat{x}$ points in the direction of increasing density $\hat{x}$ (darker region), so the flux driven by the gradient points in the $-$*grad* $\hat{x}$ direction.

The *gradient* of $\hat{x}$ is the following vector:

$$\mathrm{grad}\,\hat{x} \equiv \nabla\hat{x} = \frac{\partial\hat{x}}{\partial x}\boldsymbol{e}_x + \frac{\partial\hat{x}}{\partial y}\boldsymbol{e}_y + \frac{\partial\hat{x}}{\partial z}\boldsymbol{e}_z, \tag{6.6}$$

where $\boldsymbol{e}_k$ is the directional vector (unit vector) in the k-axis direction. That is, componentwisely,

$$\mathrm{grad}\,\hat{x} = \left(\frac{\partial\hat{x}}{\partial x}, \frac{\partial\hat{x}}{\partial y}, \frac{\partial\hat{x}}{\partial z}\right). \tag{6.7}$$

∇ is an operator called *nabla* (usually it is read as 'del') and may be understood as the following vector:

$$\nabla = \boldsymbol{e}_x\frac{\partial}{\partial x} + \boldsymbol{e}_y\frac{\partial}{\partial y} + \boldsymbol{e}_z\frac{\partial}{\partial z} = \left(\frac{\partial}{\partial x}, \frac{\partial}{\partial y}, \frac{\partial}{\partial z}\right). \tag{6.8}$$

$\nabla\hat{x}$ may be understood as the product of a vector ∇ and a scalar $\hat{x}$ (needless to say, you cannot change the order of this product, since ∇ is operating on $\hat{x}$).

Intuitively, you can imagine a landscape with altitude X given as a function of the position, and then a vector pointing the steepest ascending direction at a location $\boldsymbol{r}$ with its size give by the slope of the landscape along the vector at $\boldsymbol{r}$. The vector is 'grad X' at $\boldsymbol{r}$.

6.8 Divergence

If X is conserved, the amount of change of this quantity at a given position must be equal to the net influx of X to that position. Therefore, if we introduce an operator div (read as 'divergence') that allows us to compute the net output of X from a point based on the flux $\boldsymbol{J}_X$ at the position, the conservation law for X may be expressed as

$$\frac{\partial \hat{x}(\boldsymbol{r})}{\partial t} = -\mathrm{div}\,\boldsymbol{J}_X(\boldsymbol{r}). \tag{6.9}$$

Here, 'div' is out-going quantity, so $-$ is put. The *divergence div* $\boldsymbol{J}_X$ of the flux $\boldsymbol{J}_X$ of X at point P (the total amount of output per unit volume per unit time) may be defined as:

$$\mathrm{div}\,\boldsymbol{J}_X = \lim_{V\to P}\frac{\int_{\partial V}\boldsymbol{J}_X\cdot d\boldsymbol{S}}{\int_V d\tau}. \tag{6.10}$$

Here, $\lim_{V\to P}$ implies the limit along the sequence of nested (singly connected) volumes V converging to point P (Fig. 6.4Left) with its surface denoted by ∂V.[140] $d\boldsymbol{S}$ is the surface area element, whose direction is the outward normal direction, and whose magnitude (area) is dS (see Fig. 6.4Right). Thus, the numerator on the right-hand side is the total amount of X going out of the volume V in unit time.

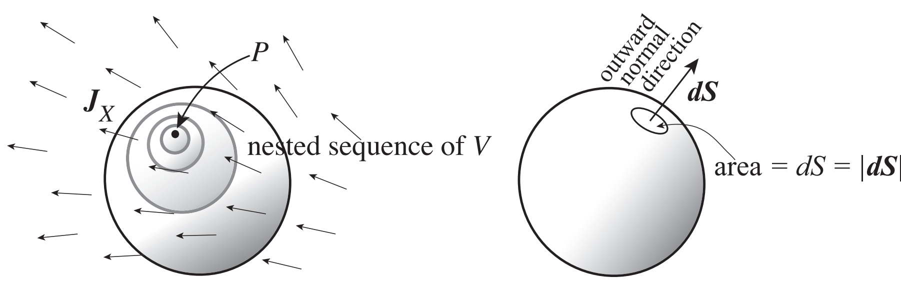

Figure 6.4: The divergence of the flux $\boldsymbol{J}_X$ at P is defined by the limit over the nested sequence of volumes V converging to a point P: *div* $\boldsymbol{J}_X = \lim_{V\to P}\int_{\partial V}\boldsymbol{J}X\cdot d\boldsymbol{S}/\int_V d\tau$.

6.9 Cartesian expression of divergence

We use the Cartesian coordinate system,

$$\begin{aligned}&\lim_{V\to P}\frac{\int_{\partial V}\boldsymbol{J}_X\cdot d\boldsymbol{S}}{\int_V d\tau}\\ =\;&\frac{[J_x(x+dx,y,z)-J_x(x,y,z)]dydz+[J_y(x,y+dy,z)-J_y(x,y,z)]dzdx+[J_z(x,y,z+dz)-J_z(x,y,z)]dxdy}{dxdydz}.\end{aligned} \tag{6.11}$$

That is,

$$\mathrm{div}\,\boldsymbol{J}_X = \frac{\partial J_x}{\partial x}+\frac{\partial J_y}{\partial y}+\frac{\partial J_z}{\partial z} = \nabla\cdot\boldsymbol{J}_X. \tag{6.12}$$

The rightmost expression implies that divergence can be formally written as the scalar product of ∇ and the flux vector. If you need a review of vector analysis, go

[140] ∂A is the standard notation for the boundary of the set A.

to, e.g., Section 2.C. of
https://www.dropbox.com/home/ApplMath?preview=AMI-2+DifferentiationRevisited.pdf

6.10 Local expression of conservation law

Suppose the density $\hat{x}$ is conserved. The total amount of X coming into the volume element $d\tau = dxdydz$, that is, $-\mathrm{div}\, \boldsymbol{J}_X\, dxdydz$ must be the increase of X in it. Therefore, we have

$$\frac{\partial \hat{x}}{\partial t} dxdydz = -\mathrm{div}\, \boldsymbol{J}_X\, dxdydz, \tag{6.13}$$

that is, the conservation equation (6.9) has been derived. If X can be produced with the rate σ per unit volume (say, due to a chemical reaction), (6.9) is modified to the following general conservation law with production:

$$\frac{\partial \hat{x}}{\partial t} = -\mathrm{div}\, \boldsymbol{J}_X + \sigma. \tag{6.14}$$

6.11 Diffusion equation

Let us first study the simplest linear transport phenomenon: the diffusion of particles. We know the number of particles is conserved without any chemical reaction. Therefore, if $\boldsymbol{J}$ is the number flux, (6.9) is

$$\frac{\partial n}{\partial t} = -\mathrm{div}\, \boldsymbol{J}. \tag{6.15}$$

We assume linear transport of particles (called *Fick's law*)

$$\boldsymbol{J} = -D\, \mathrm{grad}\, n, \tag{6.16}$$

where D is the *diffusion coefficient*. Combining these two, we get

$$\frac{\partial n(t, \boldsymbol{r})}{\partial t} = -\mathrm{div}(-D\, \mathrm{grad}\, n(t, \boldsymbol{r})) = D\nabla \cdot (\nabla n(t, \boldsymbol{r})). \tag{6.17}$$

This is the conservation law for the particle number density called the *diffusion equation*. Introducing the *Laplacian* Δ as

$$\Delta = \nabla \cdot \nabla = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}, \tag{6.18}$$

the diffusion equation reads

$$\frac{\partial n(t, \boldsymbol{r})}{\partial t} = D\Delta n(t, \boldsymbol{r}). \tag{6.19}$$

A 'pedestrian approach' to the diffusion equation will be given in **7.14**.

6.12 The meaning of Laplacian

If you understand the meaning of the Laplacian, you will feel the diffusion equation very natural. Let us consider the 1d Laplacian. It is nothing but d^2/dx^2. If we compute the second derivative numerically, we use, for example, the following discretization

$$\frac{d^2 f(x)}{dx^2} \leftarrow \frac{f'(x+\Delta x/2) - f'(x-\Delta x/2)}{\Delta x} = \frac{1}{\Delta x}\left(\frac{f(x+\Delta x) - f(x)}{\Delta x} - \frac{f(x) - f(x-\Delta x)}{\Delta x}\right), \tag{6.20}$$

so

$$\frac{d^2 f(x)}{dx^2} \propto \frac{f(x+\Delta x) + f(x-\Delta x)}{2} - f(x). \tag{6.21}$$

That is, $d^2 f/dx^2 \propto$ 'local average of f around x' $- f(x)$. You can confirm this conclusion in higher dimensional cases analogously. Generally, the Laplacian is an operator to compare the central value and the average value surrounding it. Thus, in the particle number diffusion the Laplacian computes the difference between the average n surrounding $\boldsymbol{r}$ and $n(\boldsymbol{r}, t)$. If this is positive, the diffusion equation increases $n(\boldsymbol{r}, t)$ in order for this quantity to catch up with the neighbors.

6.13 Intuitive computation of transport coefficient

To compute the transport coefficient for a quantity X we need a microscopic description of $\boldsymbol{J}_X$. Maxwell carried out this step fairly intuitively. Although it is hard to refine his argument quantitatively, as we will see soon, Maxwell's rather crude argument allows a fairly realistic estimation of Avogadro's constant.

Here, we start with a crude microscopic interpretation of a flux as the product of the flow velocity and the density (cf. **6.6**). Basically, we understand that, on the average, a molecule brings the physical quantity of our interest adopted at the location of its last collision to the location $\boldsymbol{r}$ where it is now (see Fig. 6.5). If we write the 'free vector' (a displacement vector of a molecule between successive collisions) as $\boldsymbol{l}_i$ for particle i, the last collision should have occurred at around $\boldsymbol{r} - \boldsymbol{l}_i$.

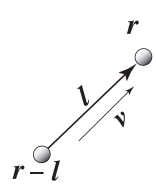

Figure 6.5: If a particle moves with velocity $\boldsymbol{v}$ along the free path $\boldsymbol{l}$ ('free vector'), on the average, the quantity of interest around $\boldsymbol{r} - \boldsymbol{l}$ transports to $\boldsymbol{r}$.

No new collision occurs until the molecule arrives at the volume element around $\boldsymbol{r}$, so the contribution of this molecule to the flux must be $x_i(\boldsymbol{r} - \boldsymbol{l}_i)\boldsymbol{v}_i$, where $x_i(\boldsymbol{r} - \boldsymbol{l}_i)$ is quantity X the molecule i acquired at its last collision. We use (6.4) to get

$$\boldsymbol{J}_X = \sum_{\boldsymbol{r}_i \in d\tau(\boldsymbol{r})} x_i(\boldsymbol{r}_i - \boldsymbol{l}_i)\boldsymbol{v}_i \Bigg/ d\tau(\boldsymbol{r}), \tag{6.22}$$

but usually it is further approximated as

$$\boldsymbol{J}_X = \langle \hat{x}(\boldsymbol{r}-\boldsymbol{l})\boldsymbol{v}\rangle = \langle \hat{x}(\boldsymbol{r})\boldsymbol{v}\rangle - \langle (\boldsymbol{l}\cdot\nabla\hat{x}(\boldsymbol{r}))\boldsymbol{v}\rangle + \cdots, \tag{6.23}$$

where the average over $\boldsymbol{l}$ and $\boldsymbol{v}$ is taken for molecules around $\boldsymbol{r}$. $\langle \hat{x}(\boldsymbol{r})\boldsymbol{v}\rangle = \hat{x}(\boldsymbol{r})\langle\boldsymbol{v}\rangle = 0$ and vanishes, because $\hat{x}(\boldsymbol{r})$ is constant in the volume element.

To compute the second term in (6.23) let us consider

$$\langle (\boldsymbol{l}\cdot\boldsymbol{A})\boldsymbol{v}\rangle = \langle \boldsymbol{v}(\boldsymbol{l}\cdot\boldsymbol{A})\rangle = \left\langle \boldsymbol{v}\sum_{i\in\{x,y,z\}} l_i A_i \right\rangle \tag{6.24}$$

for an arbitrary vector $\boldsymbol{A}$. $\boldsymbol{v}$ and $\boldsymbol{l}$ are parallel and each component of $\boldsymbol{v}$ is statistically independent, so[141*]

$$\langle v_i \ell_j\rangle \simeq \frac{1}{3}\overline{v}\ell\delta_{ij}. \tag{6.25}$$

Here, $\overline{v}$ is the average speed of the particles and ℓ is the mean-free path. We have arrived at

$$\langle \boldsymbol{v}(\boldsymbol{l}\cdot\boldsymbol{A})\rangle = \frac{1}{3}\overline{v}\ell\boldsymbol{A}. \tag{6.26}$$

Thus, we have arrived at

$$\boldsymbol{J}_X(\boldsymbol{r}) = -\frac{1}{3}\overline{v}\ell\,\mathrm{grad}\,\hat{x}(\boldsymbol{r}). \tag{6.27}$$

This is the general formula within Maxwell's approach for the flux.

6.14 Diffusion constant

For Fick's law (6.16) $\hat{x} = n$, so the diffusion constant is obtained as

$$D = \frac{1}{3}\overline{v}\ell, \tag{6.28}$$

which may also be written as

$$D = \frac{\ell^2}{3\tau}, \tag{6.29}$$

where τ is the mean free time $\tau = \ell/\overline{v}$.

As can be seen from the derivation above, the numerical factor 1/3 is not quite a definitive number.[142] The main message is that $D/\overline{v}\ell$ is a numerical factor of order unity. Then, this should be derivable dimensional-analytically. Try this derivation (then read **6.18**).

[141*]Each component of $\boldsymbol{v}$ is statistically independent, so it assumes $\pm$ independently. Both $\langle\boldsymbol{v}\rangle$ and $\langle\boldsymbol{l}\rangle$ are zero, so if $i \neq j$, $\langle v_i l_j\rangle = 0$. From the isotropy of the space we get $\langle v_1 l_1\rangle = \langle v_2 l_2\rangle = \langle v_3 l_3\rangle = \langle \boldsymbol{v}\cdot\boldsymbol{l}\rangle/3$, but $\boldsymbol{v}$ and $\boldsymbol{l}$ are parallel vectors, so their scalar product becomes the product of their lengths, i.e., mean speed $\overline{v}$ and mean free path l. Thus, we have arrived at (6.25).

[142]Besides, what average speed $\overline{v}$ to use is not very clear.

The elementary theory for shear viscosity and heat conductivity may be fun, but we will not use them in the following. Besides, as seen in **6.18**, dimensional analysis can give us equivalent results.

6.15 Shear viscosity

Suppose we have a shear flow with the velocity $\boldsymbol{V}$ in the x-direction and the velocity gradient in the z-direction as shown in Fig. 6.6.

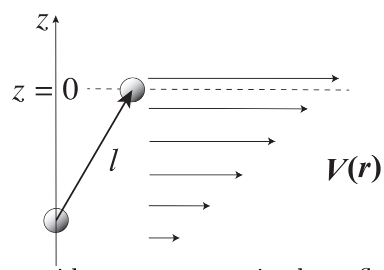

Figure 6.6: Shear flow: We consider a macroscopic shear flow, so the gradient of $\boldsymbol{V}$ must be microscopically (esp., on the scale of the mean-free path l) very small, but in the figure, it is exaggerated.

To understand the decay of this velocity gradient we study the transport of the x-component of the momentum. Due to exchange of particles between positions with different z-coordinates, larger V_x (or larger momentum density) and smaller V_x layers mix and the gradient in the z direction decays. This is the effect of *shear viscosity*.

The derivation of (6.27) immediately tells us that if the transported density is $\hat{x}$, the corresponding flux reads

$$\boldsymbol{J}_X(\boldsymbol{r}) = -\frac{1}{3}\overline{v}\ell\,\mathrm{grad}\,\hat{x}(\boldsymbol{r}). \tag{6.30}$$

To apply this general formula to the quantity we are interested in, we must identify what $\hat{x}$ is. In our present case, it must be the x-component of the momentum density

$$\hat{x} = \sum_{d\tau} mv_x/d\tau, \tag{6.31}$$

where the summation in the numerator means to take the summation of all the x-components of the momentum of the particles in the volume element $d\tau$. Therefore, (here we assume the number density n is uniform) thanks to the law of large numbers we expect only the expectation value is relevant, so

$$\hat{x}(\boldsymbol{r}) = nmV_x(\boldsymbol{r}) \tag{6.32}$$

is the right density to study. Therefore, (6.30) (or its z-component) reads

$$J_V = -\frac{1}{3}\overline{v}lnm\frac{\partial V_x}{\partial z}, \tag{6.33}$$

where J_V is the z-component of the 'x-component momentum flux'.[143] Shear viscosity η is defined by

$$J_V = -\eta \partial V_x/\partial z, \tag{6.34}$$

Comparing this with (6.33), we get the shear viscosity η:

$$\eta = \frac{1}{3} mn\overline{v}l. \tag{6.35}$$

With the already obtained estimate of l (6.2) and $\overline{v} = \sqrt{8k_BT/\pi m}$, we obtain[144]

$$\eta = \frac{2}{3d^2}\sqrt{\frac{mk_BT}{\pi^3}}. \tag{6.36}$$

This is independent of the density n as noted by Maxwell. We generally expect that the viscosity increases with density, but in gases, higher densities imply shorter free paths or a shorter mixing distance (actually the mean free path length is $\propto 1/n$) and the expected density effect is cancelled. Also notice that the viscosity increases with temperature. Although this is contrary to the behavior we usually encounter in liquids, it is easy to understand because higher temperatures imply better mixing in gases.

6.16 Elementary estimate of Avogadro's constant

To establish the reality of atoms, we wish to determine the number of particles N and their size d. Even if you could determine the mean-free path length, we can determine only the combination Nd^2. We need d or Nd^3 to get N.

Maxwell's first calculation of 1873[145] followed the method proposed by Loschmidt in 1865, who identified $\pi d^3/6$ as the volume per molecule in the liquid phase. Therefore, $(\pi d^3/6)/(1/n) = V_L/V_G$, where V_L is the molar volume of the liquid phase and V_G that of the gas phase. Thus, we obtain $d = 6\sqrt{2}(V_L/V_G)\ell$. Loschmidt estimated this as $8(V_L/V_G)\ell$, where ℓ was obtained from diffusion experiments (see (6.28)). Since we get d, we can count the number of molecules in V_L. Maxwell estimated $N_A \sim 4.3 \times 10^{23}$.

In 1873 van der Waals (1837-1923) proposed his equation of state of imperfect gases (explained in Section 25).

$$P(V - V_0) = Nk_BT - \frac{\alpha}{V}(1 - V_0/V). \tag{6.37}$$

[143] In a more advanced course, we use a tensor.

[144] If we assume that the particle mass, the cross section (d^2) and the particle thermal velocity are only relevant quantities, dimensional analysis gives essentially this result. Even if we try to take the density of the gas into account, it automatically drops out of the formula. This independence was a bit of surprise. It is a good occasion to learn rudiments of *dimensional analysis*.

[145] Maxwell's *A Treatise on Electricity and Magnetism* was published this year, so was Jules Verne's *Around the World in Eighty Days*.

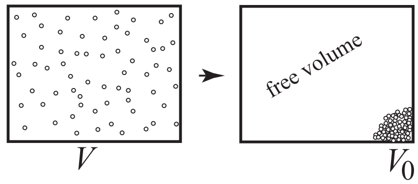

Figure 6.7: The idea of van der Waals.

His basic idea is as follows (see Fig. 6.7): Since molecules are not point masses but have volumes, they cannot run everywhere they wish (at least they must avoid each other). However, if we collect all the volumes of the molecules at a corner of the container (its volume is V_0), then, the centers of mass of the molecules could freely move around in the 'free volume' $V - V_0$. Therefore, if we ignore the attractive interactions, the 'hard-core' gas would look like an ideal gas with a reduced volume:[146]

$$P(V - V_0) = Nk_BT. \tag{6.38}$$

The remaining part of the van der Waals equation is to take care of the attractive intermolecular forces. Thus, from $V_0 \simeq bN\pi d^3/6$, where b is a geometrical constant of order unity, we can estimate the size of the molecules. Now, we know Nd^2 and Nd^3, so we can estimate N and d. The method gives an estimate of Avogadro's constant $N_A \simeq (4 \sim 6) \times 10^{23}$.[147]

6.17 Heat conductivity

The heat conductivity λ is defined as

$$\boldsymbol{J}_H = -\lambda \,\mathrm{grad}\, T, \tag{6.39}$$

where $\boldsymbol{J}_H$ is the heat flux (the thermal energy flux). The transported density $\hat{x}$ must be the thermal energy contained in the unit volume. Let us assume that the gas is a monatomic gas:

$$\hat{x} = \frac{\sum_{d\tau} m\boldsymbol{v}^2/2}{d\tau}, \tag{6.40}$$

[146] As we will show in Section 25, his idea is correct in 1-space.

[147] **⟪Definition of Avogadro's constant⟫** Since June 2019 Avogadro's constant is fixed as $N_{\mathrm{A}} = 6.022\ 140\ 76\ \times 10^{23}\ \mathrm{mol}^{-1}$. It is no more the number of atoms in a 0.012 kg of ^{12}C. Thus, the measurement of Avogadro's constant (such as quoted below) implies, since kg is defined as 1 kg $= \frac{h}{6.62607015\times 10^{-34}}\ \mathrm{m}^{-2}\mathrm{s}$, an accurate measurement of the molecular weight of a substance. ["Determination of the Avogadro constant by counting the atoms in a ^{28}Si crystal," Phys. Rev. Lett., **106**, 030801 (2011). Cf. P. Beker, "History and progress in the accurate determination of the Avogadro constant," Rep Prog Phys **64** 1945 (2001).]

so

$$\hat{x}(\boldsymbol{r}) = \frac{3}{2}nk_BT(\boldsymbol{r}), \tag{6.41}$$

where $T(\boldsymbol{r})$ is the temperature field.

(6.30) reads

$$\boldsymbol{J}_H(\boldsymbol{r}) = -\frac{1}{3}\overline{v}l\,\mathrm{grad}\left(\frac{3}{2}nk_BT(\boldsymbol{r})\right) = -\frac{1}{2}nk_B\overline{v}l\,\mathrm{grad}\,T(\boldsymbol{r}). \tag{6.42}$$

Comparing this with (6.39), we obtain

$$\lambda = \frac{1}{2}nk_B\ell\overline{v}. \tag{6.43}$$

Notice that $\eta = nmD$, $\eta/\lambda = 2m/3k_B$ and $\lambda/D = 3nk_B/2$. The last relation tells us $\lambda = c_VD$, where c_V is the specific heat per molecule of gas under constant volume.[148] Again, we should note that these relations do *not* tell us anything about the microscopic properties of the gas particles.

6.18 Dimensional analysis of transport coefficients[149]

The dimension of a quantity X is usually denoted by $[X]$. The basic dimensions are represented by the following symbols: length L, mass M and time T. For example, $[d] = L$. To obtain the dimension of a quantity, go back to its definition. For example, $[D]$ is obtained from $\boldsymbol{J} = -D\,grad\,n$ as follows. The particle number flux is the number of particles going through a unit area in unit time, so $[J] = 1/L^2T$, because the number of particles is dimensionless (a pure number). $[n] = 1/L^3$. Gradient is essentially differentiation with length, so $[grad] = 1/L$ (differentiation is something like division). Therefore, $[J] = 1/L^2T = [D]/L^4$, so $[D] = L^2/T$.

For $[\eta]$ let us go back to its definition: $J_p = -\eta\,grad\,v$, where J_p is the momentum flux, and v is the velocity. Since the dimension of momentum is ML/T, $[J_p] = (ML/T)/L^2T = M/LT^2$, $[v] = L/T$, so $[\eta] = [J_p]L/[v] = M/LT$.

For $[\lambda]$ again let us go back to its definition $J_H = -\lambda\,grad\,T$ (in this formula T is temperature, so $k_BT = E$ is energy). Therefore, $[E]/L^2T = [\lambda][E/k_B]/L$, so we obtain $[\lambda/k_B] = 1/LT$.

Thus, we obtain $[D/\eta] = L^3/M$, so $\eta/D \sim mn$ is concluded. We get $[k_BD/\lambda] = L^3 = 1/[n]$, which gives $\lambda \sim nk_BD \sim c_VD$. We also get $[k_B\eta/\lambda] = M$, which implies $\eta/\lambda \sim m/k_B$. These are the relations mentioned above.

---

[148] c_V is the energy required to raise the temperature of the molecule by 1 K under constant volume.

[149] ⟪**Introduction to dimensional analysis**⟫ See, e.g., Appendix 3.5A of Oono, Y. (2013). *The Nonlinear World*, Tokyo: Springer.

6.19 Significance of flux dependent on gradient

Due to collisions the particles cannot go straight for a long distance (actually, it is a zig-zag random walk as we will see in the next lecture). If there were no collision, the particles can move along their straight 'ballistic' trajectories, so the amount of 'X' transported must be proportional to the difference of $\hat{x}$ (not to the slope of $\hat{x}$ called gradient as we learned for linear transport phenomena) irrespective of the distance over which transportation occurs. Thus, the flux proportional to the gradient is actually a clear sign of molecular collisions occurring on the microscopic scale.

Q6-1.
(1) What is the dimension of the heat conductivity (or thermal conductivity) divided by the Boltzmann constant λ/k_B? λ is defined by

$$\boldsymbol{J} = -\lambda \,\mathrm{grad}\, T,$$

where $\boldsymbol{J}$ is the heat flux (the flux of kinetic energy; transported kinetic energy per unit time through unit area).
(2) It is a natural guess that heat transport should be related to the amount of thermal energy carried by molecules and the transport rate of the molecules. The former may be represented by the specific heat per volume c (times temperature) and the latter by diffusion constant D. What can dimensional analysis tell you about the relation among these quantities? We already discussed this in the lecture, but you must rederive the relation purely dimensional-analytically.]

Soln.
(1) $[J] = M(L/T)^2/L^2T = M/T^3$, $[\mathrm{grad}\, k_BT] = M(L/T)^2/L = ML/T^2$. Therefore

$$[\lambda/k_B] = (M/T^3)/(ML/T^2) = 1/LT. \tag{6.44}$$

Thus $[\lambda/k_B] = 1/LT$. This is consistent with the unit of heat conductivity is W/m·K.
(2) We know $[D] = L^2/T$. The heat capacity is energy/(volume times temperature), so $[c/k_B] = 1/L^3$. Therefore, $[cD/k_B] = 1/LT$. Thus, $\lambda \propto cD$ may be concluded.

Q6-2. There is a pure gas which roughly obeys a van der Waals equation of state with the excluded volume $V_0 = 5.1 \times 10^{-5}$ m^3/mole. Note that

$$V_0 = N_A \frac{1}{2}\frac{4\pi}{3} d^3 = \frac{2\pi}{3} N_A d^3, \tag{6.45}$$

where N_A is Avogadro's constant and d is the diameter of the gas particle (atom or molecule spherically approximated).

(1) This gas has a density of 5.894 kg/m^3 under 1 atm at $T = 273$ K. What is the root-mean-square velocity of the gas particles for this gas?

(2) The diffusion coefficient was observed to be $D = 4.8\times10^{-6}$ m^2/s. Using the simple gas kinetic estimate of D in the lecture notes (i.e., $D = lv/3$), obtain the mean free path length l. Here, you may identify v with the root-mean-square velocity just computed in (i).

(3) Try to estimate Avogadro's constant from the data given above.[150]

Soln.

[150] The data here is for xenon.

(1) $\langle v^2 \rangle = 3P/\rho$, so $\sqrt{3 \times 1.013 \times 10^5 / 5.89} = 227$ m/s.

(2) $\ell = 3D/v = 6.34 \times 10^{-8}$ m.

(3) Let $V = 22.4 \times 10^{-3}$ m^3 be the volume of this gas at 1atm:

$$N_A d^2 = V/\sqrt{2}\pi\ell, \;\; N_A d^3 = 3V_0/2\pi.$$

Therefore,

$$d = \frac{3V_0}{2\pi}\frac{\sqrt{2}\pi\ell}{V} = \frac{3\ell V_0}{\sqrt{2}V},$$

which is 3.067×10^{-10} m = 3.1 Å. A reasonable value. (van der Waals radius = 2.2 Å for xenon) and

$$N_A = V/\sqrt{2}\pi\ell d^2 = \frac{V}{\sqrt{2}\pi\ell}\frac{2V^2}{9\ell^2V_0^2} = \frac{\sqrt{2}V^3}{9\pi\ell^3V_0^2} = 8.466 \times 10^{23}.$$

7 Brownian motion

Summary
$*$ Brown found the universal motion called the Brownian motion.
$*$ Einstein recognized the Brownian motion is due to thermal motion, and estimated k_B (or equivalently N_A).
$*$ Langevin explains the Brownian motion in terms of the equation of motion with a noise term (called the Langevin equation).
$*$ Brownian trajectories may be related to random walks and polymer chain conformations. $\langle \boldsymbol{r}^2 \rangle = 2\mathfrak{d}Dt$.

Key words
Brownian motion, Langevin equation, mesoscopic, Fick's law, Einstein's relation, diffusion equation, Laplacian, Einstein-Stokes relation, dimensional analysis

What you should be able to do
$*$ Be able to explain the key idea of the mesoscopic approach using Einstein's Brownian motion theory as an example.
$*$ Be able to derive Einstein's relation.
$*$ Be able to estimate the span of a random walk or a random chain polymer.

7.1 How mesoscopic particles behave

At the microscopic level molecules are colliding with the fellow molecules and are recoiling forever. What if the particle we observe is much bigger than the molecules surrounding it? The particles we can observe optically are about thousand times linearly as large as the molecules (Fig. 7.1). This means that the mass ratio is $\sim 10^9$. Thus, numerous small impulses are imparted to the big particle from the surrounding molecules. The law of large numbers tells us that the motion of the big particle must be extremely slow compared with the gas particles, and its motion is due to the '$o[N]$' part of the law of large numbers (4.4). That is, we observe a typical mesoscopic scale motion, which we now call the Brownian motion.

7.2 Mr Brown discovered a universal motion (now) called the Brownian motion

The Brownian motion was discovered in the summer of 1827[151,152] by Robert

[151] [1827: Beethoven died in March; Democratic party was founded.]
[152] The work was published the next year. See P Pearle, B Collett, K Bart, D Bilderback, D

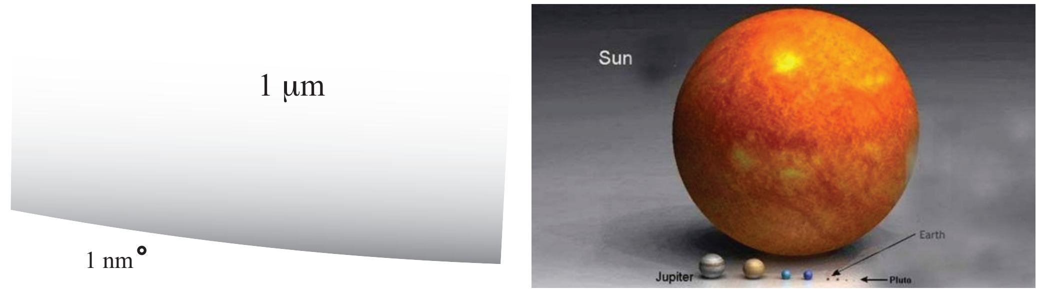

Figure 7.1: Brownian particle (1 μm radius) vs molecules (1 nm radius); The sun/the earth ratio is about 110. The ratio of the radius of the orbit of the earth (= 1 AU) and the radius of the sun is 109 (150 Gm vs. 1.4 Gm). This means the ratio of our cell (eukaryotic cell) and the molecule size is about the ratio of 1 AU and the size of the earth. Right from a nice site.

Brown.[153] We are usually given an impression that he simply observed the "Brownian motion." However, he did a very careful and thorough research to establish the *universal nature of the motion*.

Since the particles for which Brown first observed the motion came from living cells (see Fig. 7.2), initially he thought that it was a vital phenomenon. Removing the effects of advection, evaporation, etc., carefully, he tested many flowers. Then, he tested old pollens in the British Museum (he was the (founding) director of the Botanical Division), and still found active particles. He conjectured that this was an organic effect, testing even coal with no exception found. This suggested him that not only vital but organic nature of the specimens were irrelevant. He then tested numerous inorganic specimens (including a piece of Sphinx; he also roasted his specimens).

Let us watch some examples:

Nanoparticles in water:

Newman, and S Samuels, "What Brown saw and you can too," Am. J. Phys. **78**, 1278 (2010).

[153]《**Who was Mr Brown?**》[See Cook, Banks, Humboldt, ..., Bates `http://www.yoono.org/PST_Cambridge/Section9.html` for a (historical) background] Robert Brown (1773-1858) was perhaps the greatest botanist (and a great microscopist; Alexander von Humboldt (1769-1859) called him 'the glory of Great Britain') in the first half of the 19th century. He wrote (1810) a classic of systematic botany describing the Australian flora, following his expedition (1801-5). He was the first to recognize the two major classes of seed plants (1827) [P. B. Tomlinson, "Rescuing Robert Brown—The Origins of Angio-Ovuly in Seed Cones of Conifers," Bot. Rev. **78**, 310 (2012)]. He recognized the nucleus of the cell and so named it (1831; the terminology was later imported by N. Bohr to atomic physics).

Before departing for his Beagle expedition (Dec., 1831-Oct., 1836), Charles Darwin (1809-1882) asked for Brown's advice in 1831, buying a portable dissecting microscope recommended by Brown; after returning to England, Brown encouraged Darwin to visit him every Sunday morning. Later, Brown was regularly invited to parties at Darwin's home.

The participants of the now historical Linnean Society meeting, where the theory of natural selection was first read (July 1, 1858), were there mainly to listen to Lyell reading the eulogy for Brown who died on June 10 and to praise his career. Cf. J. Browne, *Charles Darwin, voyaging* (Knopf, 1995), *Charles Darwin, the power of place* (Knopf, 2002); an authoritative biography of Charles Darwin.

Figure 7.2: The pollen tube Brown observed first was from *Clarkia pulchella* (flower reddish purple, Oenotheraceae, Northwest US; the genus name commemorates Clark of the Lewis and Clark expedition (1804-6)). He observed 1/4000-1/5000 in (0.5-0.6 μm) particles in the pollen tube. From the quoted booklet: "the first plant examined proved in some respects remarkably well adapted to the object in view. This plant was *Clarkia pulchella*, of which the grains of pollen, taken from antherae full grown, but before bursting, were filled with particles of granules of unusually large size, perhaps slightly flattened, and having rounded and equal extremities. While examining the form of these particles immersed in water, I observed many of them very evidently in motion ..." [USDA photo]

http://www.youtube.com/watch?v=cDcprgWiQEY&feature=topics
Simulations
http://www.youtube.com/watch?v=PtYP8uoN0lk&feature=topics (excellent; comparison of small and large particles)
This may be the best (again):
http://falstad.com/gas/. Go to Setup Brownian motion.
http://labs.minutelabs.io/Brownian-Motion/ may be fun.

7.3 General properties of Brownian motion

Curiously enough, there was no work published about Brownian motion between 1831 and 1857, but the phenomenon was well known. From 1850s new experimental studies began by Gouy (1854-1926) and others. The established facts included (you would find them very easy to understand in terms of molecular bombardment on mesoscopic particles):

(1) Its trajectory is quite erratic without any tangent lines anywhere.
(2) Two Brownian particles are statistically independent even when they come within their diameters.
(3) Smaller particles move more vigorously.
(4) The higher the temperature, the more vigorous the Brownian motion.
(5) The smaller the viscosity of the fluid medium, the more vigorous the motion.
(6) The motion never dies out.
etc.[154]

In the 1860s there were experimentalists who clearly recognized that the motion

[154] What can you conclude from these observations and dimensional analysis?

was due to the impact of water molecules. Even Poincaré (1854-1912) mentioned this motion in 1900, but somehow **no founding fathers of kinetic theory and statistical mechanics paid any attention to Brownian motion**.[155]

Due to the bombardment of water molecules, the Brownian particle executes a zigzag motion, and eventually, say, its x-coordinate[156] displaced as seen in Fig. 7.3; its source video is worth watching.

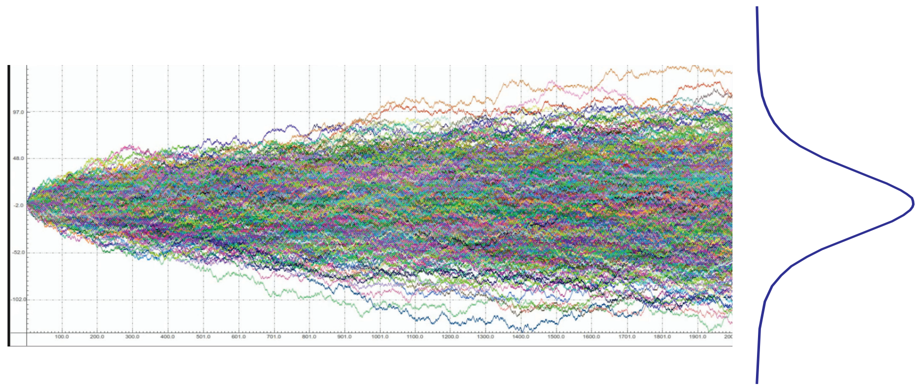

Figure 7.3: Displacement of Brownian particles along one coordinate; the x-axis is the time and the y the position of various sample particles along a line. The rightmost figure schematically describe the density of the particles at the end of the journeys. [From the video quoted above]

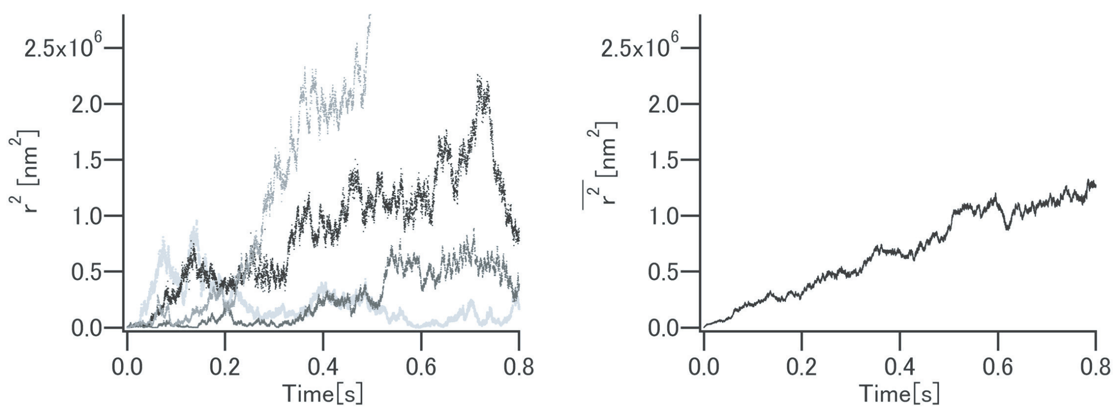

Figure 7.4: The left are four sample paths and their average is on the right. [Courtesy of Prof. Nishizaka of Gakushuin Univ.]

[155] According to H. Ezawa, they never expected the particle fluctuations large enough to be observable.

[156] This figure illustrates originally a 1D Brownian motion, but it also illustrates the behavior of a particular component of the position vector of a single Brownian particle, since all the orthogonal coordinates of a 3D Brownian particle position vector is statistically independent.

As you see in Fig. 7.4 the salient feature of the Brownian displacement $\Delta\boldsymbol{r}$ is

$$\langle \Delta\boldsymbol{r}^2 \rangle \propto t, \tag{7.1}$$

where $\langle\ \rangle$ is the ensemble average (you repeat the experiment again and again or do many (mutually not interfering) experiments simultaneously, and average the results) and t is time. The proportionality constant is related to (proportional to) the diffusion constant as we will see soon.

7.4 Langevin's explanation of the Brownian motion

Closely following Paul Langevin's argument,[157] let us demonstrate indeed $\langle \Delta\boldsymbol{r}^2 \rangle \propto t$.

Let us try to describe the motion of a Brownian particle classical mechanically. Let $\boldsymbol{r}$ be its position vector, and m its mass. Newton's equation of motion requires the forces acting on the particle. Since the particle is being hit 'randomly,' we expect a random force $\boldsymbol{w}$ (whose direction and magnitude change incessantly and erratically) acting upon the particle. If the Brownian particle moves at a constant velocity $\boldsymbol{v}$, then it would be hit by more particles of the medium on its front than on its back (imagine running in the rain). Therefore, it is natural to expect a force opposing the motion (i.e., drag) whose magnitude is proportional to the speed. Therefore, the equation of motion reads

$$m\frac{d^2\boldsymbol{r}}{dt^2} = -\zeta\frac{d\boldsymbol{r}}{dt} + \boldsymbol{w}, \tag{7.2}$$

where ζ is a positive constant describing the relation between the particle velocity and the resistive or frictional force the particle feels from the medium. Let us try to make an equation for $r^2 = \boldsymbol{r}\cdot\boldsymbol{r}$ by scalar-multiplying $\boldsymbol{r}$ to this equation. Since

$$\boldsymbol{r}\cdot\frac{d^2\boldsymbol{r}}{dt^2} = \frac{d}{dt}\left(\boldsymbol{r}\frac{d\boldsymbol{r}}{dt}\right) - \left(\frac{d\boldsymbol{r}}{dt}\right)^2 = \frac{d}{dt}\left(\frac{1}{2}\frac{d\boldsymbol{r}^2}{dt}\right) - \left(\frac{d\boldsymbol{r}}{dt}\right)^2, \tag{7.3}$$

we have

$$\frac{m}{2}\frac{d^2r^2}{dt^2} - m\left(\frac{d\boldsymbol{r}}{dt}\right)^2 = -\frac{\zeta}{2}\frac{dr^2}{dt} + \boldsymbol{w}\cdot\boldsymbol{r}. \tag{7.4}$$

Let us 'ensemble-average' this equation. That is, we prepare many such Brownian particles and average the equations for them. Let us denote this averaging procedure by $\langle\ \rangle$. Since averaging procedure is linear and time-independent, we can exchange the order of differentiation and averaging. Thus, we obtain

$$\frac{m}{2}\frac{d^2\langle r^2\rangle}{dt^2} - m\left\langle\left(\frac{d\boldsymbol{r}}{dt}\right)^2\right\rangle = -\frac{\zeta}{2}\frac{d\langle r^2\rangle}{dt} + \langle\boldsymbol{w}\cdot\boldsymbol{r}\rangle. \tag{7.5}$$

[157] Paul Langevin, "Sur la théorie du mouvement brownien," C. R. Acad. Sci. Paris **146**, 530-533 (1908). A translation may be found in D. S. Lemons and A. Gythiel, "Paul Langevin's 1908 paper "On the Theory of Brownian Motion" ["Sur la théorie du mouvement brownien," C. R. Acad. Sci. (Paris) 146, 530-533 (1908)]," Am. J. Phys., **65**, 1079 (1997).

Langevin says, "The average value of the term $\boldsymbol{w} \cdot \boldsymbol{r}$ is evidently null by reason of the irregularity of the complementary forces $\boldsymbol{w}$." Also, thanks to the equipartition of kinetic energy in equilibrium, the second term on the LHS is known:

$$\frac{1}{2}m\left\langle\left(\frac{d\boldsymbol{r}}{dt}\right)^2\right\rangle = \frac{3}{2}k_BT, \tag{7.6}$$

where k_B is the Boltzmann constant and T is the absolute temperature of the system.[158]

If we introduce

$$z = \frac{d\langle r^2\rangle}{dt}, \tag{7.7}$$

(7.5) reads

$$\frac{m}{2}\frac{dz}{dt} + \frac{\zeta}{2}z = 3k_BT. \tag{7.8}$$

Notice that this '3' is the spatial dimensionality $\mathfrak{d}$. This implies after a sufficiently long time,[159] the time derivative dz/dt should vanish and $z = 6k_BT/\zeta$ (note that 6 here is $2\mathfrak{d}$), or

$$\langle r^2\rangle = \frac{6k_BT}{\zeta}t = \frac{2\mathfrak{d}k_BT}{\zeta}t. \tag{7.9}$$

That is, the absolute value of the displacement during time t is proportional to $\sqrt{t}$. See Fig. 7.3.

7.5 Relation to random walk

As we have seen, due to random bombardment by fluid particles a Brownian particle executes an erratic motion. Let $\Delta\boldsymbol{r}_i$ be the total displacement between time $(i-1)\tau$ and $i\tau$, where

τ is a mesoscopic time scale which is very small from our point of view (say, 1 ms). Then, we may model the movement of the particle by a *random walk* (Fig. 7.5). After n steps (after $t = n\tau$), the total displacement of the Brownian particle is given by

$$\boldsymbol{r}(t) = \Delta\boldsymbol{r}_1 + \Delta\boldsymbol{r}_2 + \cdots + \Delta\boldsymbol{r}_n. \tag{7.10}$$

Let us compute the mean square displacement:

$$\langle r^2\rangle = \sum_i\langle\Delta r_i^2\rangle + 2\sum_{i<j}\langle\Delta\boldsymbol{r}_i\cdot\Delta\boldsymbol{r}_j\rangle. \tag{7.11}$$

[158] Since it is very hard to measure the velocity of the Brownian particles, the equipartition of kinetic energy was hardly directly proved, so some people even doubted this.

[159] which is actually a mesoscopic scale relaxation time: $\tau \simeq m/\zeta$. This is very short for a macroscopic observer like us.

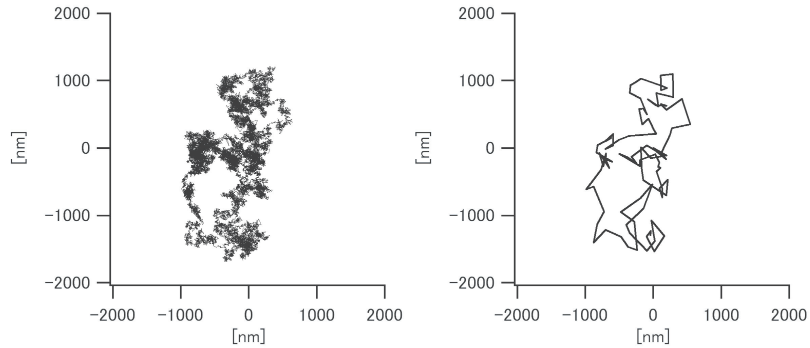

Figure 7.5: Actual observation results of a latex particle trajectory for 3.3 sec. Left: every 1/8000 sec; Right: every 1/30 sec. [Courtesy of Prof. Nishizaka of Gakushuin U]

Since the movement of the Brownian motion is uniform (e.g., throughout the duration of the motion the displacements are statistically the same), we may expect $\langle \Delta r_1^2 \rangle = \langle \Delta r_2^2 \rangle = \cdots$. Since there is no systematic direction to move into, $\langle \Delta \boldsymbol{r}_i \rangle = 0$. Since $\Delta \boldsymbol{r}_i$ are totally random (statistically independent), we expect that the average $\langle \Delta \boldsymbol{r}_i \cdot \Delta \boldsymbol{r}_j \rangle = \langle \Delta \boldsymbol{r}_i \rangle \cdot \langle \Delta \boldsymbol{r}_j \rangle = 0$ for $i \neq j$. Therefore, (7.11) implies

$$\langle r^2 \rangle = n \langle \Delta r_i^2 \rangle \propto t, \tag{7.12}$$

which is consistent with (7.9).

7.6 Let us look at 3D random walk samples

Let us observe 3D random walks (NN = 10000 steps), using the following R program (you can download R.app from CRAN https://cran.r-project.org):

```
install.packages("ggplot2")
```

Probably, you are asked to choose a CRAN mirror site. Choose, say, USA(KS).

```
install.packages("rgl")

library(ggplot2)
library(rgl)
```

The actual program begins here. (If you wish to reset the shape, simply rerun the whole program by copying the following)

```
NN <- 10000
m <- matrix(numeric(3*NN), ncol = 3)
for (i in 2:NN)
{
 q <- rnorm(3)
 qn <- q/sqrt(q[1]^2 + q[2]^2 + q[3]^2)
```

```
 m[i, ] <- m[i-1, ] + qn
}
df <- setNames(data.frame(m, seq(1, NN)),c("x", "y", "z"))
plot3d(df, xlim = c(-sqrt(NN), sqrt(NN)), ylim = c(-sqrt(NN), sqrt(NN)),
zlim = c(-sqrt (NN), sqrt (NN)), type = "l")
```

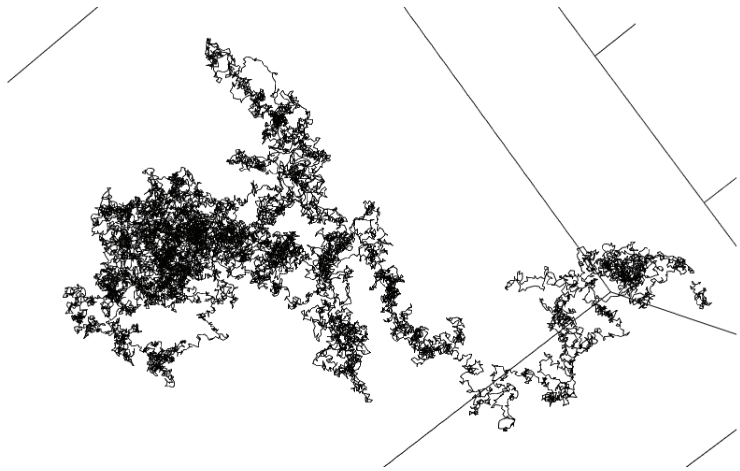

Figure 7.6: The program in **7.6** gives a 3D rotatable figure like this.

7.7 Polymer chain as a trajectory of random walk

We can consider a random walk on a lattice (see a problem at the end of this lecture). Let $\boldsymbol{\ell}_i$ be the ith step of the walk. This vector must be one of the bond vectors making the lattice. Starting from the origin, a random walk of n steps on a lattice would reach

$$\boldsymbol{R}(n) = \boldsymbol{\ell}_1 + \boldsymbol{\ell}_2 + \cdots + \boldsymbol{\ell}_n. \tag{7.13}$$

If the lattice spacing is a, then the consideration above (or (7.12)) tells us

$$\langle \boldsymbol{R}(n)^2 \rangle = na^2. \tag{7.14}$$

We may interpret the trajectory of a random walk as a conformation of a polymer consisting of n monomers (without any steric interactions among monomer units except perhaps for bond angle constraints). Then, $\boldsymbol{R}(n)$ is the end-to-end vector of the polymer chain, and the mean square end-to-end distance satisfies (7.14).

7.8 Einstein guessed the Brownian motion is due to thermal motion

That the cause of the Brownian motion is thermal motion of molecules was quantitatively demonstrated for the first time by Einstein in 1905,[160] three years before Langevin's work discussed above. You can understand the original paper in about a month, but not yet, because Einstein invented statistical mechanics by himself and used it to calculate the driving force for Brownian particles.

7.9 Einstein's approach was consciously mesoscopic

Einstein did not invent the word 'mesoscopic,' but his work consciously treated the Brownian particle as a mesoscopic object. This was the reason why his work was not instantly understood as a key paper in thermal physics.

Einstein considered the diffusion process of a collection of Brownian particles. The diffusion flux $\boldsymbol{J}$ may be written as

$$\boldsymbol{J} = -D \,\mathrm{grad}\, n, \tag{7.15}$$

where n is the number density of the Brownian particles. D is defined by this equation (Fick's law). We computed the diffusion constant in the gas phase through computing the flux.[161] Einstein did a similar thing for a suspended particle in a fluid medium.

7.10 Einstein's theory of Brownian particle flux

Einstein's key idea was that a Brownian particle may be treated both as a large molecule and as a tiny macroscopic particle at the same time (i.e., virtually, he introduced the '*mesoscopic scale*' description of Nature):
(a) Since we regard Brownian particles as molecules, we may apply Dalton's law of partial pressures. We assume the number density n of the Brownian particles is very small, so they do not interact with each other; we may regard the collection as an ideal gas (the particles are treated microscopically):

$$P = nk_BT. \tag{7.16}$$

(This P corresponds to the osmotic pressure due to the solute = Brownian particles as will be discussed in Lecture 20.)
(b) The average of mesoscopic quantities must be understandable macroscopically (i.e., in terms of macroscopic laws); Einstein did not explicitly say this, but as emphasized repeatedly, this is the key mesoscopic feature. Let $\boldsymbol{f}$ be the average

[160] "Über die von der molekularkinetischen Theorie der Wärme geforderten Bewegung von in ruhenden Flüssigkeiten suspendierten Teilchen," Ann. Phys. **17**, 549 (1905) [On the motion of suspended particles in stationary fluid required by the molecular kinetic theory of heat.]

[161] However, do not confuse the formula obtained in **6.14** (i.e., $D = \overline{v}\ell/3$, which describes the diffusion of molecules in a gas) and Einstein's formula for suspended particles in a fluid.

force acting on each particle (see Fig. 7.7). The total force acting on the slice in the figure is $n\boldsymbol{f}Adr$, but this must be the same as the force due to the partial pressure difference

$$n\boldsymbol{f}Adr = -A[P(\boldsymbol{r}+d\boldsymbol{r}) - P(\boldsymbol{r})] = -A\,\mathrm{grad}\,P\,dr, \tag{7.17}$$

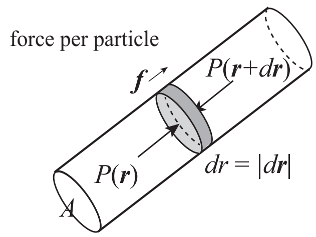

Figure 7.7: The total force acting on the thin slice of thickness $dr = |d\boldsymbol{r}|$ may be understood as the force due to the pressure difference, so $nA\boldsymbol{f}dr = A(P(\boldsymbol{r}) - P(\boldsymbol{r}+d\boldsymbol{r})) = -A\,\mathrm{grad}\,P(\boldsymbol{r})dr$, which gives (7.18).

That is,

$$n\boldsymbol{f} = -\mathrm{grad}\,P. \tag{7.18}$$

On the average a Brownian particle behaves as a macroscopic particle, so its (average) velocity $\boldsymbol{v}$ due to pushing by $\boldsymbol{f}$ must obey

$$\zeta\boldsymbol{v} = \boldsymbol{f}, \tag{7.19}$$

where ζ is the friction constant between the particle and the surrounding fluid (drag coefficient) (used in Langevin's approach **7.4**).

The diffusion flux $\boldsymbol{J}$ is

$$\boldsymbol{J} = n\boldsymbol{v} = n\boldsymbol{f}/\zeta \tag{7.20}$$

so (7.18) tells us that (assuming the temperature is uniform)

$$\boldsymbol{J} = -\frac{k_BT}{\zeta}\mathrm{grad}\,n. \tag{7.21}$$

7.11 Einstein's formula

Comparing (7.21) with the definition of the diffusion constant (7.15), we obtain

$$D = k_BT/\zeta, \tag{7.22}$$

which is called *Einstein's relation*. This equation allows us to obtain k_B or, since the gas constant R is known, to calculate Avogadro's constant N_A.

Einstein's original paper used $\zeta = 6\pi a\eta$, where a is the radius of the Brownian particle, and η is the shear viscosity of the fluid. Thus, the original Einstein's relation reads (often called the *Einstein-Stokes formula*)

$$D = \frac{k_B T}{6\pi a\eta}. \tag{7.23}$$

Here, Stokes' law is used that gives the drag force acting on a sphere of radius a moving at velocity $\boldsymbol{v}$ relative to the surrounding fluid: $\boldsymbol{f} = 6\pi a\eta\boldsymbol{v}$.[162]

$D \propto k_B T/a\eta$ may be concluded with the aid of dimensional analysis. Since dimensional analysis is quite important, let us derive this relation dimensional-analytically (almost repeating a part of our discussion in **6.18**. As noted before, an introduction to dimensional analysis is available:
http://www.yoono.org/Y_OONO_official_site/LectureSlides_504_files/DAmemo.pdf.

7.12 Dimensional analytic 'derivation' of Einstein's formula
If you know the unit of a quantity, it is easy (pragmatic) to obtain its dimension from the unit. For example, the diffusion constant is measured in the unit m^2/s, so $[D] = L^2/T$. If you do not know such information, you should go back to the definition. For example, to obtain $[\eta]$ let us go back to its definition: $J_p = -\eta\,\mathrm{grad}\,v$, where J_p is the momentum flux, and v is the velocity. Since the dimension of momentum is ML/T, $[J_p] = (ML/T)/L^2T = M/LT^2$, $[v] = L/T$, so $[\eta] = [J_p]L/[v] = M/LT$. k_BT has the dimension of energy, $[k_BT] = M(L/T)^2$.

Let us determine D. In dimensional analysis, first we must itemize all the quantities we believe relevant. In the present example, diffusion should be slow with large a or large η, and also it is related to thermal motion, so T should matter; T always appears with k_B, so we may conclude that D should depend on a, η and k_BT.

$[D]$ does not contain M, so we should get rid of M: $[k_BT/\eta] = (ML^2/T^2)/(M/LT) = L^3/T$. Therefore, $k_BT\eta/a$ must have the same dimension as D. Thus, $D \propto k_BT/a\eta$. No other combination is possible.

7.13 Displacement of particles by diffusion

Einstein's relation (7.22) with (7.9) due to Langevin implies

$$\langle \boldsymbol{r}^2 \rangle = 2\mathfrak{d}Dt. \tag{7.24}$$

Einstein, before Langevin, derived this equation in a different way (as discussed below), studying the time evolution of the number density $n(\boldsymbol{r}, t)$ of the Brownian particles that obeys the diffusion equation. We know the number density obeys the diffusion equation (6.19):

$$\frac{\partial n}{\partial t} = D\Delta n, \tag{7.25}$$

where Δ is the *Laplacian*:

$$\Delta = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}. \tag{7.26}$$

[162]Its derivation is not very trivial; see, for example, Landau-Lifshitz, *Fluid Dynamics*.

The easiest method to solve (7.25) is to use the Fourier transformation (see Appendix 6A), but here we simply quote the result. If n is normalized with the total number of particles, we get the probability density distribution of the Brownian particles $P(\boldsymbol{r}, t)$. Needless to say, P obeys the same diffusion equation. Let us assume at $t = 0$, all the probability is concentrated at the origin. Then,

$$P(\boldsymbol{r}, t) = \left(\frac{1}{4\pi D t}\right)^{\mathfrak{d}/2} e^{-\boldsymbol{r}^2/4Dt}. \tag{7.27}$$

Therefore, after t, the mean square displacement must be[163*]

$$\langle \boldsymbol{r}(t)^2 \rangle = 2\mathfrak{d} D t. \tag{7.29}$$

That is, if we observe the mean square displacement of a particle, then the diffusion constant D of the collection of such particles may be measured. Jean Perrin (1870-1942) implemented this measurement and obtained Avogadro's constant (see a problem at the end of this lecture **Q7.1**).[164]

Two more approaches to derive the diffusion equation are described below.

7.14 Pedestrian approach to diffusion equation
Let $\rho(t, \boldsymbol{r})$ be the density distribution function of a particular gas particle at position $\boldsymbol{r}$ and at time t.[165] Then,

$$\rho(t + \tau, \boldsymbol{r}) = \langle \rho(t, \boldsymbol{r} + \Delta \boldsymbol{r}) \rangle, \tag{7.30}$$

where the average here is about the 'next' free vector $\Delta \boldsymbol{r}$. Subtracting $\rho(t, \boldsymbol{r})$, the left-hand side reads

$$\rho(t + \tau, \boldsymbol{r}) - \rho(t, \boldsymbol{r}) = \frac{\partial \rho}{\partial t}\tau + \cdots. \tag{7.31}$$

The right-hand side reads

$$\rho(t, \boldsymbol{r} + \Delta \boldsymbol{r}) - \rho(t, \boldsymbol{r}) = \sum_{i=1}^{3} \Delta x_i \frac{\partial}{\partial x_i}\rho(t, \boldsymbol{r}) + \frac{1}{2}\sum_{i,j=0}^{3} \Delta x_i \Delta x_j \frac{\partial}{\partial x_i}\frac{\partial}{\partial x_i}\rho(t, \boldsymbol{r}) + \cdots. \tag{7.32}$$

[163*] Do not forget that (7.27) is a Gaussian density distribution in $\mathfrak{d}$-space. Since $\boldsymbol{r}^2 = x_1^2 + x_2^2 + \cdots + x_{\mathfrak{d}}^2$, (7.27) is actually a product of $\mathfrak{d}$ independent Gaussian density distributions for each orthogonal component x_i:

$$P(x_i, t) = \left(\frac{1}{4\pi D t}\right)^{1/2} e^{-x_i^2/4Dt}. \tag{7.28}$$

This is a one-dimensional Gaussian density distribution, so we immediately see $\langle x_i^2 \rangle = 2Dt$. Consequently, we have $\langle \boldsymbol{r}^2 \rangle = \mathfrak{d}\langle x_1^2 \rangle = 2\mathfrak{d}Dt$.

[164] J. Perrin, *Atoms* (Constable, 1916) translated by D. L. Hammick.
Available on line: https://archive.org/details/atomsper00perruoft.

[165] You could write $\rho(t, \boldsymbol{r}) = \langle \delta(\boldsymbol{r} - \boldsymbol{r}_1(t)) \rangle$, where $\boldsymbol{r}_1(t)$ the location of particle 1 at time t and the average is the conditional probability that $\boldsymbol{r}_1(0) = \boldsymbol{0}$ with probability one and the rest of the gas is in equilibrium.

We must average this over possible free vectors $(\Delta x_1, \Delta x_2, \Delta x_3)^T$:

$$\langle \Delta x_i \rangle = 0, \tag{7.33}$$

$$\langle \Delta x_i \Delta x_j \rangle = \delta_{ij} \frac{1}{3} \langle (\Delta \boldsymbol{r})^2 \rangle. \tag{7.34}$$

Thus, combining all the above we get a diffusion equation! Notice that $n\rho$ is the number density $n(t, \boldsymbol{r})$. Noting that our '3' is actually the spatial dimensionality $\mathfrak{d}$, we have

$$\frac{\partial \rho}{\partial t} = \frac{\langle (\Delta \boldsymbol{r})^2 \rangle}{2\mathfrak{d}\tau} \Delta \rho. \tag{7.35}$$

From this, at least we may conclude that $D \propto \overline{v}\ell$.

7.15 Overdamped Langevin equation without external force

If there is no systematic force, the Langevin equation reads

$$\frac{d\boldsymbol{r}}{dt} = \boldsymbol{\nu}. \tag{7.36}$$

This should describe the trajectory of a Brownian particle = random walk. We assume

$$\langle \nu \rangle = 0, \ \langle \boldsymbol{\nu}(t)^T \boldsymbol{\nu}(s) \rangle = AI\delta(t-s), \tag{7.37}$$

where A is a positive constant representing the noise amplitude (squared). This implies that there is no memory in noise (different times are uncorrelated). Since three components are uncorrelated,

$$\langle \nu_x(t) \nu_y(s) \rangle = 0, \text{ etc.} \tag{7.38}$$

In order to determine A, let us solve (7.158), assuming that the particle starts from the origin:

$$\boldsymbol{r}(t) = \int_0^t ds\, \boldsymbol{\nu}(s). \tag{7.39}$$

From this we obtain

$$\langle \boldsymbol{r}^2(t) \rangle = \int_0^t ds \int_0^t ds' \, \langle \boldsymbol{\nu}(s) \cdot \boldsymbol{\nu}(s') \rangle = \mathfrak{d}A \int_0^t ds \int_0^t ds' \, \delta(s - s') \tag{7.40}$$

$$= \mathfrak{d}A \int_0^t ds = \mathfrak{d}At. \tag{7.41}$$

Comparing this with Langevin's result above, we conclude that

$$A = \frac{2k_B T}{\zeta}. \tag{7.42}$$

However, still we cannot relate D and A directly.

7.16 Direct connection of Langevin's and diffusion equations

We already know that the distribution of the particles governed by (7.158) should obey a diffusion equation, whose diffusion constant should be proportional to A. Of course, if we solve the diffusion equation honestly as Einstein did, we immediately know $A = 2D$, but let us avoid the solution, and proceed 'more physically.'

We can derive the equation for n more directly because

$$n(t + dt, \boldsymbol{r}) = n(t, \boldsymbol{r} - \boldsymbol{\nu}dt) \tag{7.43}$$

according to the overdamped Langevin equation. Thus, we see

$$\frac{\partial n}{\partial t}dt = \frac{1}{2\mathfrak{d}}\langle(\boldsymbol{\nu}dt)^2\rangle\Delta n = \frac{A}{2}\Delta n dt \tag{7.44}$$

That is, $A = 2D$. Thus, 'without solving the diffusion equation', we have related the noise amplitude A and the diffusion coefficient D of particles driven by the noise.

7.17 Einstein's fundamental idea: summary

Let us summarize Einstein's fundamental idea, which is the key idea of the current nonequilibrium statistical mechanics:

> Microscopic fluctuations can build up mesoscopic fluctuations whose dynamics is on the average governed by the laws of macroscopic time evolution.

The Brownian motion is a mesoscopic motion that is a result of building up of microscopic fluctuations. Its decay is described by a macroscopic dissipative dynamics.

This was later more clearly stated by Onsager as the *regression hypothesis*.

7.18 Noise in the Langevin approach

We started with Langevin's theory based on a stochastic differential equation. If there is an external force $\boldsymbol{F}$, it may be generalized as

$$m\frac{d^2\boldsymbol{r}}{dt^2} = -\zeta\frac{d\boldsymbol{r}}{dt} + \boldsymbol{F} + \boldsymbol{w}. \tag{7.45}$$

Usually, we may assume that m is small and ζ is large (i.e., the over-damped condition). Then, we may ignore the acceleration term, and the equation is rewritten as

$$\frac{d\boldsymbol{r}}{dt} = \frac{\boldsymbol{F}}{\zeta} + \boldsymbol{\nu}, \tag{7.46}$$

where $\boldsymbol{\nu}$ is a noise. This equation is also called the Langevin equation (actually, this is the usual one).

Now, we wish to model the noise $\boldsymbol{\nu}$. We assume its all components are statistically independent, so let us study its x-component ν_x as a representative. $\nu_x(t)$ as a function of time changes quite rapidly and erratically, so we assume its ensemble average to satisfy

$$\langle\nu_x(t)\rangle = 0, \tag{7.47}$$

and

$$\langle\nu_x(t)\nu_x(s)\rangle = A\delta(t-s), \tag{7.48}$$

where A is a positive numerical constant. This implies that there is no memory in noise (different times are uncorrelated). Since three components are uncorrelated,

$$\langle\nu_x(t)\nu_y(s)\rangle = 0, \text{ etc.} \tag{7.49}$$

In order to determine A, let us solve (7.158), assuming that the particle starts from the origin:

$$\boldsymbol{r}(t) = \int_0^t ds\, \boldsymbol{\nu}(s). \tag{7.50}$$

From this we obtain

$$\langle \boldsymbol{r}^2(t) \rangle = \int_0^t ds \int_0^t ds' \,\langle \boldsymbol{\nu}(s) \cdot \boldsymbol{\nu}(s') \rangle = \mathfrak{d} A \int_0^t ds \int_0^t ds' \,\delta(s - s') \tag{7.51}$$

$$= \mathfrak{d} A \int_0^t ds = \mathfrak{d} A t. \tag{7.52}$$

Comparing this with (7.9), we can determine A as

$$A = \frac{2k_B T}{\zeta} = 2D. \tag{7.53}$$

This is called a *fluctuation-dissipation relation*, determining the noise (i.e., fluctuation) 'amplitude (squared)' A in terms of temperature T and friction constant ζ (i.e., dissipation).

7.19 Qualitative understanding of fluctuation-dissipation relation

Qualitatively, the fluctuation-dissipation relation (FDR) may be understood as follows (see Fig. 7.8). If the force in (7.158) is conservative (has a potential U) as

$$\boldsymbol{F} = -\mathrm{grad}\, U \tag{7.54}$$

our Langevin equation becomes

$$\frac{d\boldsymbol{r}}{dt} = -\frac{\nabla U}{\zeta} + \boldsymbol{w}. \tag{7.55}$$

Since the particle tends to be trapped in U, in equilibrium, we should expect the Boltzmann distribution $\propto e^{-\beta U}$ for the particle position $\boldsymbol{r}$ when the system described by (7.45) reaches an equilibrium state.

For example, if the viscosity of the suspending liquid is large, ζ is large, and as can be seen from (7.55), the effect of the systematic force due to the potential energy becomes relatively small. If the noise amplitude is not reduced appropriately, then obviously the distribution would spread too much. In other words, when the ambient liquid is viscous, large noise pushes the particle away from the potential minimum. Before the particle reaches the minimum, another noise kicks the particle further away from the potential minimum. Thus, a larger damping effect must be balanced with a smaller noise amplitude for the Langevin equation to describe the equilibrium state correctly. This is actually (5) in the summary of observations of the Brownian motion at the beginning of this lecture.

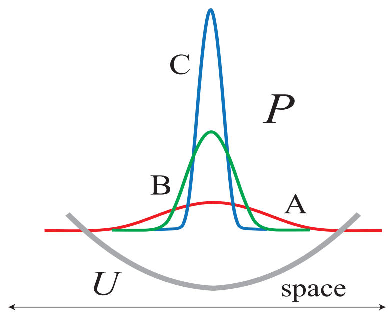

Figure 7.8: Illustration of the fluctuation-dissipation relation for a Brownian particle in a potential U. P is the probability density to find the particle at the given location with: Blue: too small noise; Green: just right noise; Red: too large noise for a given T and ζ. To reproduce the correct equilibrium state, the noise must be carefully chosen.

7.20 Smoluchowski equation and Einstein relation

The fluctuation-dissipation relation is usually derived from the condition that the equilibrium distribution of the particles is correctly described by the Boltzmann factor.[166] To close our discussion of the Brownian motion the approach to the fluctuation-dissipation relation through the front door will be explained.

Let us derive the transport equation for the number density. This is what Einstein did when there was no force. Now with an external force, how should we proceed? Since our system is linear, the force is not strong. Thus the flux must be the superposition of the flux due to the gradient of n and the one driven by the force. The latter reads (recall the flow velocity $\times$ the density of the quantity transported is the flux, and the flow velocity due to the driving by the force due to the potential U reads $\zeta \boldsymbol{v} = -\nabla U$))

$$n \times \boldsymbol{v} = -n\frac{1}{\zeta}\nabla U. \tag{7.56}$$

Therefore, the total flux reads with the aid of (7.53)

$$\boldsymbol{J} = -\frac{A}{2}\nabla n - \frac{1}{\zeta}n\nabla U. \tag{7.57}$$

The conservation of particles reads

$$\frac{\partial n}{\partial t} = -\mathrm{div}\,\boldsymbol{J}. \tag{7.58}$$

[166]Notice that even the above 'back door' derivation imports the equilibrium result as the equipartition of energy or the formula for the pressure.

7.21 Smoluchowski equation and fluctuation-dissipation relation

Combining (7.58) and the formula for the flux (7.57) gives the following equation called the *Smoluchowski equation*

$$\frac{\partial n}{\partial t} = \nabla \cdot \left(n \frac{1}{\zeta} \nabla U + \frac{A}{2} \nabla n \right). \tag{7.59}$$

In equilibrium, the time derivative must vanish, so

$$n \frac{1}{\zeta} \nabla U + \frac{A}{2} \nabla n = 0, \tag{7.60}$$

because this must vanish far away from the potential, or

$$\frac{2}{A\zeta} \nabla U + \nabla \log n = 0. \tag{7.61}$$

This implies that

$$n \propto e^{-2U/A\zeta} \tag{7.62}$$

which must be proportional to the Boltzmann factor **5.12**. Consequently, we must conclude that

$$A\zeta/2 = k_B T. \tag{7.63}$$

$A = 2k_B T/\zeta$ is the fluctuation-dissipation relation, but it is the Einstein relation itself.

Appendix 7A: How to obtain (7.27)

Use of Fourier transformation is the best. Fourier transformation $\mathcal{F}$ is defined as follows (in 3-space):

$$[\mathcal{F}f](\boldsymbol{k}) \equiv \tilde{f}(\boldsymbol{k}) = \left(\frac{1}{2\pi}\right)^3 \int d^3\boldsymbol{x}\, f(\boldsymbol{x})\, e^{i\boldsymbol{k}\cdot\boldsymbol{x}}. \tag{7.64}$$

Notice that differentiation becomes multiplication:

$$[\mathcal{F}(\nabla f)](\boldsymbol{k}) = -i\boldsymbol{k}\tilde{f}(\boldsymbol{k}). \tag{7.65}$$

This can be demonstrated by (essentially an integration by parts)

$$\begin{aligned}
[\mathcal{F}(\nabla f)](\boldsymbol{k}) &= \left(\frac{1}{2\pi}\right)^3 \int d^3\boldsymbol{x}\, \nabla f(\boldsymbol{x})\, e^{i\boldsymbol{k}\cdot\boldsymbol{x}} \\
&= \left(\frac{1}{2\pi}\right)^3 \int d^3\boldsymbol{x} \left[\nabla \left(f(\boldsymbol{x})\, e^{i\boldsymbol{k}\cdot\boldsymbol{x}}\right) - i\boldsymbol{k} f(\boldsymbol{x})\, e^{i\boldsymbol{k}\cdot\boldsymbol{x}}\right]. \qquad (7.66)
\end{aligned}$$

The first term in the second line above vanishes (assuming f vanishes at infinity), and we get (7.65).

From $\tilde{f}$ we can recover f by the inverse transformation:

$$f(\boldsymbol{x}) = [\mathcal{F}^{-1}\tilde{f}](\boldsymbol{x}) = \int d^3\boldsymbol{k}\, \tilde{f}(\boldsymbol{k})\, e^{-i\boldsymbol{k}\cdot\boldsymbol{x}}. \tag{7.67}$$

Let us Fourier transform the diffusion equation (7.25). We get

$$\frac{d\tilde{n}(t,\boldsymbol{k})}{dt} = -Dk^2\tilde{n}(t,\boldsymbol{k}). \tag{7.68}$$

This is an ordinary differential equation ($\boldsymbol{k}$ is a mere parameter). The initial condition is $n(0,\boldsymbol{x}) = \delta(\boldsymbol{x})$ (i.e., initially all the particles are at the origin). Its Fourier transform is

$$\tilde{n}(0,\boldsymbol{k}) = 1/8\pi^3. \tag{7.69}$$

Therefore, the solution to (7.68) is

$$\hat{n}(t,\boldsymbol{k}) = \frac{1}{8\pi^3} e^{-Dk^2t}. \tag{7.70}$$

Now, we inverse-transform this to get

$$\begin{aligned}
n(t,\boldsymbol{r}) &= \int_{\mathbb{R}^3} d^3\boldsymbol{k}\, \frac{1}{8\pi^3} e^{-Dk^2t - i\boldsymbol{k}\cdot\boldsymbol{r}} && (7.71)\\
&= \frac{1}{8\pi^3} \int_{\mathbb{R}^3} d^3\boldsymbol{k}\, e^{-tD(\boldsymbol{k}+i\boldsymbol{r}/2Dt)^2 - r^2/4Dt} && (7.72)\\
&= \frac{1}{8\pi^3} \left(\frac{\pi}{tD}\right)^{3/2} e^{-r^2/4Dt} = \left(\frac{1}{4\pi tD}\right)^{3/2} e^{-r^2/4Dt}. && (7.73)
\end{aligned}$$

The procedure from (7.71) to (7.72) is the completion of square in the exponent (see **5.8**), and then the calculation from (7.72) to (7.73) is just the multiplication of three 1D normalization calculation results.

Appendix 7B: Time scales, large deviation principle and Langevin equation

7.22 Three 'infinitesimal times,' dt, δt, Δt

Let us go back to the basic observation that our world often allows descriptions at three levels with distinct length scales: macro- (1 m), meso- (1 μm), and micro- (1 nm) scales.

Parallel to these length scales there should be representative time scales for these three levels. Here, we are interested in the time scale to describe the changes (motions). For us macro-organisms two time points apart less than ($\sim$)1 ms ($= 1 \times 10^{-3}$ s) cannot be recognized as two separate tie points. Thus, to describe the macro world surrounding us the time increment Δt of this size is small enough. To describe microscopic dynamics atomistically we need the time increment dt of 1 ($\sim$)fs ($= 1 \times 10^{-15}$ s). This suggests that to describe mesoscopic scales we would need the time increment δt of ($\sim$)1 ns ($= 1 \times 10^{-9}$ s). During this time a gas particle around us runs about 0.1 μm and the size of Brownian particle is about 1μm, so to describe fluctuations (noises) this δt is a reasonably sufficiently small time increment.[167] The three time increments (= time scales required to describe changes) are illustrated in Fig. 7.9.

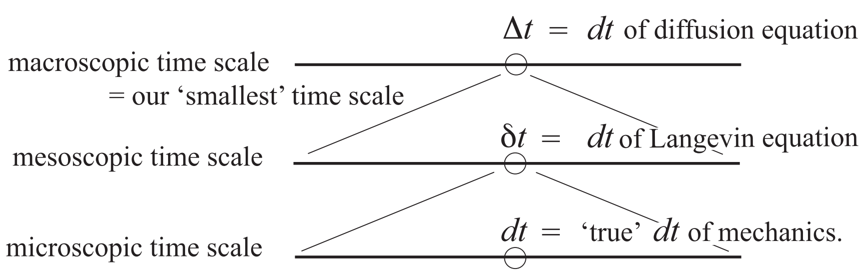

Figure 7.9: dt is the microscopically infinitesimal time scale (perhaps 10^{-15} s or less). Δt is the 'infinitesimal time scale' for us macroorganisms (perhaps, 10^{-3} s), which is usually written as dt from our point of view. δt is the 'infinitesimal time scale' in the mesoscopic world, and dt in the Langevin equation may be this time scale.

7.23 We are almost eternal microscopically

Let us try to understand these time increments intuitively. The change occurring at the ms scale may be regarded as 'the change during an infinitesimal time' (for transport phenomena), so dt in the transport equation is actually Δt (perhaps about 1 ms). To describe the true molecular dynamics dt is of order fs ($= 10^{-15}$ s) or less,

[167]That is the 'width' of the δ-function appearing in the characterization of the Gaussian noise in the Langevin equation.

so from this 'true dt' point of view, Δt is almost eternal.

Note that 10^9 s is about 31.7 a (= years). If dt is 1 s, Δt corresponds to 32 ka; If dt is 1 min, Δt corresponds to 1.9 Ma; If dt is 1 d, Δt corresponds to 2.74 Ga; cf., the Earth was born 4.56 Ga ago.

The macroscopic and microscopic time scales are very disparate. Connecting them are mesoscopic phenomena characterized by a time scale δt of the order, perhaps, 1 ns. If δt is 1 d, Δt is about 2.7 ka, dt is 0.86 sec. If δt is 1 s, Δt corresponds to 11.6 d and dt is 1 μs. If δt is one day, then Δt corresponds to 27 ka and dt corresponds to 0.86 s. If δt is 1 s, then Δt corresponds to 100 days and dt is 1 μs. We know many biophysical processes have mesoscopic time scales. For example, throwing 20 coins to have all H is almost sure in our 1 sec, if the trial is done every δt.

7.24 Time averaging to get mesoscopic results

At the macroscopic scale, if the deviation from equilibrium is gentle, we see transport phenomena.[168] The macro time derivative $\partial X/\partial t$ in the diffusion equation is actually the ratio of the change ΔX during Δt and Δt:

$$\text{macro derivative } \frac{dX}{dt} = \frac{X(t+\Delta t) - X(t)}{\Delta t}, \tag{7.74}$$

but the fundamental theorem of calculus tells us that this is the time average during Δt of the microscopic derivative (usually identified with the true mathematical derivative):

$$\frac{\Delta X}{\Delta t} = \frac{1}{\Delta t}\int_t^{t+\Delta t} \frac{dX}{dt} dt. \tag{7.75}$$

The relation between the mesoscale derivative and the microscopic true derivative is analogous:

$$\frac{\delta X}{\delta t} = \frac{1}{\delta t}\int_t^{t+\delta t} \frac{dX}{dt} dt. \tag{7.76}$$

Note, furthermore,

$$\frac{\Delta X}{\Delta t} = \frac{1}{\Delta t}\int_t^{t+\Delta t} \frac{\delta X}{\delta t} \delta t, \tag{7.77}$$

which gives (7.75) with an appropriate succession of the δt time intervals.

7.25 Law of large numbers and macroscopic time change

The microscopic time derivative is deterministic but unpredictable, and it has only

[168]Here, 'gentle' means that the macroscopic observables changes sufficiently slowly that the law of large numbers hold on the space-time scale where the macrovariable changes are infinitesimal.

a microscopic time-scale memory (extremely forgetful from our time scale). That is, after, say, 0.1 ps we may expect that dX/dt behaves statistically independently. Thus, the ratio appearing on the right-hand-sides of (7.75) and (7.76) may be understood as empirical expectation values just as S_N/N in the law of large numbers. Since $\Delta t/dt \gg 1$ is really large, for $\Delta X/\Delta t$ the law of large numbers should hold, and we may ignore its fluctuations. This is the macroscopic phenomenological law. It is deterministic. A typical example is the transport theory (Section 6).

7.26 Mesoscopics deviates from law of large numbers

In contrast, $\delta t/dt$ is large but not huge, so we must worry about fluctuations (deviations from the 'long-time' average). Thus, at the mesoscopic time scale we see Brownian motion and the equations describing this time scale are Langevin equations (Section 7). The deviation from the law of large numbers is described with the aid of the large deviation principle.

7.27 ABC of large deviation principle

The law of large numbers tells us that in the sample number $N \to \infty$ limit (here, we stick to the same notation as in Section 4 to minimize complication)

$$P\left(\left|\frac{1}{N}\sum_{k=1}^{N} X_k - E(X_1)\right| > \varepsilon\right) \to 0. \tag{7.78}$$

If N is not sufficiently large, this asymptotic relation cannot be used for empirical studies. We must refine this asymptotic law. Perhaps the most natural refinement is to try to actually evaluate how small or large this probability is. For an iid[169] stochastic variables $\{X_n\}$ with $V(X_1) < \infty$, it is known that the decay rate of the above probability is exponential:

$$P\left(\left|\frac{1}{N}\sum_{k=1}^{N} X_k - E(X_1)\right| > \varepsilon\right) \approx e^{-NI_\varepsilon}, \tag{7.79}$$

where $\approx$ implies that the ratio of the logarithms of the both sides converges to unity in the large N limit, and I_ε is a (ε-dependent) positive constant.

For physicists, the following form is convenient (statistical-mechanically explained later):

$$P\left(\frac{1}{N}\sum_{k=1}^{N} X_k \in v(y)\right) \approx e^{-NI(y)}, \tag{7.80}$$

[169] identically and independently distributed

where $v(y)$ is a volume element around y, and $I(y)$ is called the *rate function* (or *large deviation function*), satisfying

$$I(y) \begin{cases} > 0 & \text{if } y \neq \langle X_1 \rangle, \\ = 0 & \text{if } y = \langle X_1 \rangle. \end{cases} \tag{7.81}$$

The second equality is the law of large numbers. (7.80) + (7.81) is called the *large deviation principle*.[170] The rate function often behaves as

$$I(y) \simeq \frac{1}{2A}(y - \langle X \rangle)^2 \tag{7.82}$$

for not too large $|y - \langle X \rangle|$, where A is a positive constant.

Notice that $e^{-NI(y)}$ gives an estimate of the probability density of fluctuation Ny (a large fluctuation). That is, when we study $S_N = \sum_{k=1}^{N} X_k$, it is on the average $N\langle X_1 \rangle$, but there are fluctuations of significance, whose distribution can be inferred from $I(y)$.[171]

7.28 Langevin equation as a result of large deviation theory

Let us study the overdamped Langevin equation that describes the motion of a Brownian particle. If we respect the time scale, it should actually be written as (here the conserved force is replaced with a general systematic force $\boldsymbol{F}$)

$$\frac{\delta \boldsymbol{x}}{\delta t} = \frac{1}{\zeta}\boldsymbol{F} + \boldsymbol{\nu}. \tag{7.83}$$

If we average this over a macroscopic time scale, the result should yield the macroscopic law: $\boldsymbol{v} = \boldsymbol{F}/\zeta$, so

$$\frac{\Delta \boldsymbol{x}}{\Delta t} = \frac{1}{\zeta}\boldsymbol{F}. \tag{7.84}$$

This is due to the law of large numbers: Since $\Delta t/dt \gg 1$,

$$P\left(\left|\frac{\Delta \boldsymbol{x}}{\Delta t} - \frac{\boldsymbol{F}}{\zeta}\right| > \varepsilon\right) \simeq 0. \tag{7.85}$$

It is natural to expect that the mesoscopic deviation from the macroscopic behavior must be described by the large deviation principle **7.27**.

---

[170] A further mathematical requirement is that the level sets of the rate function must be convex. That is, I is a convex function.

[171] ⟪**Rate function summary**⟫ $I(y)$ has a unique minimum at $y = \langle X_1 \rangle$, its level set is convex, and if X_1 has a finite variance, I is differentiable near the global minimum at $y = \langle X_1 \rangle$. There is no book suitable to physicists, but two reviews may be accessible: a relatively new Tourchette, H. (2009). The large deviation approach to statistical mechanics, *Phys. Rep.*, **478**, 1-69 and an old one: Oono, Y. (1989). Large Deviation and Statistical Physics, *Prog. Theor. Phys. Suppl.*, **99**, 165-205.

What form of large deviation principle should we expect? Since δt is a $\delta t/dt$ collection of dt, N in (7.80) must be proportional to $\delta t/dt$. However, we do not know precisely what dt is, so let us write

$$P\left(\frac{\delta \boldsymbol{x}}{\delta t} - \frac{\boldsymbol{F}}{\zeta} \in v(\boldsymbol{\nu})\right) \approx \exp\left[-\delta t\, I(\boldsymbol{\nu})\right], \tag{7.86}$$

where v denotes the volume element around $\boldsymbol{\nu}$, and the large deviation function I should read

$$I(\boldsymbol{\nu}) = \frac{1}{2A}\boldsymbol{\nu}^2, \tag{7.87}$$

where A is a positive constant to be determined below (but, as we will learn, it turns out to be exactly the same A introduced in (7.32)). If we use this for (7.86), we obtain the density distribution function $f(\boldsymbol{\nu})$ for the noise:

$$f(\boldsymbol{\nu}) \propto \exp\left\{-\frac{\delta t}{2A}\boldsymbol{\nu}^2\right\}. \tag{7.88}$$

Thus, fluctuations are Gaussian, and[172*]

$$\langle \boldsymbol{\nu}^2 \rangle = \mathfrak{d} A/\delta t, \tag{7.89}$$

where $\mathfrak{d}$ is the spatial dimensionality.

The variance looks unpleasant with the mesoscopic infinitesimal δt appearing downstairs, but we already know what its proper interpretation should be in Section 6: the δ-function:

$$\delta(t-s) = 0 \text{ for } t \neq s, \tag{7.90}$$

$$\delta(t-s)\, dt = 1 \text{ for } t = s. \tag{7.91}$$

In short, basically, the 'needle' of length $1/dt$ located at $t = s$ is $\delta(t-s)$. Thus, the real meaning of (7.89) is[173]

$$\langle \boldsymbol{\nu}(\boldsymbol{t}) \cdot \boldsymbol{\nu}(s) \rangle = \mathfrak{d} A \delta(t-s), \tag{7.92}$$

or

$$\langle \boldsymbol{\nu}(t) \boldsymbol{\nu}^T(s) \rangle = A I \delta(t-s), \tag{7.93}$$

where I is the $\mathfrak{d} \times \mathfrak{d}$ unit matrix (do not forget that our vectors are column vectors; ^{T} implies transposition: 'column $\leftrightarrow$ row'). If we demand the fluctuation-dissipation relation, we must impose

$$A = 2k_B T/\zeta. \tag{7.94}$$

[172] $\boldsymbol{\nu}$ is a $\mathfrak{d}$-dimensional (column) vector $(\nu_x, \nu_y, \cdots)^T$ (^{T} implies transposition) and each component satisfies $\langle \nu_x^2 \rangle = A/\delta t$. Therefore, $\langle \boldsymbol{\nu}^2 \rangle = \mathfrak{d} A/\delta t$.

[173] Here 'dt' is really δt, so the $\delta(t-s)$ is the delta function for the mesoscopic time scale. That is, from the microscopic point of view it has a width of order δt (as we already discussed). For simplicity, we use only one symbol for δ-functions.

7.29 Langevin equation: practical summary

Let us write down the Langevin equation governing an overdamped Brownian particle with a friction coefficient ζ in the potential U satisfying the fluctuation-dissipation relation (e.g., (7.94)) at temperature T as a summary. The equation reads (here δt is written as dt)

$$\frac{d\boldsymbol{x}}{dt} = -\frac{1}{\zeta}\frac{\partial U}{\partial \boldsymbol{x}} + \boldsymbol{\nu}(t), \tag{7.95}$$

with the Gaussian noise satisfying $\langle \boldsymbol{\nu}(t) \rangle = 0$ and

$$\langle \boldsymbol{\nu}(t)\boldsymbol{\nu}(s)^T \rangle = \frac{2k_BT}{\zeta} I \delta(t-s), \tag{7.96}$$

where I is the $\mathfrak{d} \times \mathfrak{d}$ unit matrix. (7.96) tells us that the memory duration of the noise is almost instantaneous at the mesoscopic time scale.

Q7.1 [Modern version of Perrin's experiment].
One experiment replicating Perrin's experiment in a modern setting uses polystyrene particles of diameter (i.e., $2a$) 0.5 μm suspended in a buffer solution of viscosity $\eta = 1.03 \times 10^{-3}$ Pa·s at $T = 300$ K. A two-dimensional stage was recorded by a microscope with a CCD camera, and its x coordinate is measured as a function of time. The mean square average displacement in x is observed as $\langle x^2 \rangle = 15.6 \times 10^{-13} t$ m^2 after t seconds. Assuming that you know the gas constant $R = 8.31$ J/mol·K, estimate Avogadro's constant N_A.

Solution.
The relation we use is $\langle x^2 \rangle = 2Dt$ and the Einstein-Stokes relation $D = k_B T / 6\pi a \eta$. Therefore, $k_B = (3\pi a\eta/T) \times 15.6 \times 10^{-13} = 1.26 \times 10^{-23}$, or $N_A = R/k_B = 6.58 \times 10^{23}$.

Q7.2 [Lattice random walks]
On a triangular lattice or a honeycomb lattice (see Fig. 7.11) with the same edge (i.e., lattice bond) length ℓ is a random walker.

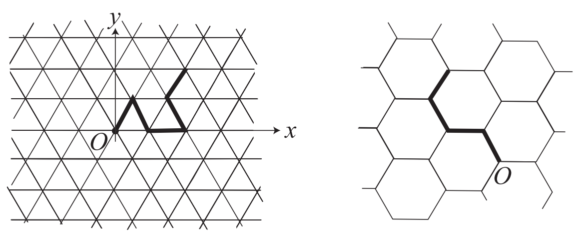

Figure 7.10: Triangular lattice (left) and honeycomb lattice

The walker starts from the origin O and walks along the edges. At every second she chooses randomly any of the edges connected to her current position and moves to the nearest neighbor lattice point along the chosen edge. You can assume that she completely forgets at what lattice point she was previously (i.e., all the steps are statistically independent). If her ith step displacement is denoted by vector $\boldsymbol{a}_i$, the total displacement during time t seconds is given by

$$\boldsymbol{R} = \boldsymbol{a}_1 + \boldsymbol{a}_2 + \cdots + \boldsymbol{a}_t. \tag{7.97}$$

Here, all the step vectors $\boldsymbol{a}_i$ are lattice bond vectors.
(1) After t seconds on which lattice (T = triangular or H = honeycomb) can she be further away from the origin on the average? That is, choose the correct relation from the following and justify your choice: $T > H$, $H > T$ or $H = T$.
(2) Now, on the triangular lattice due to a strong wind blowing constantly in the $+x$ direction, the walker tends to choose $+x$ direction with probability 0.5, but still chooses the remaining five directions randomly (with probability 0.1 for each).

(a) What is the average position (x and y coordinates) of the walker after t seconds?

(b) What is the variance of the y-coordinate after t seconds?

(c) What is the mean square displacement $\langle R^2\rangle$ of the walker after t seconds?

Solution.
(1) Thanks to the statistical independence of steps and the average step displacement being zero (i.e., $\langle \boldsymbol{a}_i\rangle = 0$, so $\langle \boldsymbol{a}_i \boldsymbol{a}_j\rangle = \ell^2\delta_{ij}$), we obtain

$$\langle \boldsymbol{R}^2\rangle = \sum_{i=1}^{t} \langle \boldsymbol{a}_i^2\rangle. \tag{7.98}$$

Here, $\langle\ \rangle$ is an ensemble average. Obviously, $\langle \boldsymbol{a}_i^2\rangle = \ell^2$, so $\langle R^2\rangle = t\ell^2$. Does this calculation depend on spatial dimension or the lattice structure?

We have $H = T$.

This might be slightly counterintuitive, because the honeycomb lattice walk seems less 'zig-zag' than the other case. Do not forget that there is a significant probability (1/3) to retrace the immediate-past step to return to the same position the walker was 2 sec ago.

(2) (a) The position after t seconds is given by (7.97). Therefore, the average position is $\langle \boldsymbol{R}\rangle = t\langle \boldsymbol{a}_1\rangle$.

$$\langle \boldsymbol{a}_i\rangle = 0.5(\ell, 0) + 0.1\ell \sum_{k=1}^{5} \left(\cos\frac{k\pi}{3}, \sin\frac{k\pi}{3}\right), \tag{7.99}$$

but from the symmetry without actual calculation

$$\langle \boldsymbol{a}_i\rangle = 0.5(\ell, 0) + 0.1(-\ell, 0) = (0.4\ell, 0). \tag{7.100}$$

Therefore, $\langle \boldsymbol{R}\rangle = (0.4\ell t, 0)$.

(b) Let us write $\boldsymbol{R} = (X, Y)$. Then, $Y = \sum_{i=1}^{t} y_i$, where y_i is the y-component of the ith step vector. We know $\langle Y\rangle = 0$, so using the statistical independence of steps, we have

$$V(Y) = \langle Y^2\rangle = \sum_{i=1}^{t} \langle y_i^2\rangle, \tag{7.101}$$

where

$$\langle y_1^2\rangle = 0.6 \times 0 + 0.4\left(\ell \sin\frac{\pi}{3}\right)^2 = 0.3\ell^2 \tag{7.102}$$

Therefore, $V(Y) = 0.3\ell^2 t$.

(c) We need

$$\langle \boldsymbol{R}^2\rangle = \sum_{i=1}^{t} \langle \boldsymbol{a}_i^2\rangle + \sum_{i\neq j} \langle \boldsymbol{a}_i \cdot \boldsymbol{a}_j\rangle. \tag{7.103}$$

Although each step is statistically independent (so you may write $\langle \boldsymbol{a}_i \cdot \boldsymbol{a}_j\rangle = \langle \boldsymbol{a}_i\rangle \cdot \langle \boldsymbol{a}_j\rangle$), its average is not zero in this case, so you cannot ignore the cross terms. There are $t(t-1)$ cross terms, but they are all the same:

$$\langle \boldsymbol{a}_i \cdot \boldsymbol{a}_j\rangle = \langle \boldsymbol{a}_i\rangle \cdot \langle \boldsymbol{a}_j\rangle = \langle \boldsymbol{a}_1\rangle^2. \tag{7.104}$$

We have already computed $\langle \boldsymbol{a}_1 \rangle = (0.4\ell, 0)$. Obviously, $\langle \boldsymbol{a}_i^2 \rangle = \ell^2$

$$\langle \boldsymbol{R}^2 \rangle = \ell^2 t + 0.16\ell^2 t(t-1). \tag{7.105}$$

What is the variance of $\boldsymbol{R}$?

Q7.3 [Average position of Brownian particles]
Suppose two identical Brownian particles are released from the same point on a two dimensional stage. Assume that the diffusion constant of the particles is $D = 1.5 \times 10^{-12}$ m^2/s.
What is the root mean-square displacement of the average position of these two particles after 1 hr.

Solution.

$$(1/4)\langle (\boldsymbol{r}_1 + \boldsymbol{r}_2)^2 \rangle = (1/2)\langle \boldsymbol{r}_1^2 \rangle = dDt = 2 \times 1.5 \times 10^{-12} \times 3600 = 1.08 \times 10^{-8}. \tag{7.106}$$

Therefore, the root mean-square displacement of the average position is 1.04×10^{-4} m $\simeq 104$ μm.

To answer such problems, first itemize what you need: two Brownian particles are mentioned, so we need two position vectors $\boldsymbol{r}_1$ and $\boldsymbol{r}_2$. Since the position of the center of mass is asked, let us express it as $\boldsymbol{R} = (\boldsymbol{r}_1 + \boldsymbol{r}_2)/2$. Then, do simple algebra without thinking:

$$\langle \boldsymbol{R}^2 \rangle = \frac{1}{4}\langle \boldsymbol{r}_1^2 + \boldsymbol{r}_2^2 + 2\boldsymbol{r}_1 \cdot \boldsymbol{r}_2 \rangle = \frac{1}{4}(\langle \boldsymbol{r}_1^2 \rangle + \langle \boldsymbol{r}_2^2 \rangle + \langle 2\boldsymbol{r}_1 \cdot \boldsymbol{r}_2 \rangle). \tag{7.107}$$

Now, you must look at the result and think about a bit of the actual situation. Both the particles are identical, so the average should not depend on particles $\langle \boldsymbol{r}_1^2 \rangle = \langle \boldsymbol{r}_2^2 \rangle$, and as already noted far before Einstein, two Brownian particles are statistically independent if apart more than their sizes. We study a long time behavior, so, except for a very short time near the starting point, these two particles are statistically independent. Consequently,

$$\langle \boldsymbol{r}_1 \cdot \boldsymbol{r}_2 \rangle = \langle \boldsymbol{r}_1 \rangle \cdot \langle \boldsymbol{r}_2 \rangle. \tag{7.108}$$

The space is isotropic, so there is no preferred direction to wander: $\langle \boldsymbol{r}_1 \rangle = \langle \boldsymbol{r}_2 \rangle = 0$. Hence,

$$\langle \boldsymbol{R}^2 \rangle = \frac{1}{2}\langle \boldsymbol{r}_1^2 \rangle. \tag{7.109}$$

The rest is as above.

Q7.4 [Diffusion of proteins]
There are two proteins of mass m and M. Let us assume that the protein molecules are spherical and its average densities are the same. We know $M/m = 100$. For a

smaller molecule to diffuse across a fixed length L in a cell it takes 0.23 s on the average. What is the best guess of the time needed for the larger protein to diffuse across the same distance L?

Solution.
$\langle r^2 \rangle = 2\mathfrak{d}Dt$, and $D = k_BT/6\pi a\eta$. This means Dt is the same, so t/a is the constant. Since we assume that the proteins are spherical and with the same density, $a \propto M^{1/3}$. That is, $t/M^{1/3}$ is constant. Hence, $t = 0.23(M/m)^{1/3} = 1.07$ s.

As warned repeatedly, do not use the gas phase formulas to calculate the diffusion constant in liquids.

Discussion 4

We discuss mean-free path, random walks and Brownian motion.

D4.1 [Mean free path and diffusion]
Consider a (ideal gas) mixture consisting of two chemically distinct species A and B. The number density of chemical species A (resp., chemical species B) is n_{A} (resp., n_{B}), the diameter of particle A (resp., particle B) is d_{A} (resp., d_{B}) and its mass is m_{A} (resp., m_{B}).
(1) Using the simple idea of the swept volume (Fig. 6.1), calculate the mean free path for A moving through the gas of B (i.e., $n_{\mathrm{A}} = 0$) step by step as:

(i) Get the cross section σ_{AB} of the cylinder: the cross section σ_{AB} of the cylinder (the swept volume by A colliding with B) can be written in terms of d_{A} and d_{B}.
(ii) The number of B particles in this swept volume should be the number of collisions experienced by a single A with B. This tells you how to compute the mean free path ℓ_{AB} of particle A in gas B under the assumption that B molecules are not moving.
(iii) How can you take the motion of B into account (approximately; cf. (6.1) $\to$ (6.2)? We need the relative speed: the relative speed is, on the average, the average relative speed of particles A and B that can be estimated as (5.69), where m should be the reduced mass μ (you must write it in terms of m_{A} and m_{B}).

(2) What is the diffusion constant (correctly speaking, it is called the mutual diffusion constant D_{AB}) of minority A through majority B? Use our elementary result (6.28).

(3) Suppose B is shear minority and diffusing through the A gas. What is D_{BA}?

(4) We imagine a particle of A is running and hitting B. Using the results of (i) - (iii) in (1), estimate the total number Z_{AB} of collisions per unit time that occur between particles A and B in a unit volume.

(5)* Obtain Z_{AA}, the number of collisions among A's in a unit volume per unit time.

(6)* Can you obtain D_{AA} (the so-called self-diffusion constant)? Is it a physical quantity?

Solution.
(1)
(i) Particles A and B can collide, if their centers of mass is within distance $(d_{\mathrm{A}} + d_{\mathrm{B}})/2$, so the collision cross section is given by

$$\sigma_{\mathrm{AB}} = \frac{\pi}{4}(d_{\mathrm{A}} + d_{\mathrm{B}})^2. \tag{7.110}$$

(ii) The condition must be

$$\sigma_{\mathrm{AB}} \times \ell_{\mathrm{AB}} \times n_{\mathrm{B}} = 1 \tag{7.111}$$

or

$$\ell_{\rm AB} = \frac{1}{\sigma_{\rm AB} n_{\rm B}} = \frac{1}{\pi[(d_{\rm A}+d_{\rm B})/2]^2 n_{\rm B}}. \tag{7.112}$$

(iii) If B molecules are also moving, we must reduce (7.112) with the ratio of the relative speed of A and B and the speed of A. (5.74) tells us the mean relative speed $v_{\rm AB}$ must be

$$v_{\rm AB} = \sqrt{\frac{8k_BT}{\pi\mu}} = \sqrt{\frac{8(m_{\rm A}+m_{\rm B})k_BT}{\pi m_{\rm A} m_{\rm B}}}. \tag{7.113}$$

The latter is just (5.69) with $m = m_{\rm A}$, so the ratio must be $\sqrt{(m_{\rm A}+m_{\rm B})/m_{\rm B}}$. Thus we get

$$\ell_{\rm AB} = \frac{1}{\sigma_{\rm AB} n_{\rm B}}\sqrt{\frac{m_{\rm B}}{m_{\rm A}+m_{\rm B}}} = \frac{\sqrt{m_{\rm B}}}{[\pi(d_{\rm A}+d_{\rm B})/2]^2\sqrt{(m_{\rm A}+m_{\rm B})}n_{\rm B}}. \tag{7.114}$$

This indeed gives our formula (6.2), if A and B are identical.

(2) In (6.28) $\overline{v}$ is the speed of A and ℓ must be $\ell_{\rm AB}$. Therefore,

$$D_{\rm AB} = \frac{1}{3}\frac{1}{\pi[(d_{\rm A}+d_{\rm B})/2]^2 n_{\rm B}}\sqrt{\frac{8k_BT}{\pi m_{\rm A}}}. \tag{7.115}$$

Here the numerical factor $2\sqrt{2}/3 \approx 1$ should not be paid much attention (so ignored below).

(3) By symmetry, we get

$$D_{\rm BA} = \frac{1}{\pi[(d_{\rm A}+d_{\rm B})/2]^2 n_{\rm A}}\sqrt{\frac{k_BT}{\pi m_{\rm B}}}. \tag{7.116}$$

(4) To count the number $z_{\rm AB}$ of collisions between a particular particle of A and B particles in one second, we can imagine a 'swept cylinder' of cross section $\sigma_{\rm AB}$ times length $v_{\rm AB}$ (see (7.113)) and then count all B particles in it:

$$z_{\rm AB} = \pi\left[\frac{d_{\rm A}+d_{\rm B}}{2}\right]^2\sqrt{\frac{8(m_{\rm A}+m_{\rm B})k_BT}{\pi m_{\rm A} m_{\rm B}}}n_{\rm B}. \tag{7.117}$$

This is for one particle of A and there are $n_{\rm A}$ in a unit volume, so

$$Z_{\rm AB} = n_A z_{\rm AB} = \pi\left[\frac{d_{\rm A}+d_{\rm B}}{2}\right]^2\sqrt{\frac{8(m_{\rm A}+m_{\rm B})k_BT}{\pi m_{\rm A} m_{\rm B}}}n_{\rm A}n_{\rm B}. \tag{7.118}$$

Notice that this is symmetric as you expect: $Z_{\rm AB} = Z_{\rm BA}$.

(5) Perhaps, you may think equating quantities with suffix A and those with B

suffices by replacing B $\to$ A. Wrong, because A particles are indistinguishable. In the case of A and B, a collision due to A coming from 'right' and B coming from 'left' and that due to B coming from 'right' and A coming from 'left' are distinct. If B is A, then these two collisions are identical, so (7.118) with A = B double-counts the number of AA-collisions. Therefore,[174]

$$Z_{\mathrm{AA}} = \frac{1}{2}\pi d_{\mathrm{A}}^2\sqrt{\frac{8k_BT}{\pi m_{\mathrm{A}}}}n_{\mathrm{A}}^2 = \pi d_{\mathrm{A}}^2\sqrt{\frac{2k_BT}{\pi m_{\mathrm{A}}}}n_{\mathrm{A}}^2. \tag{7.119}$$

(6) Strictly speaking, the particle 'self-diffusion' coefficient D_{AA} is meaningless, because we cannot track a particle A in the crowd (cloud?) of A's. D_{AA} is not observable, so it is meaningless empirically.

If there is a spatial nonuniformity in the particle distribution, it diffuses away as described by a diffusion equation, so there is some sort of diffusion constant D_{A}. This is sometimes called the collective diffusion constant, which is observable (so meaningful). However, it is questionable that D_{A} is related to the formula D_{AA}.

D4.2 [Random walker with wind]

On a triangular lattice or a square lattice (see Fig. 7.11 A & B) with the edge length a is a random walker.

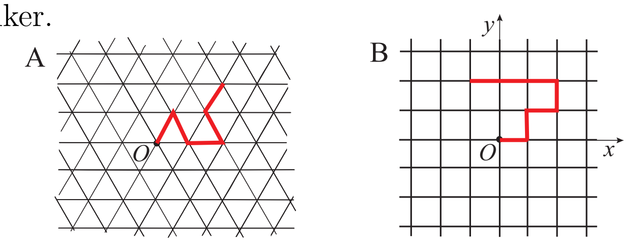

Figure 7.11: 2D random lattice walks: Triangular lattice (A) and square lattice (B)

The walker starts from the origin O and walks along the edges. At every second she chooses randomly any of the edges connected to her current position and moves to the nearest neighbor lattice point along the chosen edge. You can assume that she completely forgets what lattice point she was at less than 1 second (i.e., all the steps are statistically independent).

(0)* After N ($\in \mathbb{N}^+$, positive integers) steps, on the average which random walker can go farther away from the origin in Fig. 7.11 A or B? Justify your guess.

(1) What is the mean square displacement $\langle \boldsymbol{R}^2 \rangle$ of the walker after t seconds on the triangular lattice, where $\boldsymbol{R} = (X, Y)$ is the location of the walker at time t?

(2) What is the mean square displacement $\langle \boldsymbol{R}^2 \rangle$ of the walker after t seconds on the

[174] Although I said the numerical prefactor is not important, IF you use the same approximations, the overall multiplier 1/2 in the result must be respected.

square lattice?

(3) Now, on the square lattice due to a strong wind blowing constantly in the $+x$ direction, the walker tends to choose $+x$ direction with probability 0.5, but still chooses the remaining three directions randomly (with probability 1/6 for each).

(i) What is the average position (x and y coordinates) of the walker after t seconds?

(ii) What is the variance of the y-coordinate (i.e., $V(Y)$) after t seconds?

(iii)* What is the mean square displacement $\langle \boldsymbol{R}^2 \rangle$ of the walker after t seconds?

(iv)* Find the variance $V(X) + V(Y)$. Can this decrease due to the wind?

Solution.

(0) The same. Really? Isn't the random walk trajectory on the triangular lattice more folded than that on the square lattice? Explain (qualitatively).

(1), (2) Let $\boldsymbol{r}_i$ be the vector denoting the ith step. The total displacement after t steps $\boldsymbol{R}$ reads

$$\boldsymbol{R} = \sum_{i=1}^{t} \boldsymbol{r}_i. \tag{7.120}$$

Therefore, thanks to the statistical independence of steps and the average step displacement being zero, we obtain

$$\langle \boldsymbol{R}^2 \rangle = \sum_{i=1}^{t} \langle \boldsymbol{r}_i^2 \rangle. \tag{7.121}$$

Obviously, $\langle \boldsymbol{r}_i^2 \rangle = a^2$, so $\langle R^2 \rangle = ta^2$.

$*$ Does this calculation depend on spatial dimensionality or the lattice structure?

(3)

(i) The position after t seconds is

$$\boldsymbol{R} = \sum_{i=1}^{t} \boldsymbol{r}_i. \tag{7.122}$$

Therefore, the average position is $\langle \boldsymbol{R} \rangle = t \langle \boldsymbol{r}_1 \rangle$.

$$\langle \boldsymbol{r}_1 \rangle = 0.5(a, 0) + [(-a, 0) + (0, a) + (0, -a)]/6 = (a/3, 0). \tag{7.123}$$

Therefore, $\langle \boldsymbol{R} \rangle = ((1/3)at, 0)$.

(ii) $Y = \sum_{i=1}^{t} y_i$, where y_i is the y-component of the ith step vector. We know $\langle Y \rangle = 0$, so using the statistical independence of steps, we have

$$V(Y) = \langle Y^2 \rangle = \sum_{i=1}^{t} \langle y_i^2 \rangle, \tag{7.124}$$

where

$$\langle y_1^2 \rangle = (2/3) \times 0 + (1/3)a^2 = a^2/3. \tag{7.125}$$

Therefore, $V(Y) = a^2 t/3$.
(iii) We need

$$\langle \boldsymbol{R}^2 \rangle = \sum_{i=1}^{t} \langle \boldsymbol{r}_i^2 \rangle + \sum_{i \neq j} \langle \boldsymbol{r}_i \cdot \boldsymbol{r}_j \rangle. \tag{7.126}$$

Although each step is statistically independent (so you may write $\langle \boldsymbol{r}_i \cdot \boldsymbol{r}_j \rangle = \langle \boldsymbol{r}_i \rangle \cdot \langle \boldsymbol{r}_j \rangle$), its average is not zero in this case, so you cannot ignore the cross terms. There are $t(t-1)$ cross terms, but they are all the same:

$$\langle \boldsymbol{r}_i \cdot \boldsymbol{r}_j \rangle = \langle \boldsymbol{r}_i \rangle \cdot \langle \boldsymbol{r}_j \rangle = \langle \boldsymbol{r}_1 \rangle^2. \tag{7.127}$$

We have already computed $\langle \boldsymbol{r}_1 \rangle = a/3$. Obviously, $\langle \boldsymbol{r}_i^2 \rangle = a^2$. Therefore, (7.126) reads

$$\langle \boldsymbol{R}^2 \rangle = a^2 t + \frac{1}{9} a^2 t(t-1) = \frac{1}{9} a^2 t^2 + \frac{8}{9} a^2 t. \tag{7.128}$$

(iv) The sum of the variances are

$$V(X) + V(Y) = \langle \boldsymbol{R}^2 \rangle - \langle X \rangle^2 - \langle Y \rangle^2 = \frac{1}{9} a^2 t^2 + \frac{8}{9} a^2 t - \left(\frac{1}{3} at \right)^2 = \frac{8}{9} a^2 t, \tag{7.129}$$

which is smaller than $a^2 t$.[175]

D4.3 [Solving Langevin equation].
We wish to consider a Brownian particle suspended in an equilibrium fluid of temperature T. Let us start with the **original**[176] Langevin equation in the following form (but in the one dimensional space)

$$m \frac{dv}{dt} = -\zeta v + w(t), \tag{7.130}$$

where v is the 1D-velocity, m is the mass of the Brownian particle, ζ is the friction constant, and $w(t)$ is the noise force due to bombardments by molecules of the fluid.

(1) Assuming that the noise $w(t)$ is given as a function of t, find v as a function of time. You may assume that the initial velocity is v_0.

(2) If we wait for a sufficiently long time (that is, t is sufficiently large), the initial velocity should be totally forgotten, so in order to understand the long-time behavior we may assume $v_0 = 0$ without any loss of generality. After confirming this (or giving

[175] Of course, this is due to the artificial setting that the wind speed is really constant; in reality probably the wind speed fluctuates wildly, so the variance could be much larger with the wind.
[176] not the overdamped version.

your argument for this), compute the ensemble average $\langle v(t)^2 \rangle$ of $v(t)^2$ in terms of the time correlation function of the noise $\varphi(s-s') = \langle w(s)w(s') \rangle$, where $\langle\ \rangle$ denotes the ensemble average. Notice that since the fluid in which the particle is suspended is in equilibrium, φ does not depend on the absolute time, but only on the time lapse between s and s'.

(3) We may assume that the noise changes so randomly and so rapidly that $w(s)$ and $w(s')$ at different times are statistically independent and their averages are zero. Therefore, we may write

$$\varphi(s-s') = \langle w(s)w(s') \rangle = C\delta(s-s'), \tag{7.131}$$

where C is a positive constant (the square noise amplitude). After a long time (i.e., in the $t \to \infty$ limit) $v(t)$ must be compatible with the equipartition of translational kinetic energy: $\langle v^2(t) \rangle = k_B T/m$, so we cannot choose C arbitrarily. Find C in terms of $k_B T$ and ζ.[177]

Solution.
(1) Solving the ODE

$$\frac{dv}{dt} = -(\zeta/m)v + w(t)/m, \tag{7.132}$$

we get (see below, if you need an explanation)

$$v(t) = v_0 e^{-(\zeta/m)t} + \int_0^t ds\,(w(s)/m)e^{-(\zeta/m)(t-s)}. \tag{7.133}$$

⟪How to solve (7.130)⟫
A standard way to get this is the variation of parameters: If $w \equiv 0$, we easily get the general solution as

$$v(t) = Ae^{-(\zeta/m)t}. \tag{7.134}$$

Now, we assume the integration constant A is a function of t as

$$v(t) = A(t)e^{-(\zeta/m)t} \tag{7.135}$$

and put this in the original ODE. We obtain

$$A'(t)e^{-(\zeta/m)t} - (\zeta/m)Ae^{-(\zeta/m)t} = -(\zeta/m)Ae^{-(\zeta/m)t} + w(t)/m \tag{7.136}$$

or

$$A'(t) = (w(t)/m)e^{(\zeta/m)t}. \tag{7.137}$$

This may be solved easily as

$$A(t) = A(0) + \int_0^t ds\,(w(s)/m)e^{(\zeta/m)s}. \tag{7.138}$$

[177]This is also a fluctuation-dissipation relation. You might wonder why the answer is different from the fluctuation-dissipation relation we discussed in the lecture. Note the difference in the definitions of the noise for overdamped and not overdamped cases.

Therefore, the general solution to the original ODE reads

$$v(t) = A(0)e^{-(\zeta/m)t} + \int_0^t ds\,(w(s)/m)e^{-(\zeta/m)(t-s)}. \tag{7.139}$$

We immediately identify $A(0) = v_0$.

(2) If t is sufficiently long, since m and ζ are positive, the first term in our solution becomes indefinitely small, so we need not pay attention to the initial condition. We may set $v_0 = 0$:

$$v(t) = \int_0^t ds\,(w(s)/m)e^{-(\zeta/m)(t-s)}. \tag{7.140}$$

From this we obtain

$$v(t)^2 = \int_0^t ds \int_0^t ds'\,(w(s)/m)e^{-(\zeta/m)(t-s)}(w(s')/m)e^{-(\zeta/m)(t-s')}, \tag{7.141}$$

which, upon ensemble averaging, gives

$$\langle v(t)^2\rangle = \frac{1}{m^2}\int_0^t ds \int_0^t ds'\,e^{-(\zeta/m)(2t-s-s')}\langle w(s)w(s')\rangle = \frac{1}{m^2}\int_0^t ds \int_0^t ds'\,e^{-(\zeta/m)(2t-s-s')}\varphi(s-s'). \tag{7.142}$$

(3) Introducing (7.131) into the above equation, we get

$$\langle v(t)^2\rangle = \frac{C}{m^2}\int_0^t ds \int_0^t ds'\,e^{-(\zeta/m)(2t-s-s')}\delta(s-s'). \tag{7.143}$$

An easy integration gives

$$\langle v(t)^2\rangle = \frac{C}{m^2}\int_0^t ds\,e^{-2(\zeta/m)(t-s)} = \frac{C}{2m\zeta}\left(1 - e^{-2\zeta t/m}\right). \tag{7.144}$$

That is, in the $t \to \infty$ limit, we get

$$\langle v(t)^2\rangle \to \frac{k_BT}{m} = \frac{C}{2m\zeta}. \tag{7.145}$$

Thus, we have fixed C as

$$C = 2k_BT\zeta. \tag{7.146}$$

As noted in the footnote 165, this relates the noise (amplitude squared C) and the dissipation (ζ), so it is a respectable fluctuation-dissipation relation. The noise ν in the text (the overdamped version) is $\nu = w/\zeta$, so the amplitude of ν is our C obtained here divided by ζ^2. Thus, our whole story is consistent.

D4.4 [Following Perrin using the Boltzmann factor]
Perrin counted the number of suspended Brownian particles with radius $r = 0.212$ μm with density 1206 kg/m^3. His result at $T = 288$ K is shown in Fig. 7.12. Since the gas constant $R = 8.314$ J/mol·K is obtainable from the ideal gas law (you need P, V and T, and the definition of mole), from his data we can estimate Avogadro's constant N_A. How good is it?

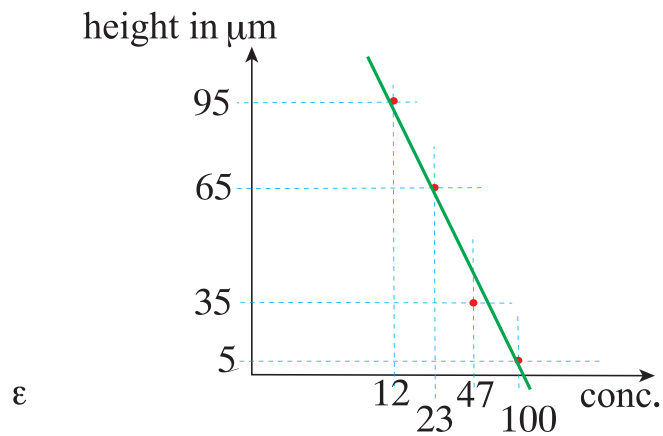

Figure 7.12: Sedimentation equilibrium observed by Perrin

In the figure the unit of the concentration may be anything, since we need only the ratios.

Solution.
This is a simple Boltzmann factor question. The potential energy difference of the particle of radius r due to the height difference h is, if the particle of density ρ is suspended in a fluid of density ρ_0, $(4\pi r^3/3)(\rho - \rho_0)gh$; you must take the buoyancy into account. Therefore, the number density $n(h)$ at height h obeys

$$n(h) = n(0) \exp\left(-\frac{(4\pi r^3/3)(\rho - \rho_0)ghN_A}{RT}\right), \tag{7.147}$$

where R is measurable using an ideal gas. The experimental result can give a:

$$\log \frac{n(h)}{n(0)} = -\frac{(4\pi r^3/3)(\rho - \rho_0)ghN_A}{RT} = -ah \tag{7.148}$$

Therefore, we can calculate

$$a = \frac{(4\pi r^3/3)(\rho - \rho_0)gN_A}{RT} = \frac{(4\pi(0.212 \times 10^{-6})^3/3)(1206 - 1000) \times 9.8N_A}{8.314 \times 288} = 0.0337{\times}10^{-18}N_A. \tag{7.149}$$

The slope is obtained from the graph Fig. 7.12; roughly,

$$a = \left(\log \frac{100}{12}\right) \Big/ 95 \times 10^{-6} = 2.23 \times 10^4. \tag{7.150}$$

Thus, $N_A = (2.23 \times 10^4 / 3.37 \times 10^{-20}) = 6.6 \times 10^{23}$. Perhaps, too good.

Exercise 4

E4.1 [Elementary estimates for Argon gas]
At 300 K and 1 atm 1 mole of argon gas (molecular weight 40) occupies a volume of 24.6 liters. The diameter of argon molecule is 2.9 Å. You may treat an argon molecule as a hard ball.
(1) What is the root mean-square velocity $\sqrt{\langle \boldsymbol{v}^2\rangle}$ of an argon molecule?
(2) What is the average distance between nearest pair of argon molecules?
(3) What is the mean free path ℓ?
(4) How many collisions on the average each argon molecule experiences in one second?
(5) What is your estimate of the isotope diffusion constant[178] for ^{39}Ar? You may ignore the isotope mass difference.

Solution.
(1) We use Bernoulli's equation

$$PV = \frac{1}{3}Nm\langle v^2\rangle, \tag{7.151}$$

where m is the mass of argon molecule. Therefore, $(M = Nm)$

$$\langle \boldsymbol{v}^2\rangle = \frac{3PV}{M} = \frac{3\times 101325\times 24.6\times 10^{-3}}{0.04} = 1.87\times 10^5. \tag{7.152}$$

Thus, $\sqrt{\langle \boldsymbol{v}^2\rangle} = 432$ m/s.

(2) If we can make a cube containing one molecule on the average, its edge length should be the representative distance between the nearby pair of molecules. The volume of the cube is

$$\mathrm{v} = 24.6\times 10^{-3}/6.02\times 10^{23} = 4.08\times 10^{-26} \ \Rightarrow \mathrm{v}^{1/3} = 3.4\times 10^{-9}, \tag{7.153}$$

that is 3.4 nm.

(3) We use

$$\ell = \frac{1}{\sqrt{2}\pi d^2 n}. \tag{7.154}$$

Since $n = 6.02\times 10^{23}/24.6\times 10^{-3} = 2.44\times 10^{25}$ $(= 1/\mathrm{v})$,

$$\ell = \frac{1}{\sqrt{2}\pi(2.9\times 10^{-10})^2 2.44\times 10^{25}} = \frac{1}{91.2\times 10^5} = 1.10\times 10^{-7}. \tag{7.155}$$

Thus, $\ell = 110$ nm.

(4) In one sec a molecule can cover about 430 m, so there are about $430/1.10\times 10^{-7} =$

[178] It is almost self-diffusion, but here the diffusing particle is distinct from the 'background' argon 40.

3.94×10^9 collisions.

(5) Let us use $D = \sqrt{\langle \boldsymbol{v}^2 \rangle}\ell/3$ with $\sqrt{\langle \boldsymbol{v}^2 \rangle}$ given above ignoring the effect of the mass difference:

$$D = \frac{1}{3}\sqrt{\langle \boldsymbol{v}^2 \rangle}\ell = \frac{1}{3} \times 432 \times 1.10 \times 10^{-7} = 1.58 \times 10^{-5}\ \mathrm{m}^2/\mathrm{s}. \tag{7.156}$$

E4.2 [Fluctuation-dissipation relation]
There is a 1D harmonic oscillator in a viscous fluid, obeying the following Langevin equation:

$$\frac{dx}{dt} = -\frac{1}{\zeta}kx + \nu, \tag{7.157}$$

where ζ and k are positive constants (the viscous damping factor and the spring constant, respectively). ν is an appropriate equilibrium thermal noise.

(1) What is the amplitude (squared) of the noise ν (i.e., what is A $(= \langle \nu^2 \rangle dt)$), if the correct Boltzmann factor $e^{-kx^2/2k_BT}$ governs the equilibrium distribution of the oscillator position along the x-axis at temperature T? [You may quote the relevant formulas without working by yourself.]
(2) The distribution of x is governed by the Boltzmann factor in (1), which is a Gaussian function in this case. The root mean square displacement $\sqrt{\langle x^2 \rangle}$ of the oscillator is 1.2 nm at $T = 295$ K. What is the spring constant k? [Thus, observation of fluctuations allows us to estimate some mesoscale (or sometimes smaller scale) parameters.]
(3) If the viscosity of the fluid is large, then ζ is large, so the noise becomes small, but you must have realized that $\langle x^2 \rangle$ is independent of ζ. Despite small noise why the spread of the distribution is not small in this case? Explain this qualitatively within a couple of lines (with the usual font).

Solution.
The aim of this problem is to understand the relation between the equilibrium noise (or the random force) acting on a Brownian particle and the intensity of dissipation (or the intensity of the brake) acting on it; to maintain the particle equilibrium distribution close to the one compatible with the Boltzmann factor these two quantities cannot be arbitrarily chosen. For example, if dissipation is large and noise small, then the particle would be very tightly captured by the potential. If dissipation (brake) is small and noise large, the Brownian particle wanders off excessively.
(1) As the hint says, you can simply read off the answer: A $(= \langle \nu^2 \rangle dt) = 2k_BT/\zeta$ (the fluctuation-dissipation relation (FDR)).

Perhaps, the most elementary approach from scratch to justify FDR may be to use

$$\frac{dx}{dt} = \nu. \tag{7.158}$$

This should describe the trajectory of a Brownian particle = random walk. From this we get

$$\langle x^2(t)\rangle \;=\; \int_0^t ds \int_0^t ds' \,\langle \nu(s)\cdot\nu(s')\rangle = At. \tag{7.159}$$

On the other hand, we may follow the original Langevin argument leading to (7.8) and conclude that

$$\langle x^2\rangle = \frac{2k_BT}{\zeta}t. \tag{7.160}$$

Comparing these two, we conclude that

$$A = \frac{2k_BT}{\zeta}. \tag{7.161}$$

(2) The Boltzmann factor gives just the Gaussian distribution for x. By inspection, you can read $\sigma^2 = k_BT/k$ off. Hence, $\langle kx^2\rangle = k_BT$ or $k = k_BT/\langle x^2\rangle$ ($k_B = 1.38 \times 10^{-23}$ J/K).

$$k = 1.38 \times 10^{-23} \times 295/(1.2 \times 10^{-9})^2 = 2.83 \times 10^{-3} \text{ N/m}. \tag{7.162}$$

That is, $k = 2.83$ pN/nm (pico newton/nanometer is just the right size for biomolecules).

(3) If the fluid is very viscous, a displacement from the origin cannot decay easily. Therefore, small displacement due to small noise can accumulate to a significant total displacement.

8 Macrosystems

Summary
* If numerous particles gather, important observables are extensive (additive) or intensive.
* Even though underlying mechanics is reversible, macroscopic systems exhibit irreversibility.
* For a macroscopic system its total mechanical energy is additive with high precision.

Key words
Internal energy, reversibility of mechanics, Poincaré recurrence

What you should be able to do
* Explain why the total mechanical energy of a macroscopic system is additive.
* Explain why irreversibility naturally occurs in systems with many particles.

8.1 How to describe a macroscopic system in mechanics

We do not need any special way to describe a macroscopic system, if we wish to describe it purely mechanically. Mechanical entities are atoms and molecules, so a system is mechanically described by the system Hamiltonian whose independent variables are position and momentum vectors of particles.

The Hamiltonian of a system consisting of N point particles of mass m interacting with a potential energy $U(\boldsymbol{x}_1, \cdots, \boldsymbol{x}_N)$ has the following form

$$H = \sum \frac{1}{2} m\dot{\boldsymbol{x}}_i^2 + U(\boldsymbol{x}_1. \cdots, \boldsymbol{x}_N). \tag{8.1}$$

The first terms describe the kinetic energy K (here, K is the total kinetic energy). Usually, we may assume that U depends on the mutual positions of the particles and not on the absolute positions of the particles. The value of H is the *total mechanical energy* of the system.

Since we are interested in the 'intrinsic' properties of the system, we are not interested in the overall translation and rotation. Thus, we are interested in the Hamiltonian of the system observed from the coordinate system relative to which the system does not exhibit any overall translational and rotational motion (the co-moving coordinate system). The total mechanical energy of the system observed by the co-moving observer is understood as the 'intrinsic' mechanical energy of the system.

8.2 Conservation of mechanical energy and the first law of thermody-

namics

Unless there is an exchange of energy with the external world, the total 'intrinsic' mechanical energy (8.1) of a system sitting still relative to the observer should obviously be conserved according to the conservation of mechanical energy. In thermodynamics the total 'intrinsic' mechanical[179] energy is called the *internal energy*. Thus, the internal energy of a system must be a conserved quantity. This is the essence of *the first law of thermodynamics*.[180] This was recognized by Carnot, Mayer, Helmholtz and others, but Helmholtz most clearly recognized the first law as a consequence of the conservation of mechanical energy, especially due to the fact that intermolecular interactions have potential functions.[181]

8.3 Two crucial features of macroscopic systems

What are the salient features of a system consisting of numerous particles? Two features come to our mind: additivity of energy and irreversibility of time evolution.

8.4 Additivity of energy

The usual intermolecular interaction decays spatially sufficiently quickly (Fig. 8.1).

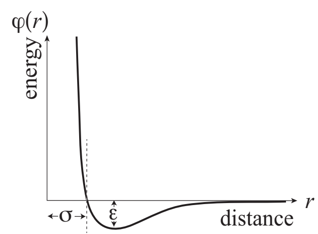

Figure 8.1: The intermolecular force potential. The repulsive portion is very steep (any steep function will do to describe it, say, $1/r^{12}$), which is due to electron-cloud overlap. The attractive potion is $1/r^6$, which is due to the induced dipole-dipole interaction (the London force). Roughly speaking, the binary intermolecular force is characterized by the repulsive (or hardcore) diameter d (the representative length scale) and the depth of the potential well ε (the representative energy scale).

If a system volume is split into two $V_1 + V_2$ with a simple boundary surface,[182] the

[179]If there are electromagnetic effects, this energy must be expanded to include the electromagnetic energy.

[180]Strictly speaking, thermodynamics discusses the systems in equilibrium, so the first law is a restricted version of the low of conservation of energy.

[181]Since no one can verify all the particles indeed obey microscopic mechanics, a more precise statement is that the empirically established first law strongly suggests that the microscopic mechanical model of a system is in terms of conserved intermolecular forces.

[182]not a fractal surface, for example; we say we split the volume into two volumes in a *van Hove* way.

sum of the total mechanical energies of the volumes is very close to the total mechanical energy of the whole system before splitting.

If the interaction energy between two particles decays faster than $r^{-\mathfrak{d}}$ in $\mathfrak{d}$-space, where r is the interparticle distance,[183] then the total interaction energy of a single molecule i near the boundary of V_1 with those in V_2 may be estimated as (see Fig. 8.2)

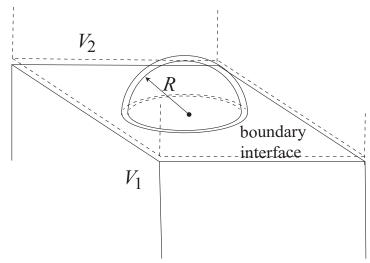

Figure 8.2: How to estimate the 'interface energy.'

$$\sum_{j \in V_2^*} \frac{1}{r_{ij}^{\mathfrak{d}+\varepsilon}} \simeq \int_{V_2^*} dy \frac{1}{|y|^{\mathfrak{d}+\varepsilon}} \propto \int_\delta^L R^{\mathfrak{d}-1} dR \, \frac{1}{R^{\mathfrak{d}+\varepsilon}} \sim \int_\delta^L dR \, \frac{1}{R^{1+\varepsilon}} \sim L^{-\varepsilon} + \text{const.} \quad (8.2)$$

Here, r_{ij} is the distance between particles i and j, V_2^* is the subset of V_2 such that the portion within distance δ from particle i is removed from V_2. This calculation shows that the relative contribution of the interaction energy that depends on the system size L becomes smaller as the system size becomes bigger. Of course, we cannot ignore the close-range contributions from the portion within distance δ of the particle as well as the constant term in (8.2), but even if we collect such contributions from all the molecules on or near the boundary, they are only proportional to $L^{\mathfrak{d}-1}$ (i.e., the surface area), so we may ignore them relative to the bulk energy $\propto L^{\mathfrak{d}}$ for macroscopic systems.

Thus, if the interaction potential decays faster than $r^{-\mathfrak{d}}$, then we may assume that the total energy is proportional to the volume of the system.

8.5 How about forces with potential $\propto 1/r$?

The Coulomb and gravitational interaction energies decay as $1/r$. For the Coulomb interaction, thanks to the shielding effect, if the system is charge-neutral, the effective interaction decays exponentially, so we need not worry about it.

For the gravity, there is no way to shield it, but the usual macroscopic objects we are interested in in statistical physics is not huge (usually about 1 m^3 or less with not

[183]Since the interactions are not totally binary, precisely speaking, we need to assume that the total interaction energies among particles is about the same order as the total contribution of the binary interactions. This is a bit delicate, but usually this is true.

a huge density like a neutron star), so we may ignore it (unless we discuss sedimentation equilibrium; even in such cases we may safely ignore gravitational interactions among the particles in the system).[184]

8.6 Why we are interested in additive quantities

To study a macroscopic system we often study additive observables that is proportional to the system size (think of internal energy). This is natural, because such observables are big for big systems. If an observable becomes smaller for larger systems, we need not pay attention to such quantities to understand the macroscopic world. Thus, we are interested in observables that are independent of the system size (*intensive quantities*) and those proportional to the amount of materials in the system (*extensive quantities*).

8.7 Time-reversal symmetry of mechanics

The world of mechanics is time-reversal symmetric (the world in which the movies played backward do not look funny). In the case of classical mechanics, Newton's equation of motion of a closed (isolated) system is an autonomous differential equation of second order without any first order derivative: For an N-particle system, generally we have

$$\frac{d^2\boldsymbol{x}_i}{dt^2} = \boldsymbol{F}_i(\boldsymbol{x}_1, \cdots, \boldsymbol{x}_N) \tag{8.3}$$

for $i = 1, \cdots, N$. Since the forces $\boldsymbol{F}_i$ are t independent in the closed system, $t \to -t$ does not change the equations.

The Schrödinger equation for an isolated system reads

$$i\hbar\frac{\partial\psi}{\partial t} = H\psi, \tag{8.4}$$

where H is a Hermitian operator independent of time. In this case $t \to -t$ might seem to alter physics, but what we observe is real, so the physics must be intact under complex conjugation.[185] Thus, quantum physics is also intact under time reversal.

8.8 In the long run we are all dead

But in the long run we are all dead and will never be resurrected. The world we live in is definitely irreversible. How come?

---

[184] If the system really becomes huge, our ordinary statistical thermodynamics does not work.

[185] Hermitian conjugation, more precisely.

8.9 Irreversibility from mechanics?

All the ambitious young men (Boltzmann 1844-1906, Einstein, 1879-1955, ...) tried to explain irreversibility from mechanics.

Boltzmann derived in 1872[186] from a pure microscopic mechanical description of atoms an equation (called the Boltzmann equation) that governs the irreversible time evolution of dilute gasses by ignoring some statistical correlations. His colleague Loschmidt (1821-1895) asked why Boltzmann could derive an irreversible equation from a reversible equation. This question made Boltzmann realize that his derivation included a sort of coarse-graining. Boltzmann explained that the initial 'non-equilibrium' states always contain more order (so inevitably subtle correlations as well), so the time evolution always drives the system to the less ordered direction; thus his equation correctly captures this tendency.

Then, in 1896, came Zermelo (1871-1953), an assistant to Planck (1858-1947) those days, who, utilizing Poincaré's recursion theorem,[187] pointed out that Boltzmann's argument was logically flawed: even if the system is coarse-grained, sooner or later the state of a closed system returns to a state indefinitely close to the starting state, so no irreversibility occurs. Boltzmann admitted the flaw, but since he was a theoretical physicist, he responded: "Young man, you know math, but you don't know physics. Think how long it takes for that to happen? It would take far longer than the age of the universe even for a very small system."

8.10 What is the lesson?

What we have learned from these debates are:
(1) Very often the initial state is special (away from equilibrium) so (even following the pure mechanics) for a long time irreversible behaviors are observed. The reason why the initial state cannot be recovered in various theories is that they discard subtle correlations (coarse-grain the system).
(2) However, if we can wait for long enough, any finite system (even after coarse-graining) almost comes back to its initial special state, but the required time is enormous, and we never experience this for macroscopic objects.

8.11 A toy model illustrating the lessons

A toy model can illustrate these points. Suppose a point is going around a unit circle with period 1 uniformly. The point is subjected to a noise that makes its angular speed fluctuate (see Fig. 8.3).

[186] [1872: Yellowstone NP established as the first NP in the world; G. Elliot: *Middlemarch* (in which Brown's famous booklet on Brownian motion showed up); C Monet: *Impression Sunrise*]

[187] Irrespective of time reversibility or irreversibility, a measure-theoretical dynamical system can return to a state indefinitely close to its initial condition.

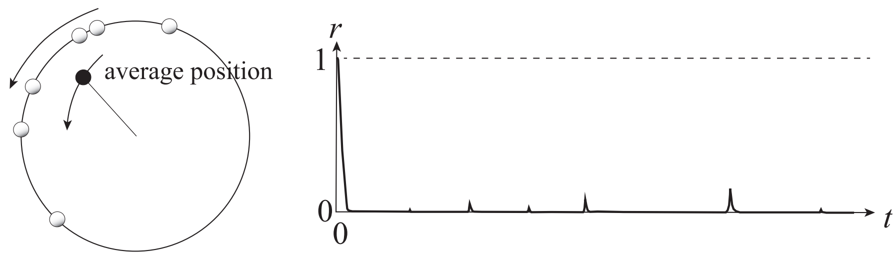

Figure 8.3: Ensemble of points with angular speeds slightly fluctuating around 2π rad/s. The averaged position spirals toward the center.

If there are only two such oscillators, their average position may become close to the origin, but then the average recovers its original amplitude fairly easily. If we have many ($N \gg 1$) such oscillators, after the average becomes close to zero, it stays small for an enormously long time, and then will return close to the original value. The waiting time for this recovery is likely to be of order e^{cN}, where c is a positive constant of order 1. [I do not know the precise quantitative results.]

Thus, as long as the system is finite, Zermelo is right, but as to the waiting time Boltzmann is right.

9 Thermodynamics: Principles

Summary
∗ Phenomenological approach is a respectable and basic method for understanding the world
∗ Equilibrium states may be described by the thermodynamic coordinates consisting of the internal energy and the work coordinates. The space spanned by the thermodynamic coordinates is called the thermodynamic space.
∗ Even if the change from one equilibrium state to another is irreversible, by devising a quasistatic path between them, changes in thermodynamic quantities may be computed thermodynamically.
∗ The first law is essentially the conservation of energy, but to describe it in terms of small number of macroscopic variables, changes (or processes) must be sufficiently slow.
∗ The second law implies that the thermodynamic space is foliated into adiabats = constant-entropy surfaces.

Key words[188]
Phenomenological approach, zeroth law, fourth law, thermodynamic coordinates, work coordinates, thermodynamic space, quasiequilibrium process, reversible process, state function, thermal contact, thermal equilibrium, temperature, conjugate pair, Clausius' law, Kelvin's law, Planck's law, adiabatic process, adiabat, Gibbs relation

What you should be able to do
∗ Explain why the thermodynamic coordinates are privileged coordinates.
∗ Understand that all three expressions of the second law mentioned here are equivalent.
∗ Demonstrate that we can introduce a state function called entropy. Also be able to explain its relation to heat.

9.1 Mechanics is not enough

As we have discussed in the last lecture, important characterization of macroscopic systems, extensivity of internal energy and irreversibility, may be understood from mechanics, so perhaps you may think mechanics can explain everything thermal as well. Unfortunately, however, we cannot confine ourselves to the discussion of closed (or isolated) systems. For example, we must discuss heat transfer, which is hard to

[188] There are many for the present section, but they are important, so you should try to memorize them at least once.

describe in terms of mechanics.[189]

We have learned that, although Brownian dynamics may well be due to underlying particle mechanics, we could set up a reasonable model (Langevin's equation) with the aid of the fluctuation-dissipation relation without directly referring to the underlying mechanics. This suggests that with a small number of postulates we can describe the key features of the macroscopic level. Such a description is a phenomenological description (phenomenology).

9.2 Phenomenological description of macrosystems

A phenomenological description of macroscopic systems is a description solely in terms of quantities that may be observed, described and defined on the macroscopic scale. If we could make a closed (complete) system of theory in terms of such quantities, the result is called a *phenomenology.* The phenomenology of macroscopic systems in equilibrium we now have is called thermodynamics. The reader must clearly recognize that, in contrast to (the supposedly more fundamental) statistical mechanics, thermodynamics survived the quantum revolution unscathed; actually it helped launching the revolution. Quantum mechanics has no problem with thermodynamics (for now), but even if quantum mechanics will be replaced by something more 'advanced,' thermodynamics will remain intact.

9.3 What is phenomenology, generally?

In physics, 'phenomenology' has not necessarily been respected; often it is almost a pejorative (e.g., in high-energy physics). However, notice that when underlying microscopic descriptions are impossible or only approximate, phenomenology may be the only realistic rational means for the human-beings to understand the world.

More generally, we may say that a self-contained description of phenomena at a given space-time scale is the general feature of phenomenology. Thus, quantum mechanics is a phenomenology at the microscopic scale. [190]

A phenomenology is not an approximate way to understand the world nor a crude version of something more accurate; thermodynamics is not an approximation of a certain more advanced and accurate theory.

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[189] Also we saw that the effect of the external world of the system cannot be completely eliminated. The long time limit ($t \to \infty$) and the 'external noise zero' limit (i.e., the pure mechanical limit) are not commutative, so purely mechanical description may well fail to describe the system reaching equilibrium after a long time.

[190] In this case, unfortunately, however, we the creator of the description is not on the same level, so a lot of difficulties ensue. Connecting different levels is always a source of conundrums and paradoxes.

9.4 Equilibrium states

A macroscopic system (a system with extremely many particles[191]) can take a special state called a *thermodynamic equilibrium state* (called an equilibrium state for simplicity). To specify the state, we introduce the concept, *generalized isolation*: a system is subjected under a generalized isolation condition if it is isolated but may be coupled to uniform field(s) conjugate to work coordinates (to be defined shortly). A macrosystem is in an *equilibrium state*, if it is left under a generalized isolated condition and eventually reaches a time-independent state.[192] Macro-observables observed at any time in equilibrium will take unchanging values forever.

A macroscopic system in equilibrium is partitioning-rejoining invariant: if a macroscopic system in equilibrium state is divided into two halves (of about the same sizes), the halves are themselves in equilibrium and if they are joined again, the result is indistinguishable from the original system as long as the thermodynamic observables are concerned (Fig. 9.1).

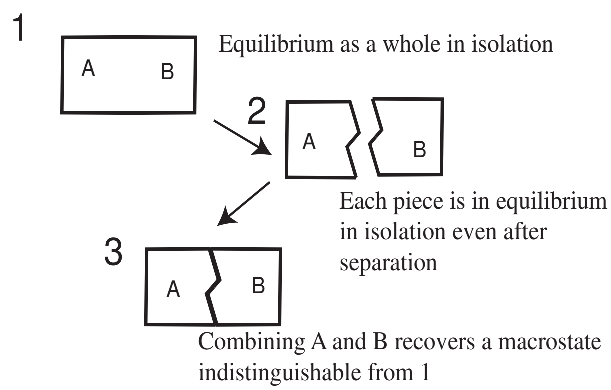


Figure 9.1: Partitioning-rejoining invariance of equilibrium states

Most textbooks are wrong: A traditional characterization of an equilibrium state is as follows: if a macrosystem is isolated and is left undisturbed for a long time, it would reach a macroscopic state (which is characterized by macroscopic observables) which would not change any further (if observed through macroscopic observables). This final state is a thermodynamic equilibrium state.

[191]⟪**What is macroscopic?**⟫ From the strictly macroscopic phenomenological point of view, since whether atoms and molecules exist or not is an irrelevant issue, it is more logical to say, “a system around us that we can see by our naked eyes” (as explained in Section 1, this characterization is actually scientific), but the book should be practical as well, so anything useful will be used to understand thermal physics.

[192]⟪**Equilibrium: another possible characterization**⟫ Equivalently, a macrosystem is in an equilibrium state, if we can devise a (macroscopically) constant and spatially uniform environment (without any dissipative currents) into which we can embed the system (with appropriate boundary conditions) and still the state does not change in time. Total isolation is a possible environment. However, not all the equilibrium states of a given system may be realized under the total isolation condition. Notice that this characterization of equilibrium never requires the isolation of a system from the external world. Also it never asks how the equilibrium state is realized. The state may be prepared in contact with a heat bath, for example.

Unfortunately, many states thermodynamics wish to consider cannot be reached this way. Thus, the traditional definition is, if not wrong, grossly incomplete.

9.5 The fourth law of thermodynamics

As already discussed intuitively **8.6**, macroscopically important observables are extensive or intensive. All the thermodynamic observables are either extensive or intensive. This is called the *fourth law of thermodynamics*.

Notice that partitioning-rejoining invariance in **9.4** makes the fourth law operationally meaningful.

9.6 Thermodynamic coordinates, a privileged set of variables

Since thermodynamics must be a phenomenology on the macroscopic scale, to construct a closed (self-contained) theoretical framework, we must carefully choose the physical quantities we deal with. The most fundamental of them are the *thermodynamic coordinates*. They are extensive quantities (= additive quantities that become important for macrosystems) and consist of internal energy E and other variables (called *work coordinates*) required to describe the macroscopic work supplied to the system that we can observe and control mechanically (electrodynamically) macroscopically. The system volume V is often among them. For a magnetic system, magnetization M is included.

Thermodynamic coordinates are a very special set of variables to describe equilibrium states that is privileged in the following sense:
(i) To understand thermodynamic coordinates we need only (macroscopic) mechanics and electromagnetism. The work that a system does or that a system is supplied can be described through the changes of these coordinates and is quantified solely electrodynamically.

Notice that we need not understand what 'heat' or 'temperature' is. Thus, as long as the thermodynamic properties are concerned, a macroscopic system is regarded as a black box with mechanically controllable handles.
(ii) The thermodynamic coordinates uniquely specify the equilibrium state. You could understand the meaning of this statement from Figure 9.2. Notice that T or P is *not* included in the thermodynamic coordinates.

9.7 Thermodynamic space

The space spanned by the thermodynamic coordinates is called the *thermodynamic space*. For a given macroscopic system, its each equilibrium state uniquely corre-

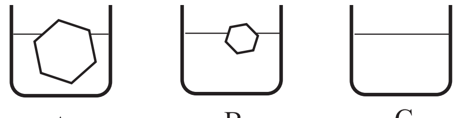


Figure 9.2: A-C contain the same amount of water at 0°C under 1 atmospheric pressure. However, their internal energies are distinct; A has the least internal energy and C the most. In elementary thermodynamics, often the temperature T appears as a key variable instead of internal energy E, but these examples clearly tell us that T cannot distinguish equilibrium states that are distinct. Analogously, in the liquid-gas phase transition under constant pressure P and T, E and V change. These examples indicate that thermodynamic coordinates are the fundamental 'privileged' set of variables to describe thermodynamic equilibrium state; generally speaking intensive variables such as T and P fail to describe states uniquely.

sponds to a point in the thermodynamic space of its own.[193]

Very Important Warning.
However, the converse is not true. That is, although any equilibrium state has its unique representative point in the thermodynamic space, even the same point may correspond to a nonequilibrium state. The crucial point is that the point in the thermodynamic space itself cannot tell us how it is changing (reversibly or irreversibly). For example, a hot coffee in a high-quality thermos very gradually cools toward the room temperature. The process could be indefinitely slow, so its state can always be infinitesimally close to a certain equilibrium state for a certain length of time. However, it is patently a state undergoing an irreversible process. Whether a point in the thermodynamic space is in equilibrium or not depends on the context (and the time scale).

9.8 Quasistatic processes

Thermodynamics wishes to study changes of equilibrium states by various processes. Not all (actually most) processes allowed to the system cannot be described in the thermodynamic space, because every point actually realizable in the thermodynamic space describes an equilibrium state of the system. Only processes that are extremely (infinitesimally) close (experimentally indistinguishably close) to equilibrium states at every moment may be expressed as continuous curves in the thermodynamic space (Fig. 9.3). In order for a process to be always close to equilibrium states it must be sufficiently slow.

However, the slowness of a process does NOT guarantee reversible changes.[194] A

[193]Some readers might question that there are much more macroscopic observables we can observe for a given object, shapes, orientation, etc. Precisely speaking, thermodynamic states are equivalence classes of macroscopically distinguishable states according to the values of the thermodynamic coordinates.

[194]Think of a hot coffee in a thermos.

Whether a given path in the thermodynamic space is reversible or not depends on the context.

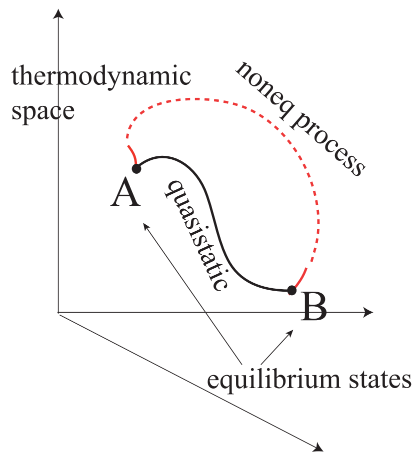


Figure 9.3: A and B are equilibrium states. A quasistatic process connecting A and B is in the thermodynamic space. From A to B a process need not be quasistatic. Then, most such processes cannot be described in the thermodynamic space (red).

quasistatic processes is a process along which both the system and its environment are (infinitesimally) close to equilibrium and can retrace their evolution precisely, i.e., 'reverse their footsteps.' Thus, a quasistatic process is also called a *retraceable processes*. Here, 'retracing' means that, after retracing the process, the world returns exactly to the original (macro)state. Thus, 'retraceable' means that, after retracing, the world returns to the state before the process occurs.

9.9 State functions

If the value of a macroscopic quantity of an equilibrium state is uniquely specified by the corresponding point in the thermodynamic space, the macroscopic quantity is called a *state function*.. That is, any observable that is a function defined on the thermodynamic space is a state function. Its value is indifferent to how the state is realized. For example, the equilibrium volume of a system is a state function; temperature is another example.

9.10 Simple system

An equilibrium system need not be spatially homogeneous at the macroscopic scale. If a system is spatially homogeneous, we call it a *simple system*.[195]

In the case of thermos, the process is undoubtedly irreversible. However, you could cool your coffee by removing heat reversibly by producing work. The path for your coffee may not be different from the case just above.

[195]If we need spatially inhomogeneous states, the system will be partitioned into sufficiently homogeneous macroscopic subsystems; if this is impossible, we will not discuss it thermodynamically in this book.

9.11 Compound system

Two or more simple systems considered as a single system with or without certain interactions among them is called a *compound system*. Even if the component simple systems are in equilibrium, the compound system as a whole may not be in equilibrium. The thermodynamic space of the compound system is the direct product of the thermodynamic spaces of the constituent simple systems. Just as in the thermodynamic space of a simple system, a point in the thermodynamic space of a compound system may correspond to a nonequilibrium state. We have to specify carefully the interactions among the constituent subsystems.

9.12 Why thermodynamics can be useful

When an initial state and a final equilibrium state are given, the change of a state function between these two states does not depend on the actual process but only on these initial and final equilibrium states. Even if the actual process connecting these two states is not a quasistatic process (i.e., does not lie in the thermodynamic space), we can thermodynamically compute the change of any state function during the process with the aid of an appropriate (appropriately devised) quasistatic process connecting the same end points. This makes thermodynamics extremely useful in practice.

9.13 Thermal contact

Empirically we know that even if there is no exchange of work or matter, two systems in contact can exchange their energies. Such a special contact is called *thermal contact*. If two systems A and B are in thermal contact and are in equilibrium as a compound system, we say A and B are in *thermal equilibrium*.

If the systems A and B are in thermal equilibrium, and if B and C are in thermal equilibrium, then so are the systems A and C. That is, the thermal equilibrium relation is an equivalence relation. This is called the *zeroth law of thermodynamics*. We can say that this equivalence relation is expressed as the equality relation between the temperatures of the systems.

Traditionally, the existence of (empirical) temperature is apparently deduced from the zeroth law, but actually, the argument is not even water tight. Besides, we do not need the zeroth law.

9.14 The first law of thermodynamics

As we have already noted, the *first law of thermodynamics* is essentially the conservation of mechanical energy (= internal energy) of the system. Mayer, Joule, Helmholtz and others established that the conservation of mechanical energy implies the existence of a state function E called *internal energy*. Its change ΔE cannot be explained solely in terms of the net work W supplied to the system, and the deficit Q is understood as the net heat given to the system:

$$\Delta E = W + Q. \tag{9.1}$$

Thus, in terms of thermodynamic coordinates that can be understood and quantified solely electrodynamically something called 'heat' whose 'true nature' is not very clear is macroscopically quantified. Notice that although E is a state function, neither W nor Q is a state function; they depend explicitly on the path connecting the initial and the final equilibrium states (the path may not be in the thermodynamic space).

9.15 Sign convention

Let us make the *sign convention* explicit. The sign is seen from the system's point of view: everything imported to the system is positive, and exported negative. For example, if you do work to the system, $W > 0$. If you get some useful work from the system $W < 0$.

9.16 Volume work

When the change is quasistatic, W and Q are determined by the equilibrium states of the system along the quasistatic path.

For example, the work $d'W$ required to change the system volume from V to $V + dV$ is given by (see Fig. 9.4)

$$d'W = -F dl, \tag{9.2}$$

if the infinitesimal displacement of the piston is dl and the external force is F.

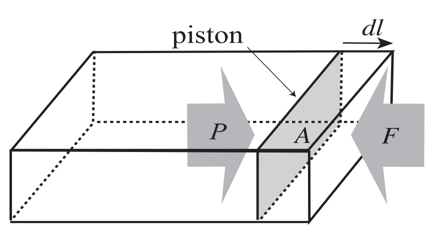


Figure 9.4: Work done by volume change.

Here, the differential expressing the infinitesimal work is written as $d'W$ instead of dW to indicate clearly that the infinitesimal is not the differential of a state function (not a perfect differential). According to our sign convention, if the system is done a work, then $d'W > 0$, but this happens when the volume shrinks, that is, when

$d\ell < 0$. Therefore, (9.2) has a minus sign. If the volume change is quasistatic, then the system pressure P and the external force F is always in balance,

$$F = A \times P, \tag{9.3}$$

where A is the cross section of the piston. Thus, we have arrived at the formula applicable to the quasistatic process:

$$d'W = -PAdl = -PdV. \tag{9.4}$$

If the process is fast, there would not be sufficient time for the system to equilibrate. For example, when we compress the system rapidly, the force necessary and the force given by (9.3) can be different; even the pressure P may not be well defined. Consequently, (9.4) does not hold (the work actually done is larger than given by (9.4)).

Thus, although the first law is essentially the conservation of mechanical energy, to write it in terms of a small number of variables, the change must be slow (quasiequilibrium).

9.17 Magnetic work

The electromagnetic work can be written as (see **Q9-2** at the end of this section)

$$d'W = \boldsymbol{B} \cdot d\boldsymbol{M}, \tag{9.5}$$

$$d'W = \boldsymbol{E} \cdot d\boldsymbol{P}, \tag{9.6}$$

where $\boldsymbol{B}$ is the magnetic field, $\boldsymbol{M}$ the magnetization, $\boldsymbol{E}$ the electric field, and $\boldsymbol{P}$ the polarization.

9.18 Prehistory of the second law

Joule quantitatively demonstrated (in 1847[196]) that work can be converted into heat,[197] and believed that work and heat were equivalent, but long before him Carnot (1796-1832) had already established (published in 1824[198]) the impossibility of complete conversion of heat into work. His brother told him (in 1844[199]) to pay attention

[196][1847: C. Bronte, *Jane Eyre*, E. Bronte, *Wuthering Heights* and W. H. Prescott, *A History of the Conquest of Peru* were published.]

[197]⟪**Work equivalent was established by Mayer**⟫ The work equivalent of heat was obtained by Mayer five years before Joule in 1842 with the aid of Mayer's cycle in **10.11**.

[198][1824: Beethoven's 9th Symphony (Karajan+BPO) premiered ; Thomson (also Kirchhoff and Smetana) was born.]

[199][1844: The first electrical telegram was sent by Morse; Goodyear patented vulcanization; Notice that Turner's famous *Rain, Steam and Speed, The Great Western Railway* (National Gallery, London) was this year (see footnote 189 below). Mozart died]

to the work of Carnot. Thomson (later Lord Kelvin) recognized the importance of Joule's work, but since he also accepted Carnot he did not believe work and heat were equivalent (Joule rejected Carnot). Thomson realized that Carnot's work could establish a universal scale of temperature, and introduced the concept of absolute temperature, but he failed to grasp the real relation between heat and work. To resolve the conflict between Joule and Carnot Thomson looked for further empirical facts, and failed to establish thermodynamics.

Clausius did not think further empirical facts were needed to resolve the conflict between Joule and Carnot. Carnot clearly recognized that only when there are hotter and colder heat baths can we produce work; there is a fundamental asymmetry between heat and work. Clausius understood this as follows: Temperature is the 'price' of energy. You cannot simply promote the price of energy (you cannot transfer energy from a colder to a hotter bath). Work corresponds to heat at $T = \infty$. Thus, thermodynamics was established by Clausius.

Now, it seems generally accepted that Clausius and Thomson (independently) constructed thermodynamics. But this is largely due to the British propaganda by Tait.[200] If Great Britain were defeated instead of Germany in WWI, the history would not have been distorted so easily.

Perhaps, a much more important prehistoric fact is that industry was far ahead.[201] Turner's painting of 1839, "The fighting Temeraire tugged to her last berth to be broken up, 1838," (Fig. 9.5) is emblematic of the era. Read the explanation on the

[200] Peter Guthrie Tait (1831-1901).

[201] ⟪**Industry was far ahead**⟫ The reader should compare the years in this footnote and those in the main text of this entry. Watt's steam engines were 1760-70, Trevithick's steam locomotive ('Puffing Devil') was 1804 and Stephenson's Locomotion for Stockton and Darlington Railway was 1825. Steamboats were earlier. Robert Fulton's boat with a Watt steam engine was 1807 (between New York and Albany 240 km for 32 hrs) [this year, Beethoven 4th symphony premiered; Jacques-Louis David, *The Coronation of Napoleon*].
Good animation of the Newcomen engine: https://www.youtube.com/watch?v=9GqVQPMCtY4
Only working Newcomen's engine at Black Country Living Museum is
https://www.youtube.com/watch?v=HC6LUWSBXjk
All above 'in one': https://www.youtube.com/watch?v=QltRwiu4U2Q

Watt was a versatile inventor: copying machine: https://www.youtube.com/watch?v=bKERVTLpGM0. Actually, this was to record the voluminous correspondence that building each engine entailed, everything had to be copied longhand [according to B. Russell, *James Watt: making the world anew* (Reaktion Books, London, 2014)].

J Hutton and Scottish Renaissance, which is the backdrop of study of heat and Watt's invention, is described in the following (geology) video (with Kelvin's blunder) https://www.youtube.com/watch?v=FYfuI2uZLmg

Robert Fulton https://www.youtube.com/watch?v=2w6x5QdswYE
Glass Stevenson's engine https://www.youtube.com/watch?v=73txXT21aZU
Replica Rocket https://www.youtube.com/watch?v=yNn0LC_9imY
no brakes https://www.youtube.com/watch?v=3woUopc1ZS4
History up to 'Rocket.' https://www.youtube.com/watch?v=wOGYZC-IJPQ

side of the painting in the National Gallery.

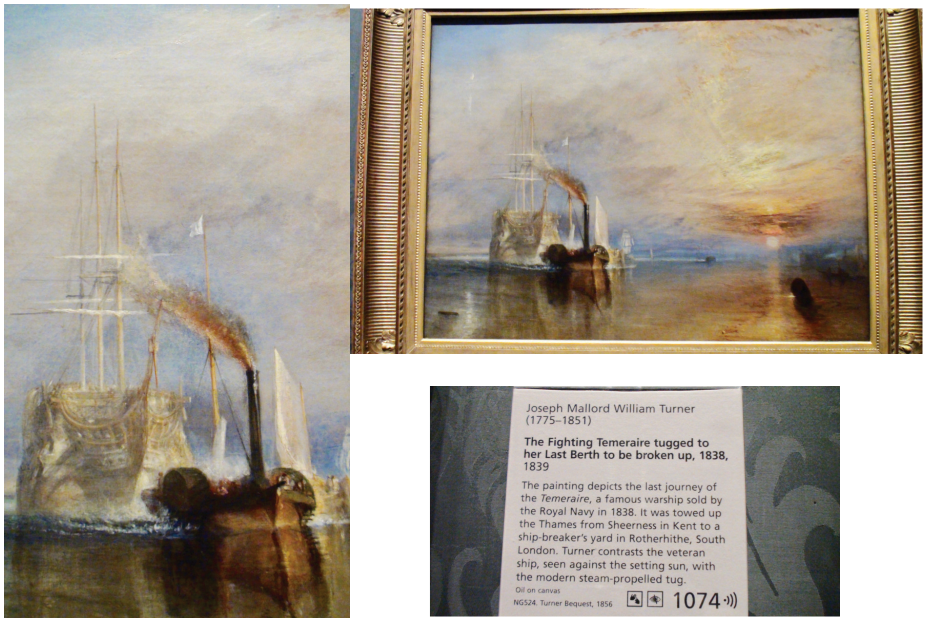


Figure 9.5: The fighting Temeraire tugged to her last berth to be broken up, 1838 (The National Gallery, London) [YO, 2019]

9.19 The second law of thermodynamics

The *second law of thermodynamics* summarizes what Carnot and Clausius clearly understood as follows. Two famous expressions are:

Clausius' principle: Heat cannot be transferred from a colder to a hotter body spontaneously.

Kelvin's principle: A process cannot occur whose only effect is the complete conversion of heat into work. (No existence of *perpetum mobile* of the second kind; there is no engine which can produce work without a radiator.)

Notice that Clausius' principle contains Kelvin's principle, if we understand work as the heat energy at $T = \infty$ as Clausius recognized.

Here, we use the second law in the following form:

9.20 Planck's principle and adiabatic process

Planck's law: In an adiabatic process if all the work coordinates return to their original value, $\Delta E \geq 0$.

Here, '*adiabatic process*' must be explained. In short, it is a process without any exchange of heat with the surroundings (a process realized in a Dewar jar).[202]

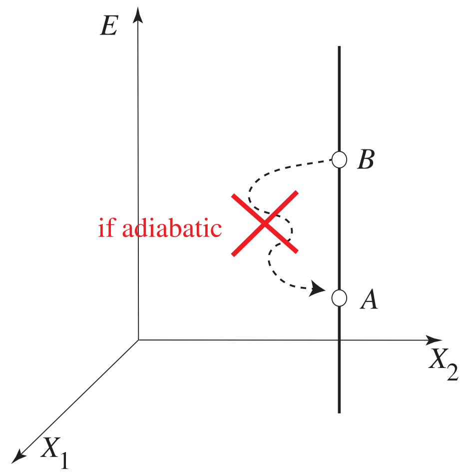


Figure 9.6: Planck's principle: A vertical move implies a purely thermal process. Adiabatically, there is no way to move from a state B to another state A that is vertically below it according to Planck's principle. Here, X_1, X_2 represent work coordinates.

The first law implies adiabatically and quasistatically[203]

$$dE = \sum_i x_i dX_i, \tag{9.7}$$

where (x_i, X_i) are conjugate pairs for work coordinates (non-thermal variables). The variables E and X_i span the thermodynamic space (of the system under study).

9.21 Planck's principle, Kelvin's principle and Clausius' principle are equivalent

None is more fundamental than the rest:

If Planck's principle is violated, then adiabatic work can reduce the system energy.

[202]There is a special wall called an *adiabatic wall* such that for a system surrounded by this wall the necessary work to bring the system from a given initial equilibrium state to a specified final equilibrium state is independent of the actual process but is dependent only on these two end states of the process. A process that can be realized in a system surrounded by adiabatic walls is an adiabatic process. Furthermore, even if a process is realized without surrounded by adiabatic walls but the same process can be realized surrounded by adiabatic walls, it is an adiabatic process. This turned about to be identical to the process without (net) heat exchange with its environment. Thus, even if a system is attached to a heat bath, a process in the system can be adiabatic. Notice that adiabatic process need not be describable in terms of pure mechanics.

[203]often 'quasistatically' is not mentioned explicitly, but to describe the process in terms differentials of state variables, the process must be sufficiently slow.

That is, work can be produced by a single heat bath. Therefore, Kelvin's principle is violated.

If Kelvin's principle is violated, then we can get work from a cold bath and do work on a hotter bath to increase its energy. Thus, Clausius' principle is violated.

If Clausius' principle is violated, then we can convert a uniform system into colder and hotter portions and produce work to make the portions to be the same temperature again by a cyclic change of the work coordinates. Thus, Planck's principle is violated.

We have roughly demonstrated, symbolically, P $\Rightarrow$ C $\Rightarrow$ K $\Rightarrow$ P. That is, all the principles mentioned here are equivalent.

9.22 Entropy was not understood by British scientists

Now, we wish to demonstrate that the second law implies the existence of a state function called 'entropy' which was introduced by Clausius. In introductory thermodynamics it seems unanimously recognized that entropy is a difficult concept to grasp. This may also be a misconception/misunderstanding spread by the British.

British people resisted to recognize entropy for a while. Even Maxwell, who used entropy correctly for the first time in England, misunderstood it initially. In reality, English speaking scientists were rescued by Gibbs who correctly understood thermodynamics.

In summary, Clausius recognized the following. The constant entropy surfaces foliate the thermodynamic space. These surfaces are called 'adiabats' or 'isentropic hypersurfaces.' If state A has a larger entropy than state B, then we can never go from A to B adiabatically.

9.23 Unique adiabat goes through an equilibrium state

At least once in your life you should try to reproduce the following explanation of the existence of entropy to your intelligent lay friends.

Choose an arbitrary point P and a vertical line L in the realizable portion of the thermodynamic space. This line is parallel to the energy axis (all the work coordinates are kept constant), along which we can change the states only by exchanging heat with the external world. Let us find a quasistatic adiabatic and reversible path[204] connecting P and L.

Suppose the path lands on L at point Q. Can we also reach other points on L in the same fashion? Planck tells us A is inaccessible; if possible, we can adia-

[204]Why is such an awkward description of the path? Reversibility does not logically guarantee quasiequilibrium; quasiequilibrium does not mean reversible. This is the reason. However, intuitively, we may say 'reversible path,' because not quasistatic reversible process is not very realistic.

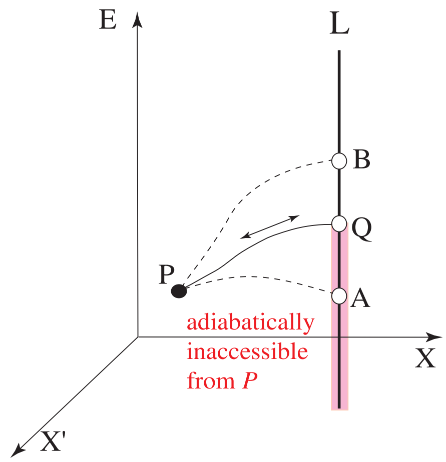


Figure 9.7: Let Q be a state on a vertical line L (along which we can move with heat exchange alone) that can be reached from state P adiabatically and reversibly. If state A can be reached by an adiabatic process from P, then adiabatically we can go from Q to A via P, violating Planck's principle. Thus, the shaded portion is inaccessible from P adiabatically. If B can be reached by an adiabatic reversible process from P, then adiabatically we can go from B to Q via P, violating Planck's principle, again. Thus, Q is unique: there is only one point on L that can be reached from P adiabatically and reversibly. (We can adiabatically go from P to B, but it is an irreversible process.)

batically go to A from Q, contradicting Planck. If we could go to B adiabatically and reversibly from P, then we can go to Q adiabatically via P, again contradicting Planck's principle. Thus, we have learned that the point on L we can reach from P adiabatically and reversibly is only Q.

Now, moving the stick L throughout the space keeping it parallel to the energy axis, we can construct a hypersurface consisting of points adiabatically and quasistatically accessible from point P (reversibility is included since it is retraceable). This is an *adiabat* containing P.

9.24 Adiabats stratify the thermodynamic space

Adiabats foliate the thermodynamic space. That is, no two different adiabatic surfaces cross each other. See Fig. 9.8 Left to understand that these sheets = adiabats

cannot cross; crossing means 'Planck' is violated. This implies that we can define a state function S, whose level sets are given by these sheets (S = constant defines an adiabat).

The adiabats do not have any 'overhangs.' As you can see from Fig. 9.8 Right, the reason is the same as that for no crossing.

Thus we have realized that the thermodynamic space is stratified (or foliated) into layers vertically stacked respecting their order.

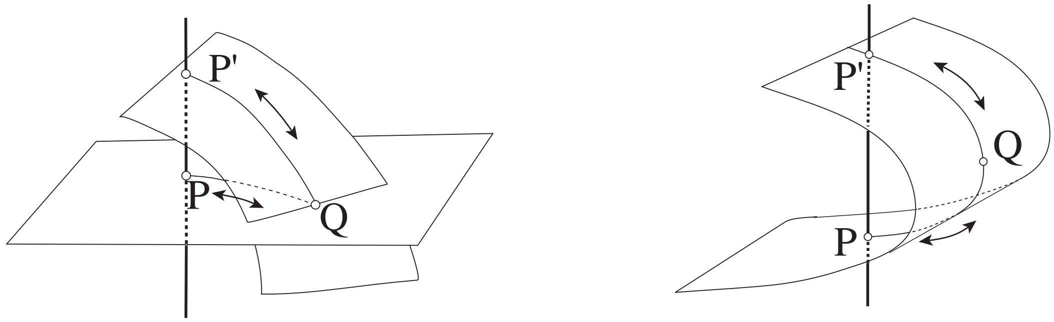


Figure 9.8: Left: If two adiabats cross or touch, then we can make a cycle that can be traced in any direction, because PQ, $P'Q$ can be traced either directions, so can be PP'. Planck's principle is violated. Right: An overhang violates Planck's principle with the same reason.

9.25 Entropy can be defined

Thermodynamic space is stratified (or foliated) into layers vertically stacked respecting their order along a line perpendicular to the work-coordinate plane (especially along the energy axis), so we can define a state function by appropriately assigning real numbers continuously according to their heights along a vertical line; in other words, we can define a state function called 'entropy' 'S' which is an increasing and continuous function of E under constant work coordinates. How can we change the value S of this function?

Obviously, we can change S by going up or down along L in Fig. 9.7 while the work coordinates being kept fixed; that is, we can change S by adding or subtracting heat Q. Since we have assumed that S increases with E, for $d'Q > 0$ we must have $dS > 0$. Therefore, we may define S so that $dS \propto d'Q$ holds. Since Q is extensive,[205] so must be S. This also tells us that we can assume S is a once differentiable function of E.

9.26 Entropy and heat

Suppose two systems are in contact through a wall that allows only the exchange of heat (that is, in thermal contact **9.13**), and they are in thermal equilibrium. Exchange of heat $d'Q$ between the thermally equilibrated systems is a reversible process (say, system I gains $d'Q_{\mathrm{I}} = d'Q$ and II $d'Q_{\mathrm{II}} = -d'Q$), so this process occurs within a single adiabat of the compound system (**9.11**, i.e., the two systems considered together as a single system). If we write $d'Q_{\mathrm{X}} = \theta_{\mathrm{X}} dS_{\mathrm{X}}$ (X = I or II), with the aid of the additivity of S,

$$0 = dS_{\mathrm{I}} + dS_{\mathrm{II}} = d'Q \left(\frac{1}{\theta_{\mathrm{I}}} - \frac{1}{\theta_{\mathrm{II}}} \right). \tag{9.8}$$

This implies $\theta_{\mathrm{I}} = \theta_{\mathrm{II}}$. If I and II are not in thermal equilibrium initially, then the

[205]That is, if we double the system, we must double the heat to reach the same thermodynamic state characterized by the same intensive parameters and densities (= extensive variables per volume).

contact causes some irreversible change, so the state of the compound system leaves the original adiabat, so $\theta_{\rm I} \neq \theta_{\rm II}$. That is, $\theta_{\rm I} = \theta_{\rm II}$ if and only if I and II are in thermal equilibrium. Hence, we may interpret the proportionality factor θ as an empirical temperature (cf. the zeroth law).

The introduced temperature can be chosen as a universal temperature T called the *absolute temperature*. Hence, in the quasistatic process we can write[206]

$$d'Q = TdS. \tag{9.9}$$

9.27 Gibbs relation

Now we can write down the infinitesimal version of the first law of thermodynamics for the quasistatic process as follows:

$$dE = TdS - PdV + \mu dN + \boldsymbol{B} \cdot d\boldsymbol{M} + \cdots. \tag{9.10}$$

This is called the *Gibbs relation*.

The chief concern of thermodynamics up to Gibbs was to formulate the second law and to prove the existence of entropy. Gibbs then utilized entropy and reformulated thermodynamics as a system even practically useful. The very starting point of this new formulation was this relation, which Gibbs wrote down for the first time. Notice that each term consists of a product of a conjugate pair: an intensive quantity and d[the corresponding (i.e., conjugate) extensive quantity]. Also do not forget the minus sign in front of PdV (recall **9.16**).

[206]《**Thermodynamic T = ideal gas T?**》 Precisely speaking, we must show that this T is identical to the T appearing in the ideal gas law. To this end we have only to consider the Carnot cycle, or to compute the efficiency η of an ideal engine. This will be done in the next lecture, but we will obtain $\eta = 1 - \theta_1/\theta_2$ (assuming that $\theta_1 < \theta_2$) [This is Thomson's fundamental idea to define temperature in a materials-free fashion]. If we use an ideal gas we obtain $\eta = 1 - T_1/T_2$, so θ and T are identical (up to the choice of units).

As we will see ideal gases contradict the third law of thermodynamics, so there are people who assert ideal gases are unphysical and should not be used to develop the basic theoretical framework; Thomson clearly thought particular material should not be used to develop basic theories. However, if pressure is sufficiently reduced, then any real gas becomes an ideal gas however low its temperature is. Therefore, as long as we clearly recognize this condition, there is no fundamental difficulty in using ideal gases to develop fundamental theories.

Q9-1 [Why thermodynamic coordinates are important].
An equilibrium state of a macroscopic system can be phenomenologically described by thermodynamics. There is a special set of variables called the thermodynamic coordinates to describe equilibriums states. Briefly explain within 10 lines (with an ordinary letter size, please) what a thermodynamic coordinate system is and why it is special.

Soln.
The thermodynamic coordinate system consists of internal energy E and (extensive) work coordinates describing macroscopic mechanical work that can be done to the system.
1. [Pure mechanical nature] Since E is essentially the mechanical (including electromagnetic) energy of the particles in the system and since work coordinates are described, controlled and measured with the aid of macroscopic mechanics (including electromagnetism), thermodynamic experiments can be described in terms of these coordinates without clear characterization of heat.
2. [Unique specification of equilibrium states] If two states have identical thermodynamic coordinates, then these states cannot be distinguished thermodynamically. Or you can say thermodynamic coordinates specify equilibrium states uniquely.

Q9-2 [Magnetic work]
The work required to increase the magnetization (= the total magnetic moment in the system) of a block in the external magnetic field $\boldsymbol{H}$ is written as $d'W = \boldsymbol{H} \cdot d\boldsymbol{M}$. We have not shown this. This is not very trivial, because not all the energy is stored in the block under study; some portion is stored as potential energy in the 'relation' between the block and the system creating the external magnetic field. We know that this potential energy is $-\boldsymbol{H} \cdot \boldsymbol{M}$ (probably, you remember that the energy of a magnetic dipole $\boldsymbol{\mu}$ is minimum, when $\boldsymbol{H}$ and $\boldsymbol{\mu}$ are parallel: $E = -\boldsymbol{\mu} \cdot \boldsymbol{H}$).

Since $\boldsymbol{M} = \sum \boldsymbol{\mu}$, where the summation is over all the magnetic dipoles in the block, let us study individual magnetic moment. We assume that the (size of the) magnetic dipole changes due to the magnetic field.

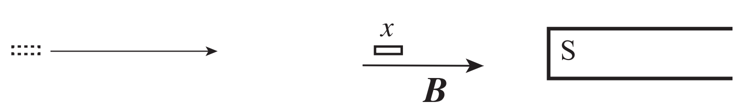


Figure 9.9: The magnetic field $\boldsymbol{H}$ is prepared by a large constant bar magnet, and the magnetic dipole initially at infinity is brought to position x along the x-axis. The field is parallel to the axis.

At position x the (x-component of the) force acting on the small magnetic dipole parallel to the x-axis (see Fig. 9.9) is given by (+ in the $+x$-direction)

$$F = \mu(H(x)) \frac{dH(x)}{dx}. \tag{9.11}$$

Since we are doing thermodynamics, we must bring the magnetic dipole from infinity slowly to the present position x. To perform such an experiment, you must apply a

force opposing the above force (i.e., $-F$) while moving the magnetic dipole.
(1) What is the work W you do to the whole system (the dipole + the bar magnet) while dragging the dipole from $-\infty$ to x? [This simply asks your work expenditure. Since the force you exert and the displacement are both given, it is an elementary question.]
(2) However, this energy W is stored not only in the block containing the magnetic dipoles, but also between the bar magnet and the dipole as the potential energy at x (as given above). Show that the energy stored in the dipole is

$$W + \mu(H(x))H(x) = \int_{\mu(0)}^{\mu(H(x))} H(x')d\mu(H(x')). \tag{9.12}$$

Therefore, $dE = HdM$ if only the magnetization (the total dipole moment $\sum \mu$) is changed among the work coordinates.

Solution.
(1) The force you exert is $-F$ (not F; without your application of brake, the 'block' would fly to the bar magnet)

$$W = -\int_{-\infty}^{x} F dx' = -\int_{0}^{H(x)} \mu(H(x'))dH(x'). \tag{9.13}$$

Here, the dependence of μ on H is explicitly written. This implies that the total work done to the system consisting of the block (containing dipoles) and the bar magnet reads

$$W = -\int_{0}^{H(x)} M(H)dH. \tag{9.14}$$

(2) Let us honestly compute this sum (9.12).

$$\begin{aligned} -\int_0^{H(x)} \mu(H(x'))dH(x') + \mu(H(x))H(x) &= -\int_0^{H(x)} \mu(H(x'))dH(x') + \int_0^{H(x)} d[\mu(H(x'))H(x')] \\ &= -\int_0^{H(x)} \mu dH + \int_0^{H(x)} d[\mu H] = \int_0^{\mu(H(x))} H(x')d\mu(H(x')). \end{aligned}$$

If we sum this over all the dipoles in the block, we get

$$\int_{M(0)}^{M(H(x))} H(x')dM(H(x')). \tag{9.15}$$

Therefore, $dE = HdM$ if only the magnetization (the total dipole moment $\sum \mu$) is changed among the work coordinates.

Q9-3 [Entropic equation of state]
Suppose we know the following equations of state of a gas:

$$T = \sqrt{E/V}, \quad P = E/V. \tag{9.16}$$

Find $S = S(E, V)$ up to an additive constant that you cannot fix.

Solution.
Let us write down dS (i.e., the Gibbs relation)

$$dS = \frac{1}{T}dE + \frac{P}{T}dV. \tag{9.17}$$

Introducing the given equations of state, we obtain

$$dS = \frac{V^{1/2}}{E^{1/2}}dE + \frac{E^{1/2}}{V^{1/2}}dV. \tag{9.18}$$

Since S is a state function, for example, $S(E, V) - S(1, 1)$ does not depend on the integration paths along which we integrate this differential form from $(E, V) = (1, 1)$ to (E, V). Therefore, let us use a convenient path that is piecewise parallel to the coordinate axes. First, let us go from $E = 1$ to E along $V = 1$, and then, we go from $V = 1$ to V along $E =$ constant:

$$S(E, V) - S(1, 1) = \int_1^E \frac{1}{E^{1/2}}dE + \int_1^V \frac{E^{1/2}}{V^{1/2}}dV = 2(E^{1/2} - 1) + 2E^{1/2}(V^{1/2} - 1). \tag{9.19}$$

In the first integral V is fixed at 1, and in the second E is fixed at its final value. Thus, we have obtained

$$S(E, V) = 2E^{1/2}V^{1/2} + \text{ const.} \tag{9.20}$$

Notice that 'miraculously' the term dependent on the starting position is cleanly separated out as a constant term. [This is, of course, guaranteed by a Maxwell's relation. You'd better check this.]

Discussion 5

We discuss basic thermodynamics (+ linear algebra we need for understanding elementary quantum mechanics).

D5.1* **[How to kill Thomson?]**[207]
In a very long thin cylinder is a gas (see Fig. 9.10). We assume that the cylinder is diathermal and everything is performed under constant temperature in a uniform gravitational field. Initially,
(I) the cylinder is horizontal. Then,
(II) the cylinder is rotated to a vertical position (slowly). Due to the gravity the top portion becomes thin.
(III) We push in the piston till the pressure at the piston is the same as in (I). Then,
(IV) the system is rotated back to the original horizontal position with the piston position fixed relative to the cylinder.
(V) After the gas density becomes uniform, let us allow the system to do work till the pressure at the piston becomes identical to that in (I).

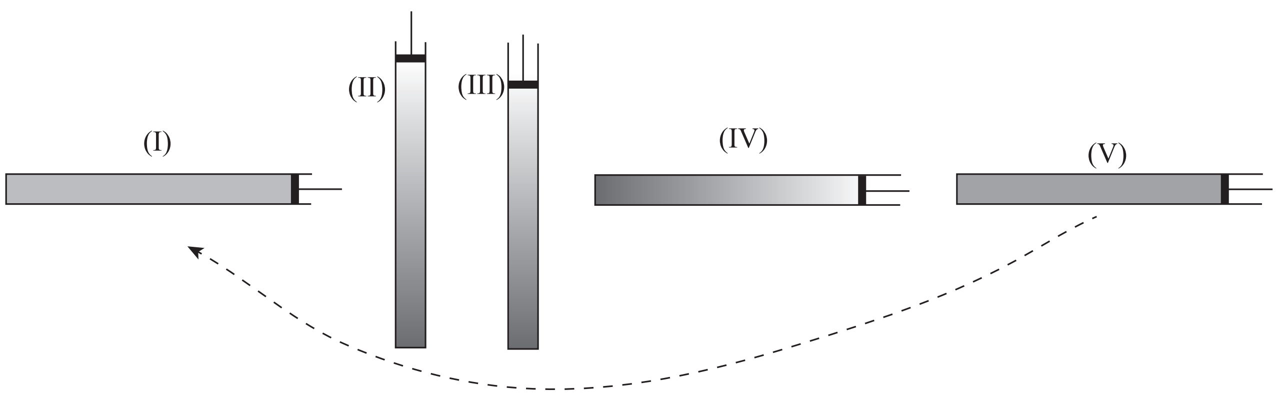


Figure 9.10: Let us kill Thomson!

Thus, we have completed a cycle. Since, the work we do in (III) is less than that we gain from (V) → (I), we have killed Thomson![208]

Is this OK?

[207]Taken with slight modification from H. Tasaki *Thermodynamics* (Baifukan 2000).
[208]Of course, you should clearly recognize that what we now call Thomson's principle was a special case of the original Clausius' principle (according to him, heat at $T = \infty$ is work), and that Thomson failed to formulate thermodynamics.

D5.2 [Adiabatic curves]
On the PV-diagram of any gas, two distinct adiabatic curves never cross. Demonstrate this. [This is almost a trivial question.]

Solution.
Look at the 'triangular' region surrounded by a high temperature isotherm and two adiabats in Fig. 9.11.

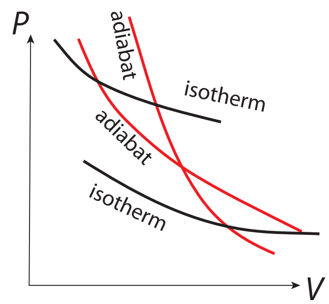


Figure 9.11: Black curves are isotherms (T const), and red curves are adiabats (actually, S const). In this diagram, two adiabats cross, but such crossing never occurs.

If we go around this cycle in the clockwise direction.

$$-\oint PdV = -\text{ the area surrounded by these three curves} < 0, \tag{9.21}$$

which is the work gained by the gas, but it is negative. That is, it can perform work using a single heat bath, violating Kelvin's law.

D5.3 [Exact and not exact differentials]
Consider a function f defined on a region $D \subset \mathbb{R}^n$. If its gradient is well defined on D, we say f is (strongly) differentiable.[209] We can write the first differential of f as

$$df = \mathrm{grad}\, f \cdot d\boldsymbol{x}, \tag{9.22}$$

where $\boldsymbol{x} \in D$ is an n-vector (independent variables $x_1, \cdots, x_n$).

Let C be any continuous curve in D connecting $\boldsymbol{x}_1$ and $\boldsymbol{x}_2$. Then,

$$f(\boldsymbol{x}_2) - f(\boldsymbol{x}_1) = \int_C \mathrm{grad}\, f \cdot d\boldsymbol{x} \tag{9.23}$$

does not depend on C. Thus, for any closed curve C in D

$$\oint_C \mathrm{grad}\, f \cdot d\boldsymbol{x} = 0. \tag{9.24}$$

[209]When we say a function is differentiable, it is always in this (strong) sense throughout these lectures. See Section 17.

If $g = (g_1, \cdots, g_n)$ is a differentiable vector, the Gauss-Stokes-Green theorem tells us for any 2-surface A

$$\int_A \sum_{i<j} (\partial_i g_j - \partial_j g_i) dx_i dx_j = \int_{\partial A} \sum_i g_i dx_i. \tag{9.25}$$

Therefore, if the integral from point P to P' of $\varepsilon = \sum_i g_i dx_i$ is independent of the paths connecting these two points in a domain D (without a hole, or more precisely, contractible to a point), then[210]

$$\partial_i g_j = \partial_j g_i. \tag{9.26}$$

If f is twice differentiable (i.e., all the first order partial derivatives of f are differentiable), then for any 2-surface A in D such that $\partial A = C$ (Gauss-Stokes-Green theorem)

$$\oint_C \mathrm{grad}\, f \cdot d\boldsymbol{x} = \int_A \sum_{i<j} \left(\frac{\partial^2 f}{\partial x_i \partial x_j} - \frac{\partial^2 f}{\partial x_j \partial x_i} \right) dx_i dx_j = 0. \tag{9.27}$$

This is true for any closed curve C in D, so we must conclude (called Young's theorem) in D

$$\frac{\partial^2 f}{\partial x_i \partial x_j} = \frac{\partial^2 f}{\partial x_j \partial x_i}. \tag{9.28}$$

This is called a Maxwell's relation in thermodynamics as we will study in detail later.[211]

The first law of thermodynamics implies that the energy form dE is closed (so the formulas corresponding to (9.28) holds).

(1) Consider

$$\varepsilon = y^2 dx + 2x(y+1)dy. \tag{9.29}$$

(i) Check that this is not closed.[212]
(ii) Integrate ε along $y = x^2$ from the origin to $(1,1)$.
(iii) Integrate ε along a part of a circle $x^2 + (y-1)^2 = 1$ from the origin to $(1,1)$ counterclockwisely.

Solution.

[210]**Remark**. If you know differential forms, you can say ε is closed ($d\varepsilon = 0$) and there is a function g such that $dg = \varepsilon$ (i.e., ε is exact; Poincaré's lemma).

[211]A 1-form ω satisfying $d\omega = 0$ is called a closed form. Thus, an exact form is a closed form (i.e., $d^2 = 0$). The converse is true on an orientable contractible domain (Poincaré's lemma: if $d\omega = 0$, there is f such that $df = \omega$).

[212]If you know differential forms, $d\varepsilon \neq 0$ is what you have to show. That is, check something like (9.28).

(i) We check the symmetry (9.28):

$$\frac{\partial y^2}{\partial y} = 2y, \quad \frac{\partial}{\partial x} 2x(y+1) = 2(y+1), \tag{9.30}$$

so ε is not closed.

Or more directly,

$$d\varepsilon = 2y dy \wedge dx + 2(y+1) dx \wedge dy = [2(y+1) - 2y] dx \wedge dy \neq 0. \tag{9.31}$$

(ii) Let us parameterize the curve as $x = t$ and $y = t^2$ ($t \in [0, 1]$).[213] The integral reads

$$\int_{y=x^2 \text{ for } x=0\to 1} [y^2 dx + 2x(y+1)dy] = \int_0^1 dt\, [t^4 dt + 2t(t^2+1)2t dt] \tag{9.32}$$

$$= \int_0^1 dt\, (5t^4 + 4t^2) = 1 + 4/3 = 7/3 \approx 2.33. \tag{9.33}$$

(iii) We set $x = \sin t$, $y = 1 - \cos t$ ($t \in [0, \pi/2]$):

$$\int_0^{\pi/2} [(1-\cos t)^2 \cos t dt + 2\sin t(2 - \cos t)\sin t dt] \tag{9.34}$$

$$= \int_0^{\pi/2} dt\, [4 - \cos t - 6\cos^2 t + 3\cos^3 t] \tag{9.35}$$

$$= 2\pi - 1 - 6 \times \frac{\pi}{4} + 3 \times \frac{2}{3} = \frac{\pi}{2} + 1 \approx 2.57. \tag{9.36}$$

(2) Consider

$$\varepsilon = y^2 dx + 2xy dy. \tag{9.37}$$

(i) Check that this is closed.
(ii) Integrate ε along $y = x^2$ from the origin to $(1, 1)$.
(iii) Integrate ε along a part of a circle $x^2 + (y-1)^2 = 1$ from the origin to $(1, 1)$. Needless
to say, you expect the answer agrees with that to (ii).
(iv) It is easy to see $\varepsilon = d(xy^2)$, so any integral of ε from the origin to (x, y) is just xy^2 irrespective of the actual integration path.

Solution.
(i) We check the symmetry (9.28):

$$\frac{\partial y^2}{\partial y} = 2y, \quad \frac{\partial}{\partial x} 2xy = 2y, \tag{9.38}$$

so ε is closed.

[213] You can simply replace y with x^2 in the integral to get the answer more easily in this case.

Or more directly,

$$d\varepsilon = 2ydy \wedge dx + 2ydx \wedge dy = [2y - 2y]dx \wedge dy = 0. \tag{9.39}$$

(ii) Let us parameterized the curve as $x = t$ and $y = t^2$ ($t \in [0, 1]$). The integral reads

$$\int_{y=x^2 \text{ for } x=0\to 1} [y^2 dx + 2xydy] = \int_0^1 dt\, [t^4 dt + 2t(t^2)2tdt] \tag{9.40}$$

$$= \int_0^1 dt\, 5t^4 = 1. \tag{9.41}$$

(iii) We set $x = \sin t$, $y = 1 - \cos t$ ($t \in [0, \pi/2]$):

$$\int_0^{\pi/2} [(1 - \cos t)^2 \cos t dt + 2 \sin t(1 - \cos t) \sin t dt] \tag{9.42}$$

$$= \int_0^{\pi/2} dt\, [2 - \cos t - 4\cos^2 t + 3\cos^3 t] \tag{9.43}$$

$$= \pi - 1 - 4 \times \frac{\pi}{4} + 3 \times \frac{2}{3} = 1. \tag{9.44}$$

(iv) $xy^2(x = y = 1) - xy^2(x = y = 0) = 1$, of course.

(3)* Let us 'prove' that under constant volume the pressure of any material is independent of temperature. The demonstration goes as follows:

The heat form dQ satisfies, according to the first law of thermodynamics,

$$dQ = dE + PdV. \tag{9.45}$$

This implies

$$\left.\frac{\partial Q}{\partial T}\right|_V = \left.\frac{\partial E}{\partial T}\right|_V, \quad \left.\frac{\partial Q}{\partial V}\right|_T = P + \left.\frac{\partial E}{\partial V}\right|_T. \tag{9.46}$$

Therefore,

$$\frac{\partial^2 E}{\partial V \partial T} = \left.\frac{\partial P}{\partial T}\right|_V + \frac{\partial^2 E}{\partial T \partial V}. \tag{9.47}$$

This implies $(\partial P/\partial T)_V = 0$. The result obviously contradicts the ideal gas law. Why?

Solution.

To go from (9.46) to (9.47) the closedness of dQ is assumed, but we know heat is path dependent, so Young's theorem (Maxwell's relation) cannot be used.

D5.4 [Very elementary questions][214]
(1) Aluminum has a density 2700 kg/m^3 at 300 K under 1 atm. Its isothermal compressibility β is 0.01385 GPa^{-1}. Assuming the compressibility is constant, estimate the work needed to compress 1 kg of aluminum block from 1 atm to 500 atm?

(2) Ammonia gas under 1 atm at 300 K flows into a heating pipe with a flow speed of 41 cm^3/s. The pipe contains a 100 Ω resistor carrying an electric current of 50 mA. The flowing ammonia gas comes out at temperature 304.1 K. What specific heat can you observe from this (and obtain it in J/K·mol)?

(3) The internal energy of one mole of a gas is given by

$$E = \frac{3}{2}RT - \frac{a}{V}, \tag{9.48}$$

where a is a positive constant. Let us adiabatically freely expand this gas from volume V_1 to volume V_2. What is the final temperature T_2, if the initial temperature is T_1?

The parameter a describes the effect of attractive interactions among gas particles. Is your result consistent with this meaning of the parameter a?

Solution.
(1) The work W we must supply satisfies

$$dW = -PdV = -P \left.\frac{\partial V}{\partial P}\right|_T dP \tag{9.49}$$

According to the definition

$$\beta = -\frac{1}{V}\left.\frac{\partial V}{\partial P}\right|_T, \tag{9.50}$$

and we may assume this to be constant, so we may use the following approximation:

$$\left.\frac{\partial V}{\partial P}\right|_T = -\beta V_0, \tag{9.51}$$

where V_0 is the volume under 1 atm, which is (in m^3)

$$V_0 = 1/2700. \tag{9.52}$$

Therefore,

$$\begin{aligned} W &= \beta V_0 \int_{P_0}^{P_1} PdP = \frac{1}{2}\beta V_0(P_1^2 - P_0^2) = \frac{1}{2} \times (0.01385 \times 10^{-9}) \times \frac{1}{2700}(5 \times 10^7)^2 \\ &= 6.4 \text{ J}. \end{aligned} \tag{9.53}$$

[214]Adapted from Moor's *Physical Chemistry*.

(2) Everywhere the pressure is constant, so the specific heat we obtain from this experiment is a specific heat under constant pressure C_P. The flow rate in moles is

$$41/(22.41 \times 10^3(300/273)) = 1.66 \times 10^{-3} \text{ mol/s}. \tag{9.54}$$

The heat energy introduced in one sec is $I^2R = 0.05^2 \times 100 = 0.25$ W, and the temperature increase due to this is 4.09 K. Therefore,

$$C_P = \frac{0.25}{1.66 \times 10^{-3} \times 4.09} = 0.0368 \times 10^3 = 37 \text{ J/K}\cdot\text{mol}. \tag{9.55}$$

(3) There is no input of heat nor work, so E must be constant:

$$\frac{3}{2}RT_1 - \frac{a}{V_1} = \frac{3}{2}RT_2 - \frac{a}{V_2}. \tag{9.56}$$

Therefore,

$$T_2 = T_1 + \frac{2a}{3R}\left(\frac{1}{V_2} - \frac{1}{V_1}\right). \tag{9.57}$$

We see the temperature decreases by expansion. Since volume expansion results in the increase of interparticle distances, the potential energy goes up, because the interaction is attractive. Therefore, the kinetic energy must go down, resulting in cooling. The effect is actually small; doubling the volume may give you order of 0.1 K temperature decrease for usual gases.

Exercise 5

E5.1 [Disparate time scales; easy question but important].
We organisms live, taking advantage of miracles (extremely rare events). Our biological time (increment) scale is 1 msec and the molecular time scale is 1 fs. Suppose you can throw 40 coins (assume all are fair) at once every 1 ps. How many times can you experience 'all up simultaneously' in 1 s on the average? If you do the throwing once every second, how many years do you expect to take for all the 40 coins to exhibit heads simultaneously? [This is an easy question; only I wish you to remember the vast time scale difference between micro and macro scales.]

Solution.
If every trial takes 1 ps, our microsystems can try 10^{12} times in one second. The probability to have all H for 40 fair coins at once is one over $2^{40} \simeq 10^{12}$. Thus, on the average this 'miracle' can happen once every second. Thus, for us it is only banal, but for an enzyme the event that it can promote a certain reaction could be a miracle.

10^{12} s is about 32 ka, so with 30 thousand years we are pretty sure this happens.

E5.2 [Elementary problem].
One mole of an ideal gas expands adiabatically against the external constant pressure $P_0 = 1.7$ atm. The gas is initially at temperature $T_1 = 273$ K and the pressure is $3P_0 = 5.1$ atm. After expansion the gas reaches a final equilibrium state. You may assume that the gas is an ideal monatomic gas. What is the final temperature T_2?

Solution.
The work done by the gas is $P_0(V_2 - V_1)$, where V_1 is the initial volume and V_2 is the final volume. The final pressure must be P_0, so $3P_0V_1 = RT_1$ and $P_0V_2 = RT_2$. Since the system is adiabatic,

$$\Delta E = -P_0(V_2 - V_1). \tag{9.58}$$

The internal energy of an ideal gas is directly related to its temperature, so

$$\Delta E = C_V(T_2 - T_1). \tag{9.59}$$

These formulas imply

$$RT_1/3 - RT_2 = C_V(T_2 - T_1). \tag{9.60}$$

Therefore, noting that $C_V = (3/2)R$,

$$T_2 = \frac{R + 3C_V}{3(R + C_V)}T_1 = \frac{1 + 9/2}{3(5/2)} \times 273 = \frac{11}{15} \times 273 = 200.2 \tag{9.61}$$

That is, 200 K.

E5.3 [Reviewing the existence of entropy].

Let us take an ideal gas system consisting of n moles of point particles (monatomic gas) and demonstrate the existence of entropy S for this system. The convenient thermodynamic space for this system is spanned by the internal energy E and the volume V. Notice that for this system the reversible infinitesimal work has the expression: $d'W = -PdV$, where P is the pressure.

(1) The internal energy E of this system depends only on the temperature T. How can you justify this statement? [Hint: a trivial question, so do not think too much. Go back to the kinetic theory. You could answer (1) and (2) at once.]

(2) Let C_V be the constant volume specific heat of this ideal gas (don't forget that it is n moles) defined by $dE/dT = C_V$. Compute it. You must know the answer, so you must be able to derive it from what we have learned up to this point in this course. [Hint: E is the total energy of the gas. What is it as a function of T?]

(3) In the figure below (Fig. 9.12; cf. Fig. 9.7) choose a point P at (E_0, V_0). The work coordinate (i.e., V in our case) of the vertical line L is V.

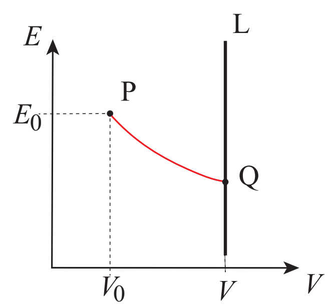


Figure 9.12: The red curve is the adiabatic and reversible process starting from P. Q is unique on L according to Planck's law.

You can reach Q reversibly and adiabatically from P. Explain why there is no point other than Q on L that can be reached from P adiabatically and reversibly.

(4) Find the E coordinate of Q in terms of V, V_0 and E_0.

(5) The surface (the red curve in Fig. 9.12) consisting of points (= equilibrium states) that may be reached from P reversibly and adiabatically should be described by a relation $f(E, V)$ = constant, where f is an appropriate function. Find or choose such a function f. (You should have virtually obtained this in (4).)[215] Show that different such curves do not cross (that is, $f(E, V) = c_1$ and $f(E, V) = c_2 \neq c_1$ do not have any common point), and also that each curve defines a function of V (i.e., there is no overhang; cf. Fig. 9.8).

(6) Thus, you have constructed 'isentropic surfaces' $f(E, V) =$ const., and you may

[215] We define dS to be proportional to $d'Q$ without any change of work coordinates **9.25**, so S must be extensive. That is, even if you double the system size $E \to 2E$, $V \to 2V$, $C_V \to 2C_V$, $n \to 2n$, the formula for dS should be intact with doubling the increments dS, dE and dV. If you take this condition into account, there is almost no freedom of choice for f, but this will not be required here, so invent your 'S' freely.

define your entropy as $S = f(E, V)$. Show that if the ideal gas gets energy only through thermal contact, then you can write the transferred heat as $d'Q = \Theta dS$, where Θ is proportional (perhaps identical) to T with S being your entropy.

Solution.
(1) The average particle energy (monatomic ideal gas!) is $(3/2)k_BT$. Since there is no interaction among particles, the energy of the system consists of kinetic energy alone. Thus, the law of large numbers tells us that the total energy is very closed to $(3/2)k_BT$ times the number of particles nN_A. Thus, $E = 3nRT/2$.

(2) We have almost answered the question in (1): $C_V = 3nR/2$. Notice that such a result cannot be obtained by thermodynamics.

(3)
(a) If we could reach from P reversibly and adiabatically to a point B above Q (cf. Fig. 9.7), then we can go to Q from B reversibly and adiabatically, violating Planck's law.
(b) If we could reach from P adiabatically to a point A below Q, then we can adiabatically reach A from Q, violating Planck's law again.
Therefore there is at most one point on L that can be reached from P reversibly and adiabatically. Notice that 'reversibility' is crucial.

(4) Since the process is quasistatic and adiabatic, we can change the system energy only by modifying the volume V. As noted at the beginning $d'W = -PdV$ is the only way to change E. Therefore,

$$dE = -PdV = -\frac{nRT}{V}dV, \tag{9.62}$$

but our coordinates are E and V, so we must write T as a function of E (and V, generally speaking). (1) and (2) tell us that $T = E/C_V$. Therefore,

$$dE = -\frac{nRE}{C_V V}dV, \tag{9.63}$$

or

$$C_V d\log E + nRd\log V = 0. \tag{9.64}$$

Integrating this, we get

$$C_V \log E + nR\log V = \text{ const.} \tag{9.65}$$

This constant is determined by the 'initial condition' P:

$$C_V \log E_0 + nR\log V_0 = \text{ const.} \tag{9.66}$$

Therefore,

$$C_V \log\frac{E}{E_0} + nR\log\frac{V}{V_0} = 0. \tag{9.67}$$

Solving this, we get

$$E = E_0(V/V_0)^{-nR/C_V} = E_0(V/V_0)^{-2/3} \tag{9.68}$$

(5) For example, we may choose

$$f(E, V) = C_V \log E + nR \log V. \tag{9.69}$$

$f(E, V) =$ const. implies $E^{3/2}V =$ constant. This is a monotone decreasing curve of V, so there cannot be any overhang. $E^{3/2}V = c_1$ and $E^{3/2}V = c_2 \neq c_1$ cannot have any common point, since these simultaneous equations cannot have any solution (or if there were, obviously $c_1 = c_2$). Thus, f foliates (or stratifies) the thermodynamic space of the ideal gas.

(6) $S = f(E, V)$ or my entropy is

$$S = C_V \log E + nR \log V. \tag{9.70}$$

Now, thermal contact means we cannot change V. E may be changed only through transfer of heat $dE = d'Q$, so

$$dS = C_V d \log E = \frac{C_V}{E} dE = \frac{1}{T} dE = \frac{1}{T} d'Q. \tag{9.71}$$

Here, you may perhaps say that I chose too convenient a function (knowing the standard result). For example, I could invent my entropy S as

$$S = f(E, V) = \log E + \frac{2}{3} \log V. \tag{9.72}$$

Now, quasiequilibrium thermal contact implies $dE = d'Q$, and $dV = 0$ (no work), so

$$dS = \frac{1}{E} dE = \frac{1}{E} d'Q \tag{9.73}$$

In our case $E \propto T$, so, although in this case the temperature scale is not the standard K scale, E is still a respectable absolute temperature.

However, as noted in footnote 1, in reality, we must respect the extensivity of S. Look at (9.72):

$$dS = \frac{1}{E} dE + \frac{2}{3V} dV \tag{9.74}$$

This unfortunately does not satisfy the 'doubling invariance' mentioned in the footnote: dS is intact under system doubling in this case. Therefore, 'my' choice is actually 'unthermodynamic.'

In contrast the choice (9.70) gives

$$dS = \frac{C_V}{E} dE + \frac{nR}{V} dV. \tag{9.75}$$

Therefore, all the coefficients of differentials are intensive (invariant), and doubling all the differential is consistent. That is, this formula is intact under doubling the system size.

E/C_V is T in our case, so $\Theta = T$, actually in our case.

10 Thermodynamics: General consequences

Summary
∗ What you should remember about thermodynamics is summarized.
∗ Under an adiabatic condition, spontaneous changes imply increasing entropy.
∗ Under an adiabatic condition, a system reaches equilibrium when its entropy becomes maximum (the principle of maximum entropy).
∗ There is a general logic to extend the results for adiabatic systems to non-adiabatic systems. This gives you Clausius' inequality.
∗ The crux of thermodynamic computation is to devise quasistatic processes.
∗ The efficiency to convert heat into work is bounded by a maximum value determined by the temperatures of the heat sources (Carnot's theorem).
∗ If $\Delta S = 0$, try to devise adiabatic reversible processes.
∗ 1 J/K·mol = 0.173 bits/molecule.

Key words
Clausius' inequality, entropy maximization principle, equilibrium conditions, reversible engine, Carnot's theorem, heat pump, entropy of mixing

What you should be able to do
∗ To compute entropy changes for simple processes.
∗ Remember the key features of the ideal gas.
∗ To be able to compute the efficiencies of an ideal engine.
∗ To show that the reversible engine is the best engine.
∗ To estimate the entropy change due to various irreversible processes.
∗ To understand entropy change intuitively in terms of the number of Yes-No questions.
∗ To draw the general $E = E(S)$ curve under constant work coordinates.

10.1 Summary of basic principles[216]

The basic laws of thermodynamics are the summary of the experiences of us macro-

[216] ⟪**Nernst's joke on the three principles**⟫ Kurt Mendelssohn writes, "When lecturing on 'his' heat theorem, Nernst was careful to point to an interesting numerical phenomenon concerning the discovery of the three fundamental laws of thermodynamics. The first one had three authors, Mayer, Joule and Helmholtz; the second had two, Carnot and Clausius; whereas the third was the work of one man only, Nernst. This showed conclusively that thermodynamics was now complete since the authorship of a hypothetical fourth law would have to be zero." (*The world of Walther Nernst: the rise and fall of German Science 1864-1941* (ebook form from Plunket Lake Press, 2015; the original 1973) Chapter 4.

scopic organisms ([**N**] indicates the closest traditional ‘N-th law’):

[**O**] There is a state called an equilibrium state. Equilibrium states of a system may be described in terms of thermodynamic coordinates (E, X_i), where E is the internal energy and X_i are work coordinates. The equilibrium state exhibits partitioning-rejoining invariance **9.4**.
[**I**] The conservation of energy: $\Delta E = Q + W$, or for infinitesimal changes $dE = d'Q - PdV + BdM + xdX$;[217] the variables appear in ‘conjugate pairs’: $(-P, V)$, (B, M), (x, X) (for a generic pair), etc. See **9.14**.
[**II**] The thermodynamic space is foliated into $S =$ constant (hyper)surfaces. With adiabatic quasistatic (thus reversible) processes we cannot get out of a given $S =$ const. surface. With work only, $\Delta S < 0$ never happens; to reduce entropy we definitely need cooling. For a quasistatic process the Gibbs relation holds: $dE = TdS + \sum_i x_i dX_i$. Often $dS = \frac{1}{T}dE + \frac{P}{T}dV - \frac{x}{T}dX + \cdots$ is convenient. See **20.3**.
[**III**] $S = 0$ in the limit $T \to 0$. This is the third law we will encounter in **16.5**.
[**IV**] Thermodynamic variables are either extensive or intensive. The total amount of an extensive quantity of a compound system is the sum of the extensive quantities of the subsystems (additivity) **9.5**.

Practically,
(i) Thermodynamics can be used to compute the state function change caused by any process connecting an initial equilibrium state A and a final equilibrium state B.
(ii) To this end we devise a convenient quasistatic path from A to B in the thermodynamic space along which we can use the Gibbs relation mentioned in [II] above.

10.2 Entropy maximization principle

Entropy cannot be reduced by any adiabatic process. Therefore, if an equilibrium state changes into another equilibrium state through modification of only the work coordinates under an adiabatic condition,[218] the entropy of the system generally increases.

Suppose the initial system is in equilibrium but with some constraints (say, compartmentalized with internal walls). If we remove the constraints, the system would evolve to a new equilibrium state (Fig. 10.1). Since the change is spontaneous, generally, this final state has a larger entropy. This is the *principle of increasing*

[217] ⟪**Standard state function symbols**⟫ We stick to the standard notations:
E: internal energy, S: entropy, T: temperature, P: pressure, V: volume, $\boldsymbol{B}$ (B or h): magnetic field, $\boldsymbol{M}$ (M): magnetization, μ: chemical potential, N: number of particles. We use X for a generic work coordinate (extensive quantity) and x for its intensive conjugate (with respect to energy).

[218] ‘Adiabatic’ implies no exchange of heat. Then, the reader may infer that thermal contact with a single heat bath is admissible if there is no net heat exchange. This is correct. Notice that ‘adiabatic condition’ does not mean $R \to 0$ (external noise zero) limit (Section 12).

entropy.[219]

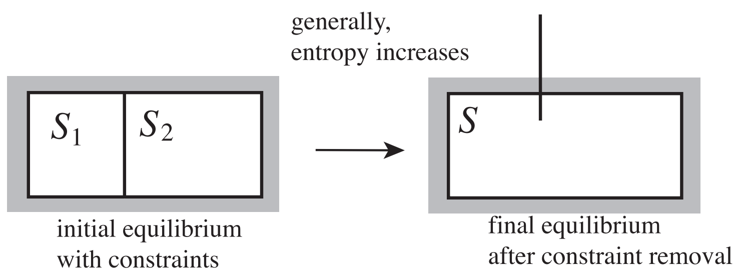


Figure 10.1: Initially, assume that the system is in equilibrium in the presence of a wall, which may be understood as a symbol of a certain constraint. The total entropy of this system as a whole (i.e., as a compound system **9.11**) is $S_1 + S_2$. The whole system is under an adiabatic condition. When the wall is removed (i.e., the constraint is removed), the system evolves to a new equilibrium state with a larger entropy spontaneously (irreversibly). That is, the final entropy S must satisfy $S \geq S_1 + S_2$ (the principle of increasing entropy).

A spontaneous change in an adiabatic system increases its entropy, so if the system entropy reaches the maximum under a given constraint, the system reaches its equilibrium state under the constraint. This is the *entropy maximization principle.*[220] Thus, the change δS of the system entropy due to any virtual change (perturbation) of the system tells us that (*stability and evolution criteria*):

$$\delta S < 0 \iff \text{the state is thermodynamically stable,} \tag{10.1}$$

$$\delta S > 0 \iff \text{the state spontaneously evolves.} \tag{10.2}$$

Therefore, the second law gives us a *variational principle* in terms of entropy to find a stable equilibrium state for an adiabatic system.

In the above description of the stability criterion, we mentioned 'virtual changes or perturbations'.[221] In reality, however, they are not virtual in most cases, but are actually produced spontaneously by thermal fluctuations. Thus, as long as thermal

[219] However, this does not claim the system entropy increases at every intermediate time during the evolution process, because thermodynamic entropy is defined only for equilibrium states.

[220] ⟪**Remark on entropy max principle**⟫ Astute readers would say that under an adiabatic condition, if entropy is maximum, then the state is in equilibrium, but the converse: if equilibrium, its entropy is maximum is not demonstrated. This is true. However, in the usual thermodynamics, this converse is postulated.

Generally speaking, even if thermodynamics tells us that a process is not forbidden, whether the system actually spontaneously realizes the process or not is a matter of kinetics or dynamics, and, logically speaking, thermodynamics cannot say anything about it. Still, in the overwhelming majority of cases thanks to thermal fluctuations, such a process actually occurs spontaneously. Therefore, we may assume that the entropy max condition is equivalent to the equilibrium condition under adiabatic conditions.

[221] δS up to this point is due to perturbations that are uniform throughout the system. However, as will be noted later in Section 19, the perturbations can be spatially non-uniform (can be localized in small regions).

fluctuations are not suppressed, whenever the system entropy can increase, the system evolves to maximize its entropy; behind any variational principle are fluctuations to substantiate it.

10.3 Entropy is concave

Let us join two systems made of the same substances to make a single system. The entropy maximization principle tells us that the entropy of the resultant compound system is given by

$$S(E, X) = \max[S(E_1, X_1) + S(E_2, X_2)], \tag{10.3}$$

where the maximum is taken over all the partitions of E and X between the two systems as $E = E_1 + E_2$ and $X = X_1 + X_2$ (X collectively denotes work coordinates). This implies with the aid of the extensivity of S (i.e., $S(\alpha E, \alpha X) = \alpha S(E, X)$)

$$S((1-\alpha)E + \alpha E', (1-\alpha)X + \alpha X') \geq (1-\alpha)S(E, X) + \alpha S(E', X') \tag{10.4}$$

for any $\alpha \in [0, 1]$. That is, S is a concave function (its graph is convex upward) of all the thermodynamic coordinates (see Fig. 10.2A). This implies that the local stability criterion (10.1) holds globally as well (under the adiabatic condition).

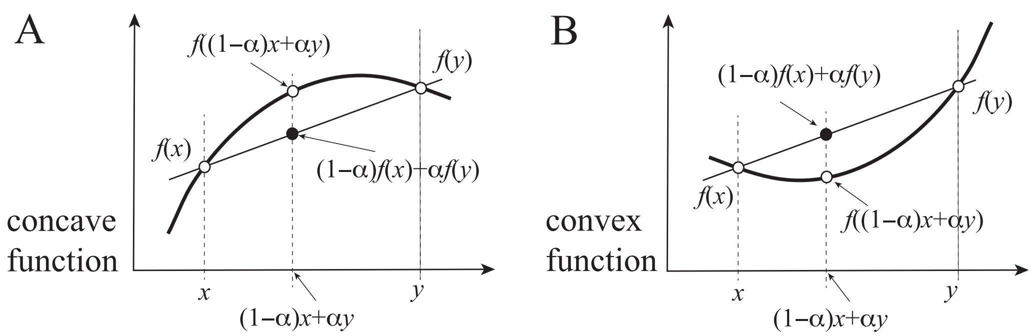


Figure 10.2: An example of the concave function A and that of the convex function B are illustrated; the resultant inequality for B is called Jensen's inequality. The black dots correspond to the right-hand sides of (10.4) and (10.8), respectively.

10.4 Internal energy minimization principle

The entropy maximization principle implies for any deviation ΔX of X from the equilibrium value[222]

$$S(E, X_{eq}) - S(E, X_{eq} + \Delta X) \geq 0. \tag{10.5}$$

[222]Since entropy is defined only for equilibrium states, this means, precisely speaking, that if, with some constraints, we make a new equilibrium state with $X + \Delta X$ and E, then (10.5) holds.

Therefore, since S is an increasing function of energy, we can increase the internal energy E in the second term to $E' \geq E$ under the $X = X_{eq} + \Delta X$ condition to satisfy

$$S(E, X_{eq}) - S(E', X_{eq} + \Delta X) = 0. \tag{10.6}$$

This implies that under the constant entropy condition, if an extra constraint to fix X at $X_{eq} + \Delta X$ is removed, then the internal energy surely decreases in equilibrium, since $E \leq E'$. That is, if the internal energy is minimized under a constant entropy condition, the system must be in equilibrium.

10.5 Internal energy is convex

Let us join two systems made of the same substances to make a single system. The energy minimization principle tells us that the internal energy of the resultant compound system is given by

$$E(S_1 + S_2, X) = \min[E(S_1, X_1) + E(S_2, X_2)], \tag{10.7}$$

where the minimum is taken over all the partitions of S and X between the two systems as $S = S_1 + S_2$ and $X = X_1 + X_2$. This implies with the aid of the extensivity of E

$$E((1-\alpha)S + \alpha S', (1-\alpha)X + \alpha X') \leq (1-\alpha)E(S, X) + \alpha E(S', X') \tag{10.8}$$

for any $\alpha \in [0, 1]$. That is, E is a convex function (its graph is convex downward) of all the variables (= entropy and work coordinates) (see Fig. 10.2B).

Let us extend our inequalities for thermally isolated systems to thermally non-isolated systems. The following argument exemplifies a standard strategy that we use repeatedly throughout statistical thermodynamics.

10.6 Extension to non-adiabatic systems

Let us extend our inequalities for thermally isolated systems to thermally non-isolated systems. The following argument is a standard strategy that we use repeatedly throughout statistical thermodynamics. To consider a system which is not isolated, that is, a system which is interacting with its environment, we construct a bigger isolated system composed of the system itself (I) and its interacting environment (II) (Fig. 10.3). We assume that both systems are macroscopic, so we may safely ignore the surface effect.

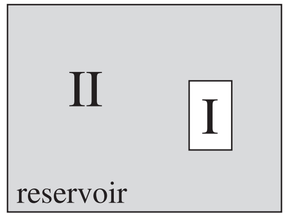


Figure 10.3: The system II is the environment for the system I we are interested in. II is sufficiently large so even if changes in I are irreversible, II remains infinitesimally close to equilibrium (i.e., any change in I causes a quasistatic change in II).

The environment is stationary (in equilibrium), whose intensive thermodynamic variables such as temperature are kept constant. To realize this we take a sufficiently big system (called a *reservoir* like a thermostat or a chemostat) as the environmental system II.[223] Even if a change is a rather drastic one for the system I itself, it would be negligible for the system II, because it is huge. Therefore, we may assume that any process in the system I is a quasistatic process for system II.

10.7 Clausius' inequality

The entropy change of the compound system I+II is given by the sum of the entropy change of the system I denoted by ΔS_{I} and that of the environment II denoted by ΔS_{II}. Since the whole system I + II is adiabatic, a natural process occurring in the whole system must satisfy (see **10.2**)

$$\Delta S_{\mathrm{I}} + \Delta S_{\mathrm{II}} \geq 0. \tag{10.9}$$

Let Q (> 0) be the heat transferred to the system I from the environment II. From our assumption, we have

$$\Delta S_{\mathrm{II}} = -Q/T_e, \tag{10.10}$$

where T_e is the temperature of the environment (system II). The minus sign is because II is losing heat to I. Combining (10.9) and (10.10) yields the following inequality:

$$\Delta S_{\mathrm{I}} \geq Q/T_e. \tag{10.11}$$

This is *Clausius' inequality* for non-adiabatic systems. This tells us when something spontaneously happens with heat exchange allowed, the actual entropy change is larger than that due to a reversible process. Of course, for adiabatic systems Q vanishes, so we recover the principe of maximum entropy **10.2**.

[223]Usually, the amount of heat transferred from a system is obtained from its temperature and heat capacity. Therefore, you might claim that if a system is huge, it would be impossible to measure its temperature change accurately, so consequently heat Q transferred may not be accurately determined. In reality, we can use a thermometer and electric heater to construct a surface (thermostat) that is maintained very accurately at a given temperature and we can measure the needed electricity to maintain it to obtain Q. Thus, virtually we can realize an ideal heat bath.

If the change in I is reversible, then $\Delta S_{\rm I} = Q/T_e$ should hold; (10.11) implies that 'excessive entropy' has been produced in I by the irreversibility of the process.

10.8 Equilibrium conditions between two systems: energy exchange possible

As an application of the entropy maximization principle, let us study the equilibrium conditions for two systems I and II interacting through various walls.

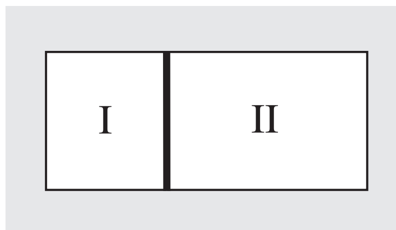


Figure 10.4: The thick vertical segment denotes the wall that selectively allows the exchange of a certain extensive quantity.

Consider a rigid impermeable wall which is diathermal. Thus, the two systems in contact through this wall exchange energy (internal energy) in the form of heat. The total entropy of the system S is the sum of the entropy of each system $S_{\rm I}$ and $S_{\rm II}$. The total internal energy E is also the sum of subsystem internal energies $E_{\rm I}$ and $E_{\rm II}$ (extensivity). We isolate the compound system and ask the equilibrium condition for the system. We should maximize the total entropy with respect to the variation of $E_{\rm I}$ and $E_{\rm II}$:

$$\delta S = \frac{\partial S_{\rm I}}{\partial E_{\rm I}}\delta E_{\rm I} + \frac{\partial S_{\rm II}}{\partial E_{\rm II}}\delta E_{\rm II} = \left(\frac{\partial S_{\rm I}}{\partial E_{\rm I}} - \frac{\partial S_{\rm II}}{\partial E_{\rm II}}\right)\delta E_{\rm I} = 0, \tag{10.12}$$

where we have used that $\delta E = 0$ or $\delta E_{\rm I} = -\delta E_{\rm II}$. Hence, the equilibrium condition is

$$\frac{\partial S_{\rm I}}{\partial E_{\rm I}} = \frac{\partial S_{\rm II}}{\partial E_{\rm II}}, \tag{10.13}$$

or $T_{\rm I} = T_{\rm II}$.

10.9 Equilibrium conditions between two systems: volume exchange possible

Consider a diathermal impermeable wall which is movable. In this case the two systems can exchange energy and volume. If we assume that the total volume of the system is kept constant, the equilibrium condition should be

$$\delta S = \frac{\partial S_{\rm I}}{\partial V_{\rm I}}\delta V_{\rm I} + \frac{\partial S_{\rm II}}{\partial V_{\rm II}}\delta V_{\rm II} = \left(\frac{\partial S_{\rm I}}{\partial V_{\rm I}} - \frac{\partial S_{\rm II}}{\partial V_{\rm II}}\right)\delta V_{\rm I} = 0, \tag{10.14}$$

and $T_{\rm I} = T_{\rm II}$, that is,

$$\frac{\partial S_{\rm I}}{\partial V_{\rm I}} = \frac{\partial S_{\rm II}}{\partial V_{\rm II}} \tag{10.15}$$

and $T_{\rm I} = T_{\rm II}$. Therefore, $P_{\rm I} = P_{\rm II}$ is also required.

Remark If the wall is adiabatic, then it cannot exchange heat, so there is no way to exchange entropy. This suggests that to use the Gibbs relation (9.10) directly is convenient. $P_{\rm I} = P_{\rm II}$ is the condition; we cannot say anything about the temperatures.

10.10 Equilibrium system has its 'individual' heat bath

It is almost never emphasized but perhaps the most important characteristic of an equilibrium macrosystem is that there is always a heat bath contact with which does not alter the equilibrium system. I call it the private (or individual) heat bath for the state.

Notice that a system attached to a heat bath cannot be described by any mechanics.[224] Thus, we may say, in equilibrium at least, thermodynamics transcends mechanics (quantum or not). Following the 19th and the 20th century tradition, we still believe smaller scales are more basic without firm empirical supporting arguments. Of course, this point of view may well be the correct way even empirically to understand our world, we should be skeptical to be faithful to the fundamental of science.

Thermodynamics through examples

Let us get familiar with thermodynamics through basic practice problems:

10.11 Mayer's relation

Demonstrate *Mayer's relation*: $C_P = C_V + R$, where C_P is the constant pressure molar specific heat and C_V the constant volume molar specific heat of an ideal gas.

First of all, we must identify the quantities in terms of thermodynamic variables. The specific heat under constant V and constant P are defined as

$$C_V = \left.\frac{\partial Q}{\partial T}\right|_V, \;\; C_P = \left.\frac{\partial Q}{\partial T}\right|_P. \tag{10.16}$$

[224] The traditional approach is to describe the heat bath as a much bigger isolated purely mechanical system. However, we must not forget that the larger the system the harder to maintain it in isolation; there is no isolated macroscopic quantum system in the world. Needless to say, you cannot enclose the system with a bigger pure mechanical system.

The first law tells us $dE = d'Q - PdV$, so

$$C_V = \left.\frac{\partial E}{\partial T}\right|_V, \quad C_P = \left.\frac{\partial E}{\partial T}\right|_P + P\left.\frac{\partial V}{\partial T}\right|_P. \tag{10.17}$$

For an ideal gas E is dependent only on T (recall that E is the kinetic energy of unhindered molecular motion for idea gases), so $dE = C_V dT$. $V = RT/P$, so

$$C_P = \left.\frac{\partial E}{\partial T}\right|_P + P\left.\frac{\partial V}{\partial T}\right|_P = C_V + R. \tag{10.18}$$

Mayer obtained this relation with the aid of *Mayer's cycle* (Fig. 10.5). Recall that ideal gas has only kinetic energy which is uniquely determined by temperature as $E = C_V T$.

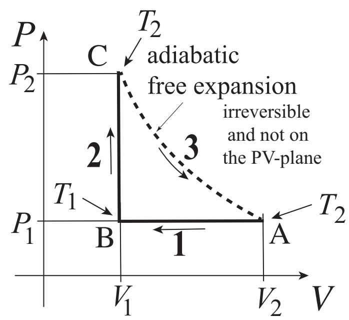


Figure 10.5: Mayer's cycle consists of isobaric compression **1**, constant volume heating **2**, and adiabatic free expansion (recall the law of constant temperature due to Gay-Lussac) **3**.

Notice that **3** in Fig. 10.5 does not change E, so for the ideal gas A and C are at the same temperature, say, T_2 (recall the law of constant temperature **2.11** (ii)). Let the temperature at B be T_1. The work supplied by the isobaric compression process **1** is $W = P_1(V_2 - V_1)$. The heat is discarded during this process simultaneously: $C_P(T_2 - T_1)$. During the process **2** heat $C_V(T_2 - T_1)$ is absorbed. Therefore, for the cycle as a whole, we have

$$0 = P_1(V_2 - V_1) + C_P(T_1 - T_2) + C_V(T_2 - T_1) = R(T_2 - T_1) + C_P(T_1 - T_2) + C_V(T_2 - T_1). \tag{10.19}$$

That is, $R - C_P + C_V = 0$.

10.12 Poisson's relation

Show that along an adiabatic quasistatic path $PV^\gamma = $ const., where $\gamma = C_P/C_V$. This is called *Poisson's relation*.

The first law implies $dE = -PdV$ (adiabatic and quasistatic!). Also $dE = C_V dT$ (ideal gas). Therefore,

$$0 = C_V dT + PdV = C_V d(PV/R) + PdV = (C_V/R + 1)PdV + (C_V/R)VdP. \tag{10.20}$$

That is, $\gamma d \log V + d \log P = 0$ with the aid of Mayer's relation.

10.13 Reversible engine: Carnot's theorem

Obtain the efficiency η (see (10.22) for the definition) of a reversible heat engine, and demonstrate that there is no engine more efficient than the reversible engine (Carnot's theorem).

A heat engine is a device that absorbs heat from a high temperature heat bath (temperature T_H) and converts a portion into work. The remaining energy is discarded to a low temperature heat bath (temperature T_L). See Fig. 10.6. Let Q_H and

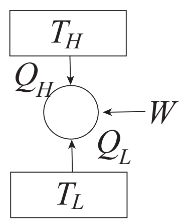


Figure 10.6: A heat engine operating between two heat baths. We assume the standard sign convention seen from the engine (the circle in the figure). Thus, $Q_H > 0$, $W < 0$ and $Q_L < 0$.

Q_L be the heats the engine absorbs from the high and low temperature heat baths, respectively, per one cycle, and W the work the engine obtains per one cycle (we expect $Q_H > 0$, $Q_L < 0$ and $W < 0$). The first law implies (since the engine does not produce energy)

$$W + Q_H + Q_L = 0. \tag{10.21}$$

The *efficiency* of an engine is the ratio of the work the engine produces (the benefit we get) to the heat it absorbs from the high-temperature reservoir (the expenditure we pay). Therefore, we define the engine efficiency as (be careful with the sign convention)

$$\eta \equiv \frac{|W|}{Q_H} = -\frac{W}{Q_H} = 1 + \frac{Q_L}{Q_H}. \tag{10.22}$$

Let ΔS_H be the entropy increase of the engine in a single cycle due to the import of heat from the high-temperature bath, and ΔS_L due to the import of heat from the low-temperature bath. Clausius' inequality (10.11) tells us that

$$\Delta S_H \geq \frac{Q_H}{T_H}, \quad \Delta S_L \geq \frac{Q_L}{T_L}. \tag{10.23}$$

Since the engine returns to the original state after a single cycle, $\Delta S = \Delta S_H + \Delta S_L = 0$:

$$0 = \Delta S_H + \Delta S_L \geq \frac{Q_H}{T_H} + \frac{Q_L}{T_L} \;\Rightarrow \frac{Q_H}{T_H} \leq -\frac{Q_L}{T_L}, \tag{10.24}$$

which implies $T_L/T_H \le -Q_L/Q_H$. Thus, we have

$$\eta = 1 + \frac{Q_L}{Q_H} \le 1 - \frac{T_L}{T_H}. \tag{10.25}$$

If the engine is reversible, it attains the maximum efficiency $\eta = 1 - T_L/T_H$. This statement is called *Carnot's theorem*.[225]

10.14 Absolute temperature scale

Thomson saw in (10.25) a possibility of introducing the universal temperature scale based solely on the thermodynamic principles free from any materials; he reached the concept of the *absolute temperature* in terms of the maximum efficiency.

10.15 The original Carnot's argument using the Carnot cycle of an ideal gas.[226] Carnot conceived the following engine (the *Carnot engine*) which utilizes an ideal gas (in this exposition, 1 mole of it) as its working substance (Fig. 10.7). This original demonstration of Carnot's theorem is much harder than the one we just saw, but may be a good elementary thermodynamics exercise:
(i) The engine does work through expansion while absorbing heat from the high temperature heat source (at T_H) (A→B in Fig. 10.7).
(ii) Then, it continues to expand while doing work and cools from T_H to T_L (B→C). Notice that this portion was Watt's novelty.
(iii) Next, the engine volume isothermally shrinks (i.e., some positive work is supplied to the engine) while discarding heat to the low temperature heat source at T_L (C→D).
(iv) Finally, the system is compressed adiabatically (again some positive work is supplied to the engine) and its temperature goes up from T_L to the original T_H (D→A).

The work added to the system (engine) is

$$W = -\oint_{ABCDA} PdV, \tag{10.26}$$

so it is equal to $(-1)\times$ the area surrounded by the warped red-hsaded quadrangle ABCD in Fig. 10.7. That is, the work done by the engine during its one cycle is the area of ABCD.

During the isothermal process A→B the engine does some work to the environment, but its internal energy is constant, because this is an isothermal process for an ideal gas; the work must be paid by the heat Q_H absorbed from the high temperature heat source at T_H. Therefore, (notice $dE = d'Q - PdV = 0$)

$$Q_H = \int_{A\to B} PdV = \int_{A\to B} \frac{RT_H}{V} dV = RT_H \log \frac{V_B}{V_A} > 0. \tag{10.27}$$

[225] If $T_H = +\infty$, then the reversible efficiency is 1. Recall **9.19**, according to Clausius, that work is heat from a bath at $T = \infty$.

[226] **《Carnot's original used the caloric theory》** The actual original argument due to Carnot relied on the caloric theory (which regarded heat as a substance called caloric), so the exposition given here cannot literally be his original argument, but a correct transliteration was done by Clausius. We need this demonstration to identify the absolute temperature introduced by the ideal gas law and θ we introduced to relate heat and entropy change in Section 9.

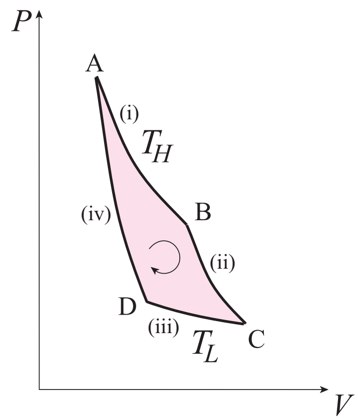


Figure 10.7: The Carnot cycle: AB and CD are quasistatic isothermal processes, and BC and DA are quasistatic adiabatic processes. BC is the key element of Watt's engine. The working substance is an ideal gas, so during the isothermal process its internal energy is constant. This implies that during isothermal processes the work the system does (or is supplied to the system) and the heat it absorbs (or it discards) must be identical. Understanding the Carnot engine with the PV-diagram was originally due to Clapeyron (1834, thus this diagram is called Clapeyron's graph), who advocated Carnot's work. The work done by the engine in one cycle is the area of the pale-red warped quadrangle.

Similarly, during the isothermal process C→D the heat $|Q_L|$ discarded (i.e., Q_L (< 0) absorbed) by the system to the low temperature heat source at T_L must be identical to the work done to the system, so we have

$$|Q_L| = -\int_{C\to D} PdV = -\int_{C\to D} \frac{RT_L}{V}dV = RT_L \log\frac{V_C}{V_D}. \tag{10.28}$$

To relate these two formulas, we need the ratios of the volumes related by quasistatic adiabatic processes. Poisson's relation **10.12** PV^γ = const. implies $TV^{\gamma-1}$ = const. Consequently, $T_H V_A^{\gamma-1} = T_L V_D^{\gamma-1}$ and $T_H V_B^{\gamma-1} = T_L V_C^{\gamma-1}$ hold. This implies that $T_H/T_L = V_D^{\gamma-1}/V_A^{\gamma-1} = V_C^{\gamma-1}/V_B^{\gamma-1}$, or $V_B/V_A = V_C/V_D$. Using this relation in (10.27) and (10.28), we obtain the equality in (10.24). The rest is identical to the argument above, and we get $\eta = 1 - T_L/T_H$.

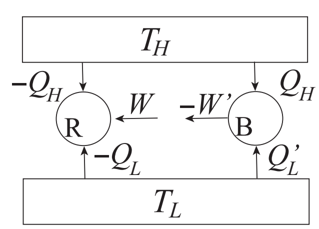


Figure 10.8: The reversible engine R (Left) is now used as a heat pump, and is driven by a (imaginary) better engine B (Right) that can produce work $|W'| > |W|$ using the identical heat sources.

Carnot's original proof of his theorem went as follows. Suppose we have an engine B better (more efficient) than the reversible engine R, which can be driven backward by supplying work. Let us drive the reversible engine R backward with engine B and use R as a 'heat pump' (see Fig. 10.8).

$|W'| > |W|$, so if we use the output of the 'better engine' to drive the reversible engine, we can still utilize the work $|W'| - |W|$. Since the net heat imported to the two engines from the hotter bath is zero, inevitably, $|Q'_L| < |Q_L|$. That is, $|Q_L| - |Q'_L|$ is absorbed from the colder bath. This implies that work has been extracted from a single heat bath, violating Kelvin's principle. Hence, there cannot be any better engine than the reversible engine.

10.16 Ideal gas: thermodynamic equation of state

The thermodynamic space of an (1 mole) ideal gas is spanned by internal energy E and volume V. Compute the entropy difference between the initial equilibrium state (E_1, V_1) and the final equilibrium state (E_2, V_2) for a 1 mole of ideal gas.

Since entropy is a state function 9.9, to compute its change between two equilibrium states, we may invent a convenient process connecting these two states. The process we can compute in detail is a quasistatic process.

The first law (or the Gibbs relation) tells us along a quasistatic process

$$dS = \frac{1}{T}dE + \frac{P}{T}dV. \tag{10.29}$$

Since for a (1 mole) ideal gas $E = C_V T$ and $PV = RT$,

$$dS = \frac{C_V}{E}dE + \frac{R}{V}dV = C_V d\log E + Rd\log V. \tag{10.30}$$

dS is a perfect differential, so we have only to integrate this along a convenient path (this is the meaning of inventing a convenient process):

$$S(E_2, V_2) = S(E_1, V_1) + C_V \log\frac{E_2}{E_1} + R\log\frac{V_2}{V_1}. \tag{10.31}$$

In contrast to the usual equation of state $PV = RT$, the relation (which should be called the true equation of state) $S = S(E, V)$ gives you 'everything' you wish to know about the ideal gas:

$$\frac{P}{T} = \left.\frac{\partial S}{\partial V}\right|_E = \frac{R}{V},\ \ \frac{1}{T} = \left.\frac{\partial S}{\partial E}\right|_V = \frac{C_V}{E}. \tag{10.32}$$

Poisson's relation $PV^\gamma =$ const. must imply $\Delta S = 0$. Since we derived Poisson's relation assuming $\Delta S = 0$, this should be, but in any case, let us check this. $P = RT/V = RE/C_V V$, so Poisson's relation implies $EV^{\gamma-1} =$ const. for an adiabatic quasistatic process. If this relation holds, then, since $R = C_P - C_V$, the system entropy does not change:

$$S(E_2, V_2) = S(E_1, V_1) + C_V\left[\log\frac{E_2}{E_1} + (\gamma - 1)\log\frac{V_2}{V_1}\right] = S(E_1.V_1). \tag{10.33}$$

or we may write with an appropriate base point E_0 and V_0 in the thermodynamic space

$$S(E, V) = S(E_0, V_0) + C_V\log(E/E_0) + R\log(V/V_0). \tag{10.34}$$

10.17 Heat exchange between two blocks: set up

There are two blocks with the same heat capacity C at temperature T_L and at T_H, respectively. If we bring these blocks to thermal equilibrium reversibly or irreversibly, what is the final common temperature T_F (Fig. 10.9)?

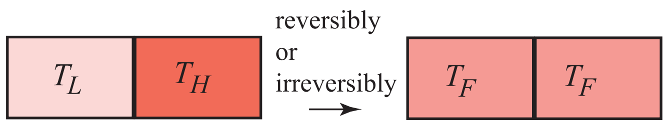


Figure 10.9: Initially, two blocks have different temperatures. What is the common temperature T_F when the blocks reach a thermal equilibrium?

10.18 Heat exchange: Irreversible case

If we make a thermal contact between them (assume that the system as a whole is thermally isolated = under an adiabatic condition), a 'perfectly' irreversible process occurs, and the final temperature is $T_F = (T_L + T_H)/2$ due to the first law and the result we obtained above. Needless to say, the final entropy of this system must be larger than the initial one, i.e., $\Delta S > 0$ (Δ always means 'final' $-$ 'initial'). To use thermodynamics, we must invent a quasistatic process connecting the initial and the final equilibrium states. We bring one block from T_L to T_F, and the other from T_H to T_F quasistatically, and then join these two. This last step does not change anything. Let us study each block separately.

An important observation is that if the heat exchange is across infinitesimal temperature difference dT, then the heat transfer is a quasistatic process (no increase of entropy).[227] Therefore, we may prepare numerous heat baths at various temperatures, and use them appropriately in turn to change the temperature of the block gradually (quasistatically). Along this process, we may use thermodynamics. Since $dQ = CdT$, $dS = CdT/T$:

$$\Delta S_1 = \int_{T_L}^{T_F} \frac{CdT}{T} = C \log \frac{T_F}{T_L}. \tag{10.35}$$

We can perform quite an analogous calculation for the other box, so combining the

[227]The entropy change due to the irreversible process of thermal contact between $T + dT$ and $T - dT$ is $\Delta S = C \log[T^2/(T^2 - dT^2)] = -C \log[1 - (dT/T)^2] \simeq C(dT/T)^2$, so it is a higher-oder infinitesimal, and may be ignored. That is, we may ignore the entropy change. See a summary starting from **10.20**.

answers, we get

$$\Delta S = \Delta S_1 + \Delta S_2 = C \log \frac{T_F^2}{T_L T_H} = 2C \log \frac{T_F}{\sqrt{T_L T_H}}. \tag{10.36}$$

Here, $T_F = (T_L + T_H)/2$. As can be seen from Fig. 10.10,

$$\Delta S = 2C \left[\log \frac{T_L + T_H}{2} - \frac{\log T_L + \log T_H}{2} \right] > 0. \tag{10.37}$$

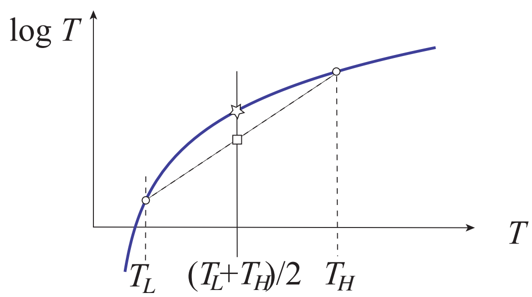


Figure 10.10: Star denotes $\log[(T_L + T_H)/2]$ and square denotes $(1/2)[\log T_L + \log T_H]$, demonstrating $(T_L + T_H)/2 > \sqrt{T_L T_H}$.

10.19 Heat exchange: reversible case

(10.36) implies that if $T_F = \sqrt{T_L T_H}$, then $\Delta S = 0$. There must be a reversible process to realize this. How can you do this? Notice that the internal energy of the system is not conserved:

$$\Delta E = 2CT_F - (CT_L + CT_H) = 2C \left(\sqrt{T_L T_H} - \frac{T_L + T_H}{2} \right) < 0. \tag{10.38}$$

Indeed this $|\Delta E|$ must be exported; the system can (must) do work.

To realize this reversible process we can set up a reversible engine between the two blocks and operate it until there is no temperature difference. Let us assume that T_H' is the temperature of the hotter block, and T_L' that of the colder block at some time point. Since by operation of the engine, the block temperatures change, so we analyze the engine working when the hotter block temperature is between T_H' and $T_H' + dT_H'$ (notice that $dT_H' < 0$). The entropy change must be zero (a reversible engine) during this temperature change:

$$dS = \frac{dQ_H}{T_H'} + \frac{dQ_L}{T_L'} = C\frac{dT_H'}{T_H'} + C\frac{dT_L'}{T_L'} = 0. \tag{10.39}$$

This implies $d\log(T_H' T_L') = 0$ or $T_L' T_H' =$ constant. That is, $T_F^2 = T_H' T_L' = T_L T_H$, or, as we know, the final temperature must be $T_F = \sqrt{T_L T_H}$.

We know the efficiency of the reversible engine, so

$$-\frac{d'W}{d'Q_H} = 1 - \frac{T_L'}{T_H'}, \tag{10.40}$$

or

$$-d'W = \left(1 - \frac{T'_L}{T'_H}\right) d'Q_H. \tag{10.41}$$

Here, $d'Q_H = -CdT'_H$, because decrease of T'_H implies positive $d'Q_H$. Therefore,

$$-d'W = -\left(1 - \frac{T'_L}{T'_H}\right) CdT'_H = \left(1 - \frac{T'_L T'_H}{T'^2_H}\right) C(-dT'_H). \tag{10.42}$$

That is, the work we can take out from the system is (note that $T_F = \sqrt{T'_L T'_H}$)

$$-\Delta W = C(T_L - T_F) + CT_H - C\frac{T_L T_H}{T_F} = 2C\left(\frac{T_L + T_H}{2} - \sqrt{T_L T_H}\right). \tag{10.43}$$

This is positive as shown before. Of course, this is a stupid way to compute ΔW; the answer is obvious from the first law. Trust thermodynamics.

In any case a (great) lesson is: if $\Delta S = 0$, there must be a reversible process to realize the change. Devise it.

We will see such an example in the next lecture.

A summary of heat and its relation to entropy changes is given here with small letters.

10.20 Heat exchange between systems with infinitesimal temperature difference is reversible

If the system exchanges no work but only heat, and if the process is quasistatic, then

$$dS = \frac{1}{T} dQ. \tag{10.44}$$

Consider the situation in Fig. 10.11, where the system is initially at temperature T_0. Suppose the specific heat of the system (assuming it is a block of material) is C.

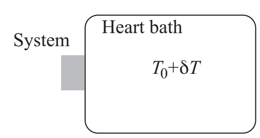


Figure 10.11: Heat contact with bath

Then, $dQ = CdT$. Therefore, the entropy increase of the system is, if we can realize a quasistatic process to 'warm up' the block,

$$\delta S_{\text{sys}} = \int_{T_0}^{T_0+\delta T} \frac{C}{T} dT = C \log \frac{T_0 + \delta T}{T_0} = C \log\left(1 + \frac{\delta T}{T_0}\right) = C\frac{\delta T}{T_0} - \frac{C}{2T_0^2}(\delta T)^2 + O[(\delta T)^3]. \tag{10.45}$$

The entropy increase of the heat bath is, since it does not change its temperature,

$$\delta S_{\text{bath}} = -\frac{C\delta T}{T_0 + \delta T} = -C\frac{C\delta T}{T_0(1 + \delta T/T_0)} = -C\frac{\delta T}{T_0} + \frac{C}{T_0^2}(\delta T)^2 + O[(\delta T)^3]. \tag{10.46}$$

Therefore, the entropy change due to this heat contact is

$$\delta S = \delta S_{\text{sys}} + \delta S_{\text{bath}} = \frac{C}{2T_0^2}(\delta T)^2 + O[(\delta T)^3]. \tag{10.47}$$

It is indeed positive (irrespective of cooling or warming!) in harmony with the second law, but it is $O[(\delta T)^2]$, so it is a higher order infinitesimal and does not add up to a finite amount. That is, the heat exchange between the systems with infinitesimal temperature difference is reversible.

10.21 Quasistatic temperature change due to heat

Exploiting the fact that the heat exchange between the systems with infinitesimal temperature difference is reversible **10.20**, we can devise a means to change the temperature of any system in a quasistatic manner (i.e., reversibly). We prepare numerous heat baths with temperatures $T_0 + \delta T$, $T_0 + 2\delta T$, $\cdots$, $T_1 - \delta T$, T_1 and bring the system with initial temperature T_0 in contact with these heat baths successively to reach the final temperature T_1.

10.22 Exchanging (finite) heat with heat bath is always irreversible

However, generally heat transfer is irreversible. Consider the effect of a single heat bath of temperature T_F. Then system whose initial temperature is T_0 will reach temperature $T_1 = T_F$ with the total entropy change given by

$$\Delta S = \int_{T_0}^{T_F} \frac{C}{T} dT - C\frac{T_F - T_0}{T_F} = C \log \frac{T_F}{T_0} - C\frac{T_F - T_0}{T_F} = C\left[\log \frac{T_F}{T_0} + \frac{T_0}{T_F} - 1\right]. \tag{10.48}$$

For $f(x) = \log x - 1/x + 1$ $f(1) = 0$ and $f'(x) = (x-1)/x^2$, so f is minimum at $x = 1$. Therefore, if $x \neq 1$, $f(x) > 0$. This means our $\Delta S > 0$ as long as $T_F \neq T_0$; irrespective of cooling or warming, heat conduction is irreversible.

10.23 Effects of intermediate temperature heat baths

Let us choose one more heat bath with temperature T_1 between T_0 and T_F. The total entropy change is given by

$$\Delta S = C \log \frac{T_1}{T_0} - C\frac{T_1 - T_0}{T_1} + C \log \frac{T_F}{T_1} - C\frac{T_F - T_1}{T_F}. \tag{10.49}$$

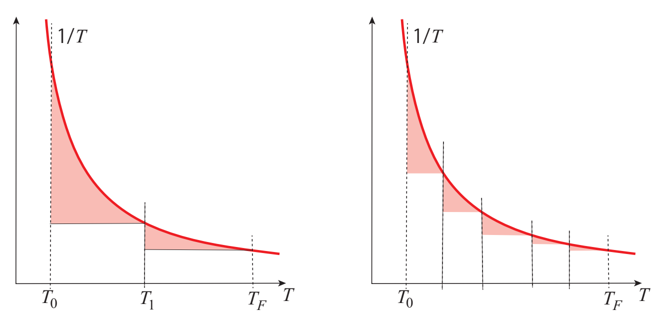


Figure 10.12: Left: One intermediate heat bath; Right: more numerous intermediate heat baths. The pale red shaded area is $\Delta S/C$.

Assuming $T_F > T_0$, let us illustrate this case and the case with more intermediate heat baths (Fig. 10.12).

In the figure the pale red shaded area is $\Delta S/C$, so increasing the intermediate heat baths filling the temperature gap reduces the 'extent of irreversibility' of head conduction; the ultimate version was already discussed in **10.21**; it is just the Riemann sum approximation of the integral.

10.24 If $\Delta S = 0$, there ought to be a reversible process

Suppose, there are two identical containers A and B containing identical amount of water, but their temperatures are distinct: A is at T_H and B at T_L ($< T_H$). A different state that A is at T_L and B at T_H obviously has the same entropy as the former case. There must be a way to change the initial state to the second one reversibly, i.e., there must be a reversible way to exchange the temperatures only. Can you do this only with heat transfer without using engines?

You can use this device to utilize the thermal energy in the used water in a bath tub to warm up the shower water, which may be the usual tap water.

10.25 Sudden doubling of volume

We know adiabatic free expansion is irreversible. Let us double the volume of an ideal gas from $V_I = V$ to $V_F = 2V$ by adiabatic sudden expansion (say, by removing the wall in Fig. 10.13).

If the gas is an ideal gas, the total kinetic energy is conserved, so the internal energy of the gas cannot change **2.11** (ii). This is an irreversible process. Since the process does not change the internal energy of the gas, we can compute the entropy change, using the formula we derived last time **10.16**, or integrating $dS = (P/T)dV$; this latter approach is equivalent to devising an appropriate quasistatic process. For one mole of the gas

$$\Delta S = R \log \frac{V_F}{V_I} = R \log 2. \tag{10.50}$$

$R = 8.31$ J/K·mol, and $\log 2 = 0.693$, so $\Delta S = 5.75$ J/K·mol.

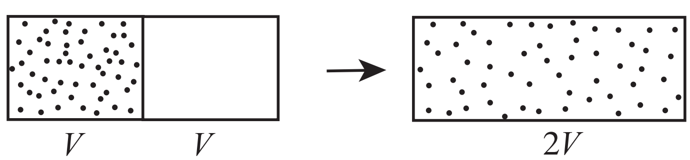


Figure 10.13: If the volume is doubled, to locate a molecule as accurately as before expansion we need to know which V (left half or right half) it is in.

10.26 Information: sneak preview

Entropy change and gain or loss of 'information' are closely related as we will see in Section 15. Here is a sneak preview.

If the volume is doubled, to locate a molecule as accurately as before the expansion we need to know which V (left or right) it is in before knowing at what location inside of one of Vs the particle is. This knowledge is obtained from a question answered by a single Yes or No ("is it in the left box?", a single YN question), so the expansion makes a state that requires one *bit* per molecule[228] extra information to describe it relative to the original state (molecules have acquired more freedom, obviously).

Therefore, it is sensible to conclude that the entropy change 5.75 J/K·mol (1 J/K·mol) is interpreted as (converted to) the information of 1 bit/molecule (0.174bit/molecule). 1 J/K·mol entropy increase corresponds to 0.174 bit/molecule of information. Notice that it is per molecule (not per mole); we are asking questions about each molecule.

10.27 What happens if we expand the gas from V to $2V$ reversibly?

This is nothing but adiabatic reversible expansion we have already discussed, but let us look at it from a slightly different angle. $\Delta S = 0$, so the internal energy must be reduced. That is, the gas can do work. You can devise a quasistatic path to $V_F = 2V$. Or, we can consider the final state $(2V, E_F)$ in the thermodynamic space, and demand the process from (V, E_I) to this final state to satisfy $\Delta S = 0$, using the equation of state $S = S(V, E)$ we already know.

First, let us devise a quasistatic process. We must gently expand the gas, so we must apply a force counterbalancing the pressure of the gas. The work done by the gas during this process is

$$\Delta W = -\int_V^{2V} P(V')\, dV'. \tag{10.51}$$

Although $PV = RT$ may be used, the temperature would change. Notice that this is a reversible adiabatic process, so we may use Poisson's relation $PV^\gamma =$ constant $= P_I V^\gamma$. Therefore,

$$\begin{aligned}\Delta W &= -P_I \int_V^{2V} \left(\frac{V}{V'}\right)^\gamma dV' = -P_I V^\gamma \frac{1}{1-\gamma}\left[(2V)^{1-\gamma} - V^{1-\gamma}\right] && (10.52)\\ &= -P_I V \frac{1}{\gamma - 1}(1 - 1/2^{\gamma-1}). && (10.53)\end{aligned}$$

This is certainly negative.

Now, let us use the equation of state $S = S(E, V)$ derived in **10.16**. We know $S(E_I, V) = S(E_F, 2V)$, so

$$C_V \log \frac{E_F}{E_I} + R \log \frac{V_F}{V_I} = 0. \tag{10.54}$$

[228]'bit' is the unit of information we can obtain from an answer of one yes-no question (YN question). We will discuss this after the introduction of canonical distribution. Here, simply accept this intuitively.

Since $R/C_V = \gamma - 1$, this reads

$$\log \frac{E_F}{E_I} + \log 2^{\gamma-1} = 0 \;\Rightarrow\; E_F = E_I/2^{\gamma-1}. \tag{10.55}$$

Indeed, $E_F < E_I$. Can you show $\Delta W = E_F - E_I$ is identical to (10.53)?

10.28 Mixing entropy

Mixing of two different substances (even without any interactions between them as in the case of ideal gases) also causes an increase of entropy (Thomson ignored this aspect of entropy). Suppose there are two kinds of ideal gas A and B (N particles each in a separate container of the same volume V). They are at the same T and P, and can be mixed at constant T and P (due to Dalton's law of partial pressures **2.10**) by removing the separating wall at the midpoint of the box (see Fig. 10.14).

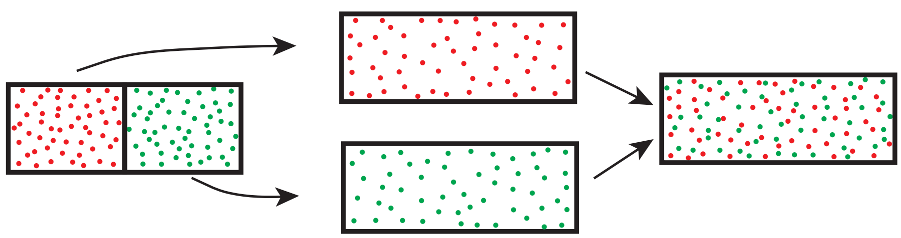


Figure 10.14: The mixing process may be considered as two irreversible volume doublings and subsequent superposition of the expanded gases; the last superposition step does not cause any thermodynamic change, because these gas particles do not interact.

If we use the information-entropy relation above, we can guess the mixing entropy. After mixing, if you pick up a single molecule, you must know whether it is A or B. Before mixing, this information was given 'for free', if you know the particle position. That is, mixing process prepares a state that requires one more bit (one extra YN question, say, "is it A?") to specify the state of its individual molecules. Therefore, $\Delta S = 2Nk_B \log 2$ is our guess (there are $2N$ particles).

The mixing process may be decomposed into the processes illustrated in Fig. 10.14. First, we expand each gas separately to prepare the state at temperature T and pressure $P/2$ (you can do so by adiabatic 'free' expansion as discussed just above), and then superpose these two gases to make the final mixture;[229] since they are ideal gases, they do not feel each other (recall Dalton's law of partial pressures). Therefore, the final superposition step does not cause any thermodynamic change and ΔS must be just the sum of the '$V \to 2V$' expansion entropy changes; our guess is correct.

[229]This is realizable with the aid of semipermeable membranes (walls that can allow only A or B to go through).

10.29 A more general case

A more general case is that the amount of A and B are different; T and P are the same but the volumes are V_A and V_B, respectively. Then, the final volume is V_A+V_B, so the free expansion entropies for A and B are

$$\Delta S_A = N_A k_B \log \frac{V_A+V_B}{V_A}, \ \ \Delta S_B = N_B k_B \log \frac{V_A+V_B}{V_B}. \tag{10.56}$$

That is, the mixing entropy is given by (notice that P, T constant $\Rightarrow N \propto V$)

$$\Delta S = N_A k_B \log \frac{N_A+N_B}{N_A} + N_B k_B \log \frac{N_A+N_B}{N_B}. \tag{10.57}$$

If we introduce the mole fraction $x_A = N_A/(N_A+N_B)$ and $x_B = N_B/(N_A+N_B)$, we can rewrite as

$$\Delta S = (N_A+N_B)k_B(-x_A \log x_A - x_B \log x_B). \tag{10.58}$$

We have learned that if we mix distinct gases A and B, entropy increases. Suppose you have two gases C and D, and wish to know whether they are distinct gases or not. OK, let us measure the mixing entropy. Is this feasible?

10.30 Entropy changes due to phase transition

Another way to change the system entropy is phase transition, e.g., melting or evaporation.[230] When a solid melts, a latent heat Q_m is absorbed at a constant temperature (= melting temperature T_m), so the system entropy changes by

$$\Delta S_m = Q_m/T_m. \tag{10.59}$$

Notice that Q_m is measured as the enthalpy change of the system. We have a similar formula for boiling:

$$\Delta S_b = Q_b/T_b, \tag{10.60}$$

where Q_b is the latent heat of evaporation (boiling heat) and T_b is the boiling temperature. For water $\Delta S_m = 21.9$ J/K·mol $= 3.7$ bits/molecule and $\Delta S_b = 109$ J/K·mol $= 18$ bits/molecules.

Can we understand these entropy changes? Upon melting, water molecules can freely orient in the 3D space. If we simply specify the orientation direction by one of the octants, 3 bits/molecules may not be unreasonable. When evaporated, the

[230] We will discuss what phase transition is statistical-mechanically in Section 25.

volume is expanded by about 1300 times, so even specifying where a molecule is requires extra $\log_2 1300 \simeq 10$ bits. Therefore, although we cannot quantitatively explain this 18 bits by such a crude idea, still we can partially understand why ΔS_b is much larger than ΔS_m.

Q10.1 [Fridge for camper].

There is a refrigerator that uses external heating process (such as used in campers with the use of LPG). Let us imagine an ideal fridge (i.e., reversible fridge) importing heat Q_H from the high temperature heat reservoir (say, a burner) at temperature T_H.

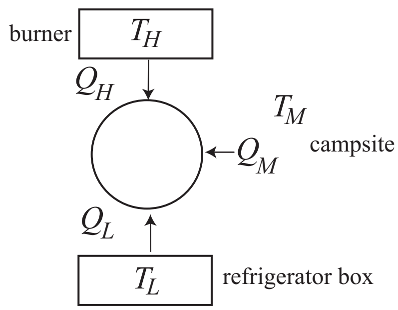


Figure 10.15: An idealized LPG fridge.

Let T_M be the temperature of the campsite. The temperature inside the cooled box is T_L ($T_H \gg T_M > T_L$ is the usual case). The energy balance of the device may be depicted as in Fig. 10.15. For this device to work as a fridge, Q_H and Q_L must be positive (i.e., the device absorbs these heats) and Q_M must be negative (this heat must be discarded). Since Q_H is supplied by some energy source, the 'goodness' of the fridge may be measured by the cost-performance ratio:

$$\eta = Q_L/Q_H. \tag{10.61}$$

(1) Write down the energy balance equation (i.e., $\Delta E = 0$ for a cycle). We strictly apply our sign convention: in $+$, out $-$.
(2) Write down the reversibility condition (i.e., $\Delta S = 0$).
(3) Using these equations, obtain η in terms of T_H, T_M and T_L.
(4) If you look at the obtained η, you will realize that this 'goodness measure' improves (increases) as T_H is raised: hotter the burner, cooler the box! Isn't it counterintuitive? Explain very briefly why it is not counterintuitive. A hint is the following 'dissection' of the fridge in Fig. 10.16 (I do not mean every such fridge contains an engine. The dissection is a conceptual dissection.)

Solution.
(1) I recommend you to stick to the algebraic sign convention: $Q_H + Q_M + Q_L = 0$.
(2) Since reversibility may be assumed for the ideal case, we may use $dS = d'Q/T$:

$$\frac{Q_H}{T_H} + \frac{Q_M}{T_M} + \frac{Q_L}{T_L} = 0$$

(3) Getting rid of Q_M, we get

$$\frac{Q_H}{T_H} + \frac{Q_L}{T_L} = \frac{Q_L + Q_H}{T_M},$$

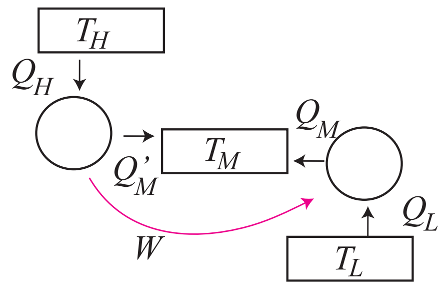


Figure 10.16: Conceptual dissection of the LPG fridge.

so

$$\frac{1}{T_H} + \eta\frac{1}{T_L} = (1+\eta)\frac{1}{T_M},$$

or (recall $T_L < T_M < T_H$)

$$\left(\frac{1}{T_L} - \frac{1}{T_M}\right)\eta = \frac{1}{T_M} - \frac{1}{T_H}$$

Therefore,

$$\eta = \frac{\frac{1}{T_M} - \frac{1}{T_H}}{\frac{1}{T_L} - \frac{1}{T_M}} = \left(1 - \frac{T_M}{T_H}\right)\frac{T_L}{T_M - T_L}.$$

This is just the product of the reversible heat engine efficiency working between T_H and T_M and the reversible refrigerator efficiency working between T_M and T_L. Thus, Fig. 10.16 is quite natural. This answers (4) as well. Increasing T_H makes the engine efficiency better, so the overall efficiency increases. Thus, the hotter the burner, the cooler the fridge (although we are not actually lowering T_L in this problem).

Q10.2 [Explosion in box]
Inside a thermally insulated (i.e., adiabatic) empty (i.e., vacuum) box of volume $10V$ is a small can of volume V containing a one mole of an ideal gas at temperature T. Now, the can is punctuated and the gas leaks out into a larger box and eventually reaches a new equilibrium state (see Fig. 10.17).

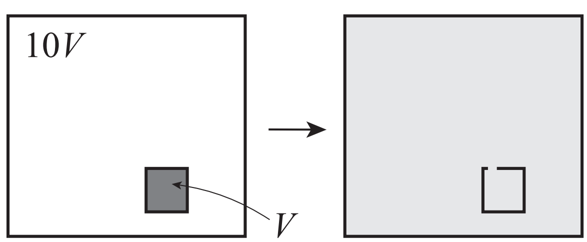


Figure 10.17: Initially, the can is filled with a gas (left) and is inside a vacuum box of volume $10V$. Then it is punctuated and the gas leaks to reach the final equilibrium state in the Right.

(1) What is the change of the total internal energy of the system due to punctuation

of the can?
(2) What is the total entropy change due to punctuation of the can?
(3) How many extra yes-no questions (i.e., how many bits/molecule) do you expect to need to specify the state (microscopic state) of a molecule compared with the state before the punctuation?

Solution.
(1) No heat nor work is exchanged with the outside world, so $\Delta E = 0$. Since our gas is ideal, this implies that the temperature (when definable) is invariant.
(2) We may use the equation of state $S = S(E, V)$. Thus,

$$\Delta S = R \log 10.$$

(3) Since $R \log 2$ corresponds to 1 bit/molecule, $\log 10/\log 2 = \log_2 10 = 3.32$ bits. Thus, on the average 3.3 questions.[231] [Recall that doubling of the volume increased the number of yes-no questions needed to specify the microscopic state of a particular molecule by one.]

We will discuss information later in more detail, but this question should be answerable, if you understand the volume doubling and volume quadrupling cases (already discussed). In the former case $\Delta S = R \log 2$ for a one mole ideal gas. This increase corresponds to one extra question about a particular molecule: is it in the right half? In the quadrupling case, $\Delta S = R \log 4$. We must ask two extra questions: is it on the right half? Then, subsequently, is it on the upper half? Thus, $\Delta S/R \log 2$ gives you the number of Yes-No questions you must further ask.

What if the hole made by punctuation is extremely small and molecules can go through it only one by one? No change, because $\Delta E = 0$ does not change, and the final volume does not change, so whatever the process is as long as the system is energetically isolated, the result cannot change. However, you may be suspicious. OK, we can actually compute the entropy change along the actual process.

This is a quasi equilibrium process BUT is not reversible. Actually, if we pay attention to a small portion $\delta N'$ of the gas going out from the can into the box, the process is patently an irreversible expansion. Thus, entropy increases. This increase may be computed, and after integrating all these infinitesimal increases δS of entropy, we get exactly the same result (as demonstrated below).

The following detailed calculation is not at all recommended, but let us follow the quasistatic process just described. Suppose N' molecules have already leaked out from the can (assume that the leakage is very slow and quasistatic). Then, the can pressure is $P = (N - N')k_B T/V$. Let $\delta N'$ be the further small amount of leak from the can. Before going out of the can, this portion $\delta N'$ occupies the volume

$$\delta V_i = \frac{\delta N'}{N - N'} V \tag{10.62}$$

[231] This means if you ask 33 yes-no questions about 10 molecules, you can get enough information.

in the can. The pressure of the outer box is $P = N'k_BT/9V$, so the volume of the escaping molecules $\delta N'$ is

$$\delta V_f = \frac{\delta N'}{N'} 9V. \tag{10.63}$$

That is, the leaked $\delta N'$ changes its volume from δV_i to δV_f. Therefore, the entropy increase due to this escape is (notice that the amount of molecules going out is $\delta N'$)

$$\delta S = k_B \delta N' \log \frac{\delta V_f}{\delta V_i} = k_B \delta N' \log \frac{9(N - N')}{N'}. \tag{10.64}$$

We should integrate this from N to $N/10$ (= the remaining amount in the can):

$$\Delta S = \int_N^{N/10} dN' \, k_B \log \frac{9(N - N')}{N'} = N k_B \log 10. \tag{10.65}$$

11 Isothermal systems

Summary
$*$ Helmholtz' free energy gives us the reversible work under isothermal condition. Generally, $\Delta A \leq W$ (pay attention to our sign convention).
$*$ Legendre transformation $f \to f^*$ has a deep meaning.
$*$ Legendre transformation preserves thermodynamics: $f^{**} = f$.

Key words
Helmholtz free energy, Legendre transformation, the Gibbs free energy, enthalpy, free-energy minimum principle

What you should be able to do
$*$ Understand the meaning of free energies.
$*$ To understand the significance of convexity of E.
$*$ To understand the meaning of Legendre transformation to preserves thermodynamics.

11.1 Relaxing isolation/adiabatic conditions

In reality, the variables $S, V, X, \cdots$ for the ordinary Gibbs relation (9.10) are often hard to control or at least awkward. For example, to keep volume constant may be more difficult than to keep pressure constant. To keep the temperature constant may be easier than an adiabatic condition.

11.2 Isothermal system

Under T constant (an isothermal condition) we should allow 'free' exchange of heat between the system and its ambient world to maintain the system temperature. Therefore, we wish to pay attention to the RHS of

$$dE - d'Q = d'W = -PdV + xdX. \tag{11.1}$$

Since (11.1) holds under a quasistatic condition, $d'Q = TdS$. T is constant, so (11.1) reads

$$dE - TdS = d(E - TS) = -PdV + xdX. \tag{11.2}$$

This implies that the introduction of the quantity

$$A = E - TS, \tag{11.3}$$

called the *Helmholtz free energy*,[232] is convenient. Notice that for an isothermal

[232] Old literatures use F.

process

$$dA = d'W. \tag{11.4}$$

Thus, ΔA is the work the system obtains by a reversible process under constant temperature (i.e., a reversible isothermal process).

11.3 ΔA by an irreversible process

Work W is always measurable with the aid of mechanics. What happens if the work exchange is not reversible under isothermal conditions?[233]

If we inject work W into the system irreversibly (= that allows some dissipation of work), the system must discard heat to the heat reservoir to maintain its temperature of the final equilibrium state. This implies that, even if you do actual work of W, effectively the system receives less energy as work. Therefore, we conclude

$$\Delta A \le W. \tag{11.5}$$

Pay attention to the sign convention: 'coming in is +'! Therefore, (11.5) implies that the work the system can do cannot be larger than $|\Delta A|$.

Suppose the system does work of amount $|W|$ ($W < 0$) to the outside. This implies that the system is supplied with the work of $-|W| = W$, so according to (11.5) $\Delta A < -|W|$ must hold. Since $\Delta A < 0$, and $|\Delta A|$ is the amount of decrease of the system free energy, when the system does work to outside, (11.5) implies

$$|\Delta A| \ge |W|. \tag{11.6}$$

That is, the work produced by the system cannot exceed the amount of the free energy lost by the system. The work we can gain from the system is bounded by $|\Delta A|$.

11.4 Relation to Clausius' inequality

You might have felt that the above argument sounds like a hand-waving argument (actually, it is not), so let us derive (11.5) from Clausius' inequality

$$\Delta S_{\mathrm{I}} \ge Q/T. \tag{11.7}$$

Here, we assume $T_e = T$. Q is the heat given to system I, so the heat bath loses Q or gains $-Q$. Let us assume system II also does work W to system I. That is, system II gains $-W$ (however, there is no guarantee that this work is completely received by system I as work). The first law applied to heat bath II reads

$$\Delta E_{\mathrm{II}} = -W - Q. \tag{11.8}$$

[233] Strictly speaking, temperature is not definable if a system is not in equilibrium, so you may well question what an isothermal irreversible process means. It means that the initial and the final temperatures are the same. Anything can happen in between. You can also understand the process as occurring in a system immersed in an isothermal bath (thermostat); still there is no guarantee that the system temperature is always well defined.

The definition of the Helmholtz free energy and an isothermal condition imply

$$\Delta E_I = \Delta A_{\rm I} + T\Delta S_{\rm I}. \tag{11.9}$$

Since the total energy is conserved (isolation),

$$0 = \Delta E = \Delta A_{\rm I} + T\Delta S_{\rm I} - W - Q. \tag{11.10}$$

Clausius' inequality implies $T\Delta S_{\rm I} - Q \ge 0$, so this implies

$$\Delta A_{\rm I} - W = Q - T\Delta S_{\rm I} \le 0. \tag{11.11}$$

This is what we wished to have.

11.5 Free energy minimum principle

If there is no exchange of work, irreversibility under isothermal condition implies

$$\delta A \le 0. \tag{11.12}$$

This implies that, if there is no spontaneous change (i.e., the state is stable), then

$$\delta A > 0. \tag{11.13}$$

That is, in the stable equilibrium state under constant $T, V, \cdots$ the Helmholtz free energy must be the global minimum. This is the *free energy minimum principle.*

11.6 Gibbs relation for A

The Gibbs relation now reads

$$dA = -SdT - PdV + xdX, \tag{11.14}$$

so we see, as designed, the natural set of independent thermodynamic variables is (T, V, X) instead of (S, V, X).

11.7 Gibbs free energy and enthalpy

It is often more convenient to study systems not only under constant temperature but also under constant pressure. Now, the system is placed in a constant pressure thermostat. Then, the work due to the volume change (the volume work $-PdV$) must be freely exchanged between the system and the external world, so we should rewrite the Gibbs relation as

$$dE - TdS + PdV = xdX + \cdots, \tag{11.15}$$

but since T and P are constant, it is convenient to introduce the following *Gibbs free energy* G

$$G = E - TS + PV \tag{11.16}$$

Quite an analogous argument as the case of the Helmholtz free energy tells us that under constant T and P, if no work other than due to volume changes exists, then

$$\delta G < 0, \iff \text{spontaneous changes can occur,} \tag{11.17}$$

$$\delta G > 0, \iff \text{the equilibrium is stable.} \tag{11.18}$$

Again, this is the principle of minimum free energy.

The Gibbs free energy may be written as

$$G = H - TS, \tag{11.19}$$

where

$$H = E + PV \tag{11.20}$$

is called the *enthalpy*.

If there is only volume works, then $d'W = -PdV$, so under constant pressure the first law reads

$$dH = dE + PdV = d'Q. \tag{11.21}$$

That is, the increase of enthalpy is the heat absorbed by the system under constant pressure. Thus, for example, if a chemical reaction occurs in a system, then the change of enthalpy is the reaction heat under constant pressure.

11.8 Legendre transformation

Formally, we can say that $E \to A = E - TS$ allows us to change the independent variables from (S, V, X) to (T, V, X). This is called (in most introductory textbooks) a *Legendre transformation*. This is, probably, one of the most mysterious parts of thermodynamics, because usually instructors do not know the true meaning of this transformation.[234]

11.9 Geometrical meaning of Legendre transformation

The transformation $E \to A = E - TS$ assumes that T in this relation satisfies $\partial E/\partial S = T$. Then, to obtain A may be understood geometrically as follows

As can be seen from Fig. 11.1, for a given T, to find on the curve $E = E(S)$ a point where the tangent is T is to find the point where the curve $E = E(S)$ and

[234]It is shocking that even an expository article of Legendre transformation in Am. J. Phys. does not mention this at all. Any reasonable instructor should know the rudiments of convex analysis.

the line $E = TS$ are the closest. Therefore, the (signed) distance between the curve $E = E(S)$ and the line $E = TS$ is A. In other words, we are actually computing $A = \min_S[E - TS]$, because to draw a tangent whose slope is T for curve $E = E(S)$ is to minimize the difference between the curve and the line $E = ST$.

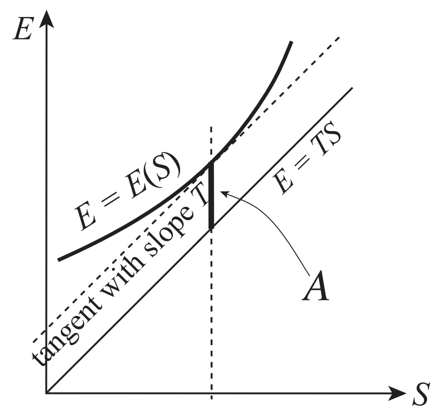


Figure 11.1: If we fix X's, E is a monotone increasing convex function of S.

11.10 Mathematically more rational definition of Legendre transformation

The true essence of the *Legendre transformation* is: a convex curve can be reconstructed from the totality of its tangent lines (→Fig. 11.2 Left), where a tangent line of a convex curve is a line sharing at least one point with the curve, and all the points on the curve are on one side of the line or on it (i.e., none on the other side). $E = E(S)$ and $-A = -A(T)$ are both convex curves.

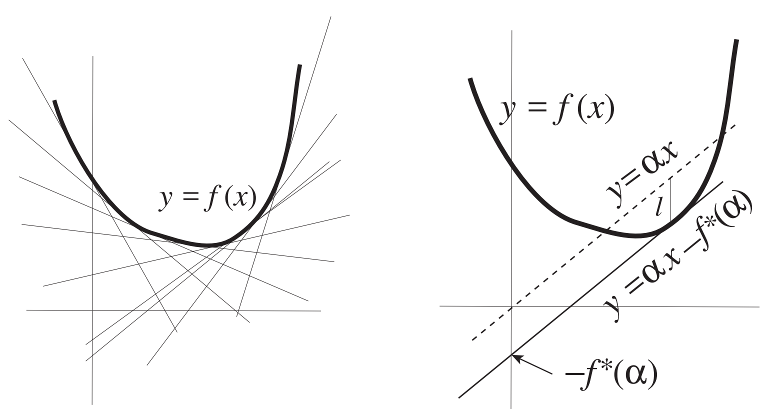


Figure 11.2: **Left**: The totality of tangent lines can recover a convex function. **Right**: l is the maximum gap between the dotted line $y = \alpha x$ and the convex curve $y = f(x)$ (we pay attention to its sign; maximum of $\alpha x - f(x)$). Therefore, if we choose $f^*(\alpha) = \max_x[\alpha x - f(x)]$, then $y = \alpha x - f^*(\alpha)$ is the tangent line in the figure. This gives a geometrical meaning of the Legendre transformation $f \to f^*$.

A line with a slope α is specified by its y-section $-f^*(\alpha)$: $y = \alpha x - f^*(\alpha)$. If this line is tangent to f, $f^*(\alpha)$ is given by the *Legendre transformation* of f (Fig. 11.2 Right):[235]

$$f^*(\alpha) = \max_x [\alpha x - f(x)]. \tag{11.22}$$

This formula is the mathematically standard definition of the Legendre transformation $f \to f^*$. Although the exposition here is for a function with one independent variable, αx may be understood as a scalar product of vector $\boldsymbol{\alpha}$ and $\boldsymbol{x}$ if f is a function of n variables $\boldsymbol{x} = (x_1, \cdots, c_n)$. Thus the general definition is

$$f^*(\boldsymbol{\alpha}) = \max_{\boldsymbol{x}} [\boldsymbol{\alpha} \cdot \boldsymbol{x} - f(\boldsymbol{x})]. \tag{11.23}$$

11.11 If f is convex, then f^* is convex, and $f^{**} = f$

The inverse Legendre transformation may be given by a symmetric procedure $f(x) = \max_\alpha[\alpha x - f^*(\alpha)]$. This can be illustrated by Fig. 11.3. This graphic demonstration uses the fact that any convex function is a primitive function of an increasing function g: $f(x) = \int^x g(x')dx'$.

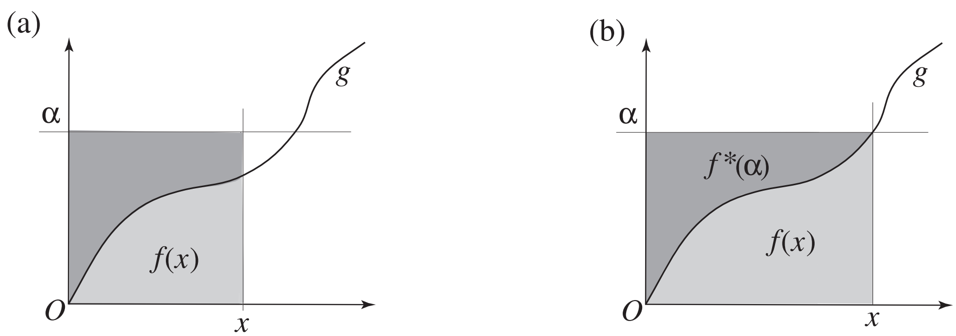


Figure 11.3: Illustration of the relation between f and f^* in 1D.

In (a) of Fig. 11.3 the pale gray area is $f(x)$. Legendre transformation maximizes the signed area $\alpha x - f(x)$, the dark gray area, by changing x, that is, the (signed) area bounded by the α-axis, the horizontal line through α, the vertical line through x, and the graph of $g(x)$. When $\alpha = g(x)$, this dark gray area becomes maximum. This is realized in (b): $f^*(\alpha) + f(x) = \alpha x$ (this equality is called *Fenchel's equality*).

From these illustrations it should be obvious that the relation between f and f^* is perfectly symmetric, so f^* is convex, and $f(x) = \max_\alpha[\alpha x - f^*(\alpha)]$, or $f^{**} = f$.

[235]'max' in such formulas are 'sup' in mathematics, but do not worry too much.

11.12 Application of Legendre transformation to thermodynamics

Thermodynamically conventional Legendre transformation tells us (recall **11.9**)

$$A = \min_S [E - TS] \tag{11.24}$$

This may be rewritten as

$$-A = \max_S [TS - E]. \tag{11.25}$$

This is a mathematically proper Legendre transformation. We know E is a convex function, so this implies that $-A$ is a convex function of T. Therefore, $f = f^{**}$ implies that

$$E = \max_S [ST - (-A)] = \max_S [ST + A]. \tag{11.26}$$

We can completely recover the thermodynamic equation of state from A.

Analogously, the Gibbs free energy **11.7** is given by

$$-G = \max_{S,V} [TS + (-P)V - E]. \tag{11.27}$$

Therefore, the inverse transformation gives

$$E = \max_{T,P} [ST - PV + G]. \tag{11.28}$$

Notice that $-P$ is the conjugate variable of V. This means $-G$ is a convex function of T and P, simultaneously.[236]

Remark E is a convex function of $S, V, X, \cdots$ (S and all the work coordinates). $-A$ is a convex function of T when other variables are fixed, and A is a convex function of work coordinates when T is fixed. However, A itself is neither convex nor concave as a function fo $T, V, X, \cdots$.

Analogously, $-G$ is convex as a function of T and P when other variables are fixed. Also G is a convex function of X (work coordinates other than V) when T and P are fixed, but G itself is usually neither convex nor concave; only when the thermodynamic space is spanned by E and V only, $-G$ is a convex function.

[236] if (Note that if $f(x)$ is a convex function, $f(-x)$ is also convex.

Q11.1 [Compression by weights]
A vertical cylinder of cross section A containing an ideal gas is equipped with a piston and is placed in a room at temperature T. Initially, on the piston is a weight of mass M (ignore the ambient pressure, or we do this experiment in the vacuum as illustrated in Fig. 11.4). Now we put another identical weight on the piston. The cylinder is rigid but does not isolate the content thermally. What is the percentage of the potential energy of the weights lost as heat, etc., to the environment?

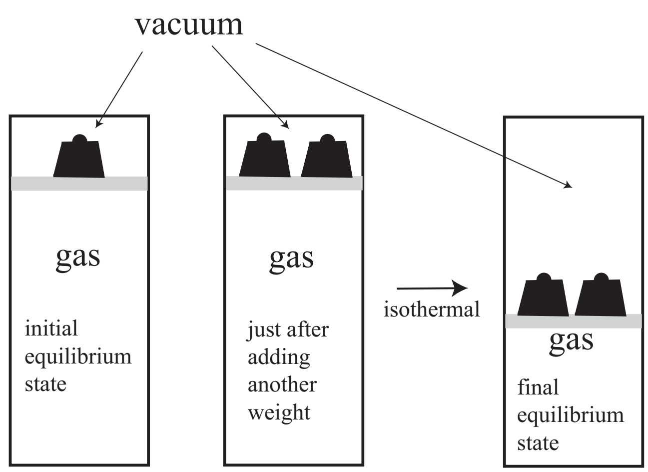


Figure 11.4: Left: the initial state; Center: just before the irreversible sinking occurs; Right: the final state.

Solution.
Let V be the initial volume. The initial pressure is $Mg/A = P$. The piston moves by $V/2A$, so $W = 2Mg(V/2A) = nRT$ is the potential energy lost from the weights between the initial and the final states. The increase of the free energy of the gas is (notice $\Delta E = 0$ for isothermal process for an ideal gas)

$$\Delta A = \Delta E - T\Delta S = -T\Delta S = -TnR\log\frac{V/2}{V} = nRT\log 2$$

Hence, $100 - 69.3 = 31\%$. We can directly obtain ΔA as well since $dA = -SdT - PdV$. T is constant, so

$$\Delta A = -\int_V^{V/2}\frac{nRT}{V}dV = nRT\log\frac{V}{V/2} = nRT\log 2. \tag{11.29}$$

A more detailed explanation is in Fig. 11.5. In this figure, A is the situation we are discussing. The work W done by the weights is the loss of their potential energy $= W = nRT$ according to our calculation above. This process is not a gentle process. Let us do this process gently by applying an appropriate force F (B in the figure). Then, the work W_{rev} (reversible work) done to the gas is the reversible work, so $\Delta A = W_{rev}$. W_{rev} is the potential energy difference $-$ the work you did through F, so clearly $W > W_{rev} = \Delta A$. Without your assistance, it is clear that the potential energy of the weights is lost as heat (and perhaps sound), and the loss should be $W - \Delta A$.

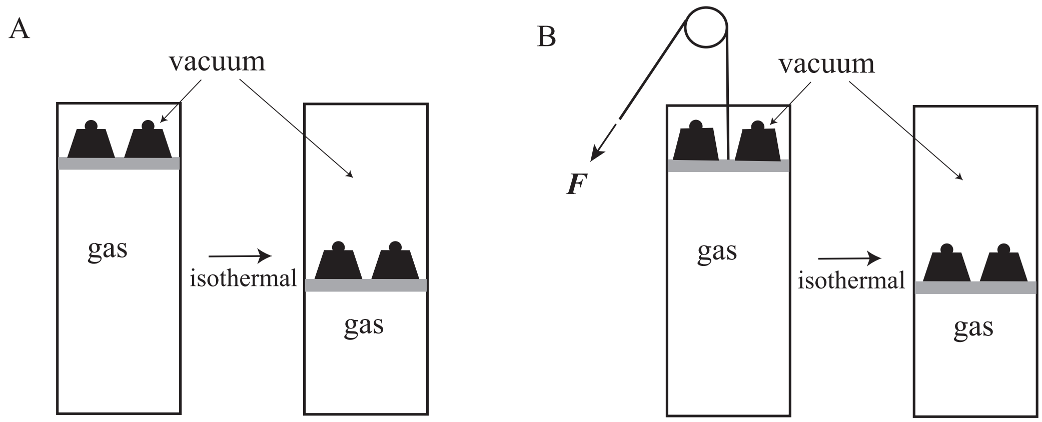


Figure 11.5: A: The actual irreversible process; Left: just after starting the dropping process; Right: the final state. B: By adjusting the force $\boldsymbol{F}$, we wish to lower the weights quasistatically

Discussion 6

We will discuss basic thermodynamics, especially entropy change due to irreversible and mixing processes.

D6.1 [Drinking bird]*
Estimate the efficiency of the 'drinking bird' toy. Assume that the room temperature is 300 K and the liquid in the bird is dichloromethane CH_2Cl_2 (boiling point is about 40 °C, density = 1.33 g/cm^3). The humidity of the room may be around 50%.

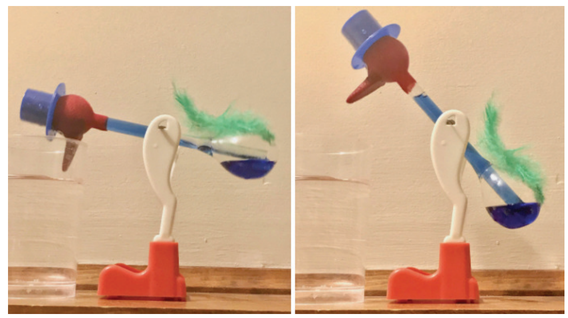


Figure 11.6: How diligent is the birdy?

Solution.
The upper limit is given by Carnot's theorem. The bird works between the room temperature $T_H = 300$ K and the temperature of the cooled head T_L, which may be 10 K lower than the room temperature. Let us assume $T_L = 290$ K.

$$\eta \simeq 1 - \frac{290}{300} = \frac{1}{30}. \tag{11.30}$$

This is probably too good for the actual bird, because the cooled liquid is mixed with the hot bottom liquid at every drinking (like the Newcomen engine). Thus, the effective heat bath temperatures are perhaps 292 - 298 K:

$$\eta = 1 - \frac{292}{298} \simeq \frac{1}{50}. \tag{11.31}$$

In any case the 'ideal' efficiency is of order 1%.

How can we actually measure it? The amount of heat going through the system may be estimated from the amount of water evaporated from the head. The work actually produced may be obtained from the volume of the dichloromethane (1.333 g/cm^3) liquid column pushed up in one cycle: 2 cm^3 for 1.5 cm per 15 sec (= period). 20 cm^3 of water ($\Delta H = 2$ J/g) is gone over 12 hrs. This seems to give about 2% (too good, perhaps). If you search a paper, there is at least one relevant, which measured 'the actual value' of 10^{-2}% (but I do not trust it very much).

D6.2 [Irreversible expansion]
A rigid cylinder is initially separated by a piston held at location P initially as in Fig. 11.7. Both the compartments contain <u>one mole</u> of identical ideal gases.

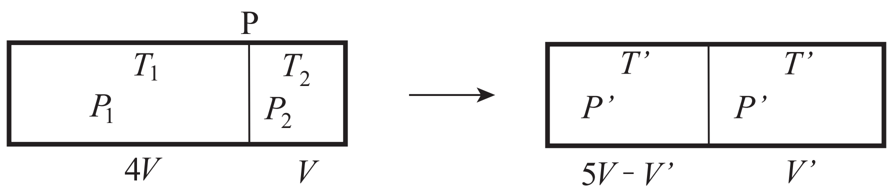


Figure 11.7: Left: the initial state; Right: the final state.

In the following no numerical calculation is required.
(1) Assume that the cylinder and the piston is diathermal, and the ambient temperature is held at T. You may assume $T_1 = T_2 = T$. The piston is suddenly allowed to move freely.

(i) What is the final state of the system (That is, what are V' and P' in terms of T)?
(ii) What is the entropy change?

Solution.
Notice that thanks to the constraint holding the piston at P, the whole system is in equilibrium (as a compound system) initially. When this constraint is removed, the system is no more in equilibrium, so no thermodynamic quantities are well defined, but eventually the system reaches a new equilibrium and all the thermodynamic quantities are again well defined. To calculate the change in any state function, you can use any path connecting the initial and the final states in the thermodynamic space.
(i) Obviously $V' = 5V/2$. Therefore,

$$V'P' = RT \tag{11.32}$$

implies

$$P' = \frac{RT}{V'} = \frac{2RT}{5V}. \tag{11.33}$$

(ii) On the left-hand side the volume is changed from $4V$ to $5V/2$, but E does not change, because there is no T change. On the right-hand side the volume is changed from V to $5V/2$.

Since entropy is a state function, we may apply

$$\Delta S = S(E_2, V_2) - S(E_1, V_1) = nC_V \log \frac{E_2}{E_1} + nR \log \frac{V_2}{V_1} \tag{11.34}$$

to each side separately. We have

$$\Delta S_{\rm L} = R\log(5/8), \quad \Delta S_{\rm R} = R\log(5/2). \tag{11.35}$$

Therefore,

$$\Delta S = \Delta S_{\rm L} + \Delta S_{\rm R} = R\log(25/16). \tag{11.36}$$

(2) Assume that the cylinder is adiabatic and the piston is diathermal. The temperatures are initially different, T_1 on the left-hand side and T_2 on the right-hand side. The piston is suddenly allowed to move freely as in (1).

(i) What is the final state of the system (That is, what are V' and P' in terms of T_1, T_2 and V)? You may assume the gas is a monatomic gas.

(ii) What is the entropy change?

(iii)* Which entropy change is larger, case (1) or case (2)? Is the answer obvious?

Solution.
(i) The initial total internal energy is ($C_V = 3R/2$)

$$E = C_V T_1 + C_V T_2. \tag{11.37}$$

Notice that this is invariant, because no work nor heat is added to or extracted from the system. Therefore, we get the final temperature T' as

$$T' = \frac{T_1 + T_2}{2}. \tag{11.38}$$

This should be obvious from symmetry.

After equilibration the pressures of the compartments are identical P'. Also the temperatures must be identical, so the volumes are both $5V/2$. Therefore,

$$(5/2)VP' = RT' \tag{11.39}$$

or

$$P' = \frac{2RT'}{5V} = \frac{R(T_1 + T_2)}{5V}. \tag{11.40}$$

(ii) The entropy change may be calculated just as in (1), but we must pay attention to the temperature change that causes the change in E.

On the left-hand side the internal energy changes from $T_1 C_V$ to $T' C_V$. Thus,

$$\frac{E_1'}{E_1} = \frac{T'}{T_1} = \frac{T_1 + T_2}{2T_1}. \tag{11.41}$$

Therefore,

$$\Delta S_{\rm L} = C_V \log\frac{T_1 + T_2}{2T_1} + R\log(5/8). \tag{11.42}$$

Analogously, we have

$$\Delta S_{\rm R} = C_V \log \frac{T_1+T_2}{2T_2} + R\log(5/2). \tag{11.43}$$

Therefore,

$$\Delta S = \Delta S_{\rm L} + \Delta S_{\rm R} = 2C_V \log \frac{T_1+T_2}{2\sqrt{T_1T_2}} + R\log(25/16). \tag{11.44}$$

(cf **10.19** for the temperature contribution to ΔS or the significance of $\sqrt{T_1T_2}$.)

(iii) ΔS for (2) is always larger than that for (1) as long as $T_1 \neq T_2$, because $(x+y)/2 \geq \sqrt{xy}$ (for nonnegative x and y; prove it.[237] It should be obvious without any calculation, since more difference is eliminated in (2) than in (1).

(3)* The same as (2) but this time the piston is also adiabatic. What can you say about the final state?

Solution.
To determine the final state, we can use the conservation of E, (11.37). Thus we have

$$T_1 + T_2 = T_1' + T_2'. \tag{11.45}$$

The final pressures must be identical on both sides. Thus,

$$P'V' = RT_1', \;\; P'(5V - V') = RT_2' \tag{11.46}$$

or

$$5VP = R(T_1+T_2). \tag{11.47}$$

Thus, P is determined, but, unfortunately, we cannot claim $V' = 5V/2$, because we cannot know T_1'. Thus, we cannot go further, thermodynamically. Thus, thermodynamically there is no definite prediction.

It is not hard to understand that the final outcome depends on the details such as how the heat generated by the friction of the piston against the cylinder wall is distributed to each compartment. That is why we cannot know the final temperatures without further information.

Important Remark
Those who did not really understand thermodynamics wrote papers to remove this 'defect' from thermal physics. You must recognize that the conclusion that there is no definite outcome is a prediction of thermodynamics; you must respect it. This uncertainty is NOT the weakness of thermodynamics; on the contrary it reinforces how powerful and reliable thermodynamics is.

[237] Using the convexity of $-\log x$ is the best as shown in Fig. 10.10).

D6.3 [Mixing two chemically distinct ideal gases][238]
(1) Assume that the system is, as a whole, adiabatic. Initially, the left-hand half (volume V) contains one mole of a monatomic ideal gas A (red) at temperature T and the right-hand half (volume V) contains two moles of monatomic ideal gas B (green) at temperature $2T$ (Fig. 11.8). After the separating wall is removed, eventually, the system reaches a new uniform equilibrium state.
(i) Find the final temperature T_F and pressure P_F.
(ii) What is the entropy increase?

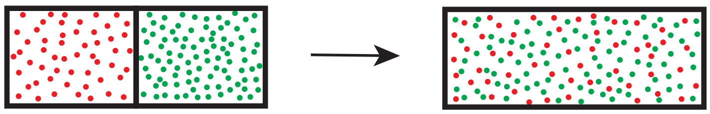


Figure 11.8: The mixing process of one + two mole distinct gases.

Solution.
(i) This is not really hard. Since the internal energy must be conserved:

$$E = C_V T + 2C_V \times 2T = 5C_V T = 3C_V T_F. \tag{11.48}$$

Thus, the final temperature is $T_F = (5/3)T$. As to the pressure, mixture or not does not matter; what matters is the total number of particles. Thus the final pressure must satisfy

$$P_F(2V) = 3RT_F = 5RT. \tag{11.49}$$

That is, $P_F = 5RT/2V$.
(ii) To find the entropy change we must find a quasistatic process that can connect the intial and the final states. Thus, we invent a process illustrated in Fig. 11.9:

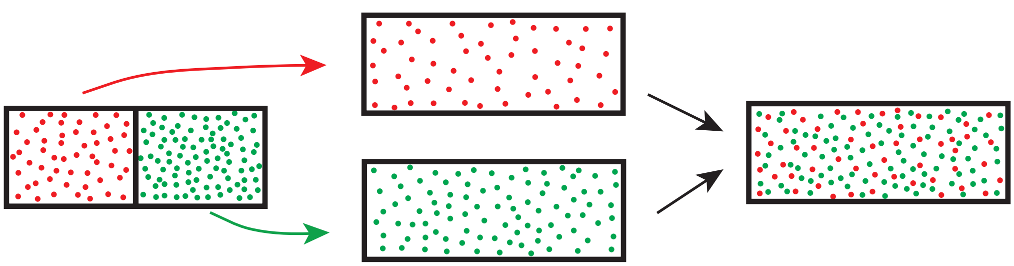


Figure 11.9: The mixing process may be considered as two expansions and subsequent superposition of the expanded gases; the last superposition step does not cause any thermodynamic change, because these gas particles do not interact. Entropy changes only along the colored arrows. The 'intermediate' states these arrows reach must have the final temperature T_F

Superposition of the end states of the colored arrows is adiabatic and reversible, so

[238] See the figure posted as a supplement to Lect 12 associated with the examples discussed in the lecture.

there is no entropy change along the black arrows. All the changes are along the colored arrows.

For the red arrow the volume of the red gas is changed from V to $2V$ and the temperature T to $T_F = 5T/3$, that is, the internal energy is from $C_V T$ to $5C_V T/3$. Therefore,

$$\Delta S_{\text{red}} = C_V \log \frac{5}{3} + R \log 2. \tag{11.50}$$

For the green arrow the volume of the green gas is changed from V to $2V$ and the temperature $2T$ to $5T/3$, that is, the internal energy is from $4C_V T$ to $10C_V T/3$ (2 moles!). Therefore,

$$\Delta S_{\text{green}} = 2C_V \log \frac{5}{6} + 2R \log 2. \tag{11.51}$$

Therefore, the total entropy change is

$$\Delta S = C_V \log \frac{125}{108} + R \log 8. \tag{11.52}$$

(2) Suppose the two gasses are indistinguishable. What is ΔS?

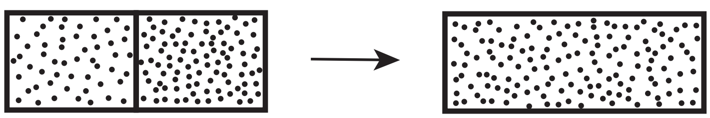


Figure 11.10: Indistinguishable gases are joined.

That is, on the left-hand side is 1 mole and the right 2 moles of identical gases. Although the volumes are identical (V), initially, the right-hand side has temperature $2T$ and the left T. The membrane is broken and eventually the system reaches a uniform equilibrium state. Assume that the system is, as a whole, adiabatic. What is ΔS?

($*$) Can you understand the difference in ΔS for (1) and (2) intuitively?

Solution.
To find the final state T and P, there is no difference from (1): Since the internal energy must be conserved:

$$E = C_V T + 2C_V \times 2T = 5C_V T = 3C_V T_F. \tag{11.53}$$

Thus, $T_F = (5/3)T$. The final pressure must satisfy

$$P_F(2V) = 3RT_F = 5RT. \tag{11.54}$$

That is, $P_F = 5RT/2V$.

(ii) To find the entropy change we must find a quasistatic process that can connect the intial and the final states. Thus, we invent a process illustrated in Fig. 11.11:

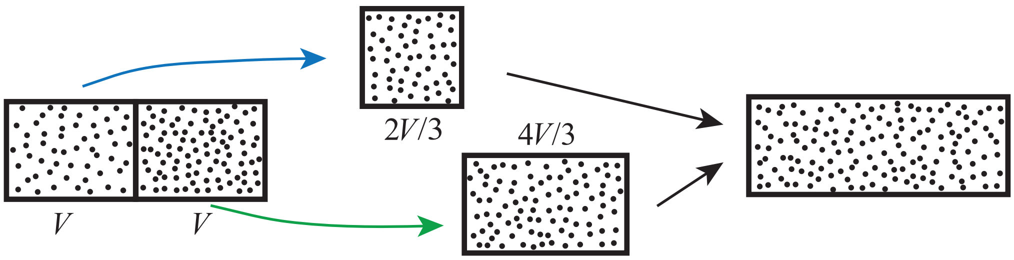


Figure 11.11: From each side we prepare the state with temperature T_F and pressure P_F with the same number densities. The last joining step does not cause any thermodynamic change.

After the processes denoted by the color arrows we prepare the gases with the same temperatures T_F and pressures P_F. The mole ratio is 1:2, so the volume ratio of the final states is also 1:2. Then, we join these two. At this final step there is no entropy change, so we have only to compute the entropy change along the colored arrows.

For the left-hand side along the blue arrow the volume changes from V to $2V/3$, and the temperature changes from T to $T_F = 5T/3$. Therefore,

$$\Delta S_{\mathrm{L}} = C_V \log \frac{5}{3} + R \log \frac{2}{3}. \tag{11.55}$$

For the right-hand side along the green arrow the volume changes from V to $4V/3$, and the temperature changes from $2T$ to $T_F = 5T/3$. Therefore, (there are 2 moles!)

$$\Delta S_{\mathrm{R}} = 2C_V \log \frac{5}{6} + 2R \log \frac{4}{3}. \tag{11.56}$$

Therefore,

$$\Delta S = C_V \log \frac{125}{108} + R \log \frac{32}{27}. \tag{11.57}$$

As you see the energetic contribution is the same as before (since energy is 'color-blind'). The entropy difference is

$$\Delta S_{\mathrm{mix}} - \Delta S_{\mathrm{pure}} = R \log \frac{8 \times 27}{32} = R \log \frac{27}{4}. \tag{11.58}$$

Can we understand this intuitively? Yes. The difference is just the mixing entropy we can understand information theoretically: do not forget there are 3 moles of particles.

$$\Delta S_{\mathrm{inf}} = -3R \times \left(\frac{1}{3} \log \frac{1}{3} + \frac{2}{3} \log \frac{2}{3} \right) = -R \log \frac{1}{3} - 2R \log \frac{2}{3} = R \log \frac{27}{4}. \tag{11.59}$$

D6.4 [Mixing and irreversibility]
Suppose mixing process is reversible. Then, show that we can violate Thomson's principle (i.e., we can do work with a single heat source).

Solution.
Through isothermally expanding the red and green gases separately (cf. the solution to **D6.3**), we can take out work from each process. Now we merge (superpose) the two gases reversibly without any work nor exchange of heat. Then, we can reversibly and adiabatically demix the mixture to go back to the original state. Thus, cyclically the heat taken from a uniform-temperature environment can be converted to work, violating Thomson.

[Comment] The question is often asked in the following manner: Suppose there is no increase of entropy due to mixing. $\cdots$. Unfortunately thermodynamics cannot tell us whether this process with $\Delta S = 0$ can be actually performed or not, so strictly speaking we cannot say anything conclusive. I must hastily add, however, that according to our experience, we can always ingenuously devise such a process. "All the thermodynamically allowed processes are realizable" is, strictly speaking, an extra principle.

D6.5 [Equation of state and entropy]
As we have learned, thermodynamics cannot give you any 'concrete information' (e.g., equations of state) for any system. These must be obtained experimentally or by microscopic modeling with the aid of statistical mechanics. Still, after determining the thermodynamic equation of state such as entropy as a function of thermodynamic coordinates, we can know every macroscopic thermal properties of the system. This is the reason why thermodynamics is emphasized in practice.

(1) For one mole of pure substance the following two relations have been empirically obtained:

$$T = cE^{2/3}/V^{1/2}, \tag{11.60}$$
$$P \propto E/V, \tag{11.61}$$

where c is a positive constant.
(i) Write down the corresponding equations for N moles of the same substance.
(ii) Find the entropy as a function of the thermodynamic coordinates E, V, N and c.

Solution.
(i) Thermodynamic variables are extensive or intensive (the fourth law **9.14**), so E

in the above equation is actually E/N, and V V/N. Therefore,

$$\begin{aligned} T &= c(E/N)^{2/3}/(V/N)^{1/2} = cE^{2/3}/V^{1/2}N^{1/6}, \quad (11.62) \\ P &= aE/V, \quad (11.63) \end{aligned}$$

where we write the proportionality relation as an equality with a multiplicative constant a, which we must fix eventually. Notice that T is indeed intensive (check this by doubling the system size).
(ii) The Gibbs relation for entropy reads

$$dS = \frac{1}{T}dE + \frac{P}{T}dV. \quad (11.64)$$

Therefore,

$$dS = \frac{V^{1/2}N^{1/6}}{cE^{2/3}}dE + \frac{aE^{1/3}N^{1/6}}{cV^{1/2}}dV = \frac{1}{c}V^{1/2}N^{1/6}E^{-2/3}dE + \frac{a}{c}E^{1/3}N^{1/6}V^{-1/2}dV. \quad (11.65)$$

Let us integrate this from (E_0, V_0) to (E, V). Since dS is exact, we can choose any integration path. Let us use $(E_0, V_0) \to (E, V_0) \to (E, V)$:

$$S(E,V) - S(E_0, V_0) = \frac{3}{c}V_0^{1/2}N^{1/6}(E^{1/3} - E_0^{1/3}) + \frac{2a}{c}E^{1/3}N^{1/6}(V^{1/2} - V_0^{1/2}) \quad (11.66)$$

The result should not depend on the mid point location (E, V_0). This implies that $2a = 3$. Thus,

$$S(E,V) - S(E_0, V_0) = \frac{3}{c}(E^{1/3}N^{1/6}V^{1/2} - V_0^{1/2}N^{1/6}E_0^{1/3}). \quad (11.67)$$

a may be determined before integration from the closedness of dS as well:

$$\frac{1}{2c}V^{-1/2}N^{1/6}E^{-2/3} = \frac{a}{3c}E^{-2/3}N^{1/6}V^{-1/2}. \quad (11.68)$$

D6.6 [Intuitive meaning of entropy: information preview].
The amount of information you can get from the answer to a YES-NO question for which you cannot guess the answer at all ('even' yes-no question) is 1 bit.[239]

If a system changes from state A to B and if we need an answer to one extra (even) yes-no question to specify the state of a molecule in system state B (say, gas phase) as accurately as in A (say, liquid phase), we say $S_{\rm B} - S_{\rm A} = R\log 2$ per 1 mole of molecules ($R = 8.314$ J/K·mol). That is, 1 bit/molecule $\Longleftrightarrow$ 5.8 J/K·mol

[239]In other words, the maximum information you can get from a single yes-no question is one bit.

or 0.17 bit/molecule $\Longleftrightarrow$ 1 J/K·mol.

The boiling temperature of acetic acid under 1 atm is 391 K, and the evaporation heat (= latent heat of evaporation) is about 23.7 kJ/mol.
(1) What is the entropy increase due to evaporation?
(2) Roughly, how many yes-no questions do you have to ask to specify the (single) molecular state in the gas phase as accurately as in the liquid phase?
(3)* The evaporation entropy of ethanol is about 110 J/K·mol. You should have realized a big difference between this value and the value you obtained in (1). This is said to be due to dimerization: acetic acid gas (around the boiling point) consists of dimers $(CH_3COOH)_2$ (due to strong hydrogen bonding, but ethanol does not make dimers in the gas phase).[240] Is the entropy difference roughly consistent with this explanation (or not)? Give your opinion with your supporting argument.

Soln.
(1) The entropy change due to evaporation is $\Delta S = 23700/391 = 60.6$ J/K·mol.
(2) This corresponds to $60.6 \times 0.17 = 10.3$ bits/molecule. That is, we need about 10 Yes-No questions to determine the state of each molecule as precisely as we can do so in the liquid phase. The volume of the gas (under the condition we are interested in) is about 200 times as large as that of the liquid.[241] This explains about 7 to 8 bits. Not very bad.
(3) Ethanol evaporation corresponds to almost 19 bits/molecule increase of entropy, so we may say that the number of questions required for ethanol is almost doubled. If we assume that roughly two molecules behave together, then the knowledge about one molecule tells us about one more molecule, so this is reasonable.

[240] Precisely speaking, there are also tetramers, and the average acetic acid molecules in a single gas particle seems about $105/60 \simeq 1.75$.
[241] According to a very crude estimate, 1 mole of acetic acid just above its boiling point occupies about 10 l, which is about 170 times as large as the liquid volume.

Exercise 6

E6.1 [Heat pump]
We could import heat from the external world (outdoors) into a room to warm it up. The set up of the analysis is always the same, Fig. 11.12:

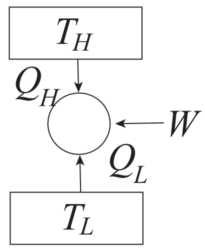


Figure 11.12: Heat pump operation requires: $Q_L > 0$, $W > 0$ and $Q_H < 0$.

W is what we invest, and $|Q_H|$ is our gain, so $|Q_H|/W$ is called the coefficient of performance. If the room temperature $T_H = 298$ K and the low-temperature heat source is the $T_L = 288$ K underground device, what is the limit of the coefficient of performance?

Solution.
For one cycle the total energy input to the heat pump must be zero:

$$Q_H + Q_L + W = 0. \tag{11.69}$$

For a single cycle the entropy increase of the device must be zero, so with the aid of Clausius' inequality ($\Delta S \geq Q/T$, **10.7**), we have

$$\frac{Q_H}{T_H} + \frac{Q_L}{T_L} \leq 0. \tag{11.70}$$

Thus,

$$\frac{Q_H}{T_H} + \frac{-W - Q_H}{T_L} \leq 0 \tag{11.71}$$

or

$$Q_H \left(\frac{1}{T_H} - \frac{1}{T_L} \right) = |Q_H| \left(\frac{1}{T_L} - \frac{1}{T_H} \right) \leq \frac{W}{T_L}. \tag{11.72}$$

Therefore, the coefficient of performance is

$$\frac{|Q_H|}{W} \leq \frac{1}{T_L} \bigg/ \left(\frac{1}{T_L} - \frac{1}{T_H} \right) = \frac{T_H}{T_H - T_L}. \tag{11.73}$$

For our case this is 298/10, about 30, a tremendous gain.

E6.2 [Explosion in a cylinder with a piston]
Inside a thermally insulated (i.e., adiabatic) empty (i.e., vacuum) cylinder of volume $10V$ is a small can of volume V containing one mole of an ideal gas at temperature $15T$. The one wall of the cylinder can move outward, if the internal pressure is higher than the external one which is $P_{\rm ex} = RT/V$. The can is punctured and the gas escapes and eventually reaches a new equilibrium state (see Fig. 11.13).

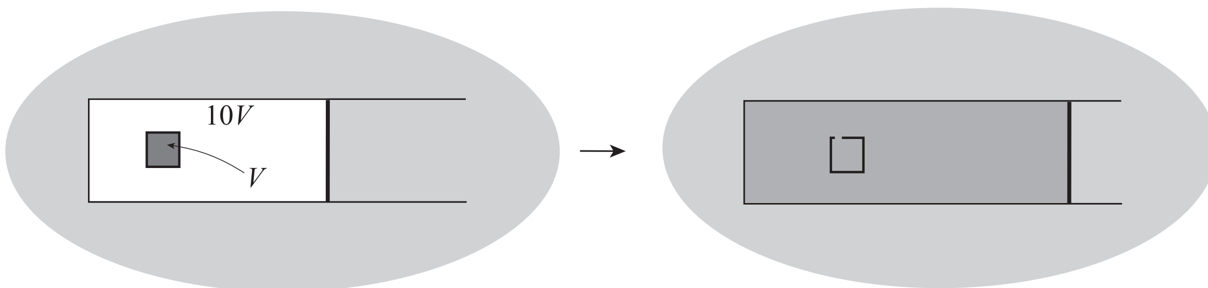


Figure 11.13: Initially, the can is filled with a gas (Left) and is inside a vacuum box of volume $10V$. Then, it is punctured and the gas escapes to reach the final equilibrium state (Right).

(1) Find the final temperature T_F and the volume V_F of the gas in the cylinder.
(2) What is the total entropy change due to puncturing the can?

Solution.
(1) The initial internal energy is $E = 15C_VT$. Let V_F be the final volume of the gas. Then, $V_F - 10V$ is the volume of the displaced external gas. This requires the system to do work: $|W| = P_{ex}(V_F - 10V)$, so the final internal energy of the gas in the cylinder is

$$E - P_{ex}(V_F - 10V). \tag{11.74}$$

Thus the final temperature of the gas is

$$T_F = (E - P_{ex}(V_F - 10V))/C_V = 15T - \frac{2}{3}T(V_F/V - 10). \tag{11.75}$$

Since the equation of state implies that

$$P_{ex}V_F = RT_F \;\Rightarrow\; \frac{V_F}{V} = \frac{T_F}{T}, \tag{11.76}$$

we get

$$T\frac{V_F}{V} = 15T - \frac{2}{3}T(V_F/V - 10). \tag{11.77}$$

That is,

$$\frac{5}{3}\frac{V_F}{V} = 15 + \frac{20}{3} = \frac{65}{3} \tag{11.78}$$

or

$$\frac{V_F}{V} = \frac{65}{5} = 13. \tag{11.79}$$

Therefore,

$$T_F = \frac{P_{ex}V_F}{R} = \frac{RTV_F}{RV} = 13T. \tag{11.80}$$

Or,

$$T_F = 15T - \frac{2}{3}T\,(13 - 10) = 13T, \tag{11.81}$$

consistent.

(2) We may use the equation of state $S = S(E, V)$. Thus,

$$\Delta S = C_V \log \frac{13}{15} + R \log 13. \tag{11.82}$$

E6.3. [General ideal gas]
Experimentally, the internal energy of a gas is volume-independent under constant temperature, and PV is a function of T only, say $PV = \phi(T)$. Show that $\phi(T) \propto T$. You may use the following Maxwell's relation

$$\left.\frac{\partial S}{\partial V}\right|_T = \left.\frac{\partial P}{\partial T}\right|_V, \tag{11.83}$$

which we will show in a month.[242]

Solution.
The first law tells us

$$dE = TdS - PdV. \tag{11.84}$$

It is said that the internal energy of a gas is volume-independent under constant temperature:

$$\left.\frac{\partial E}{\partial V}\right|_T = 0. \tag{11.85}$$

Thus, (11.84) implies

$$0 = T\left.\frac{\partial S}{\partial V}\right|_T - P = T\left.\frac{\partial P}{\partial T}\right|_V - P. \tag{11.86}$$

[242] You will understand (in Section 17) the following simple algebra:

$$\left.\frac{\partial S}{\partial V}\right|_T = \frac{\partial(S,T)}{\partial(V,T)} = \frac{\partial(S,T)}{\partial(V,P)}\frac{\partial(V,P)}{\partial(V,T)} = \frac{\partial(V,P)}{\partial(V,T)} = \left.\frac{\partial P}{\partial T}\right|_V.$$

$PV = \phi(T)$ implies

$$V \left.\frac{\partial P}{\partial T}\right|_V = \phi'(T). \tag{11.87}$$

Therefore, multiplying V to (11.86) gives us

$$T\phi'(T) = \phi(T) \;\Rightarrow\; d\phi/\phi = dT/T. \tag{11.88}$$

That is, $\phi \propto T$.

E6.4 [Mixing diatomic and monatomic gases]
Assume that the system is, as a whole, adiabatic. Initially, the left-hand half (volume V) contains <u>one mole</u> of a monatomic ideal gas A (red) ($C_V = 3R/2$) at temperature T and the right-hand half (volume V) contains <u>one mole</u> of diatomic ideal gas B (green) ($C_V = 5R/2$) at temperature $2T$. After the separating wall is removed, eventually, the system reaches a new uniform equilibrium state as illustrated in Fig. 11.14.

(1) Find the final temperature T_F and pressure P_F.
(2) What is the entropy increase? You need not get the numerical answer but may keep R as a symbol.

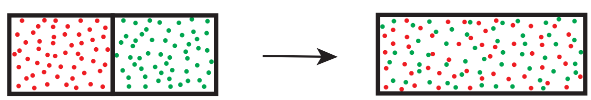


Figure 11.14: The mixing process.

Solution.
(1) Since the internal energy must be conserved:

$$E = \frac{3}{2}RT + \frac{5}{2}R \times 2T = \frac{13}{2}RT = \left(\frac{3}{2}R + \frac{5}{2}R\right) T_F = 4RT_F. \tag{11.89}$$

Thus, $T_F = (13/8)T$. As to the pressure, mixture or not does not matter; what matters is the total number of particles; there are two moles. Thus the final pressure must satisfy

$$P_F(2V) = 2RT_F = \frac{13}{4}RT. \tag{11.90}$$

That is, $P_F = 13RT/8V$.

(2) To find the entropy change we must find a quasistatic process that can connect the initial and the final states. Thus, we invent a process illustrated in Fig. 11.15 (as usual!).

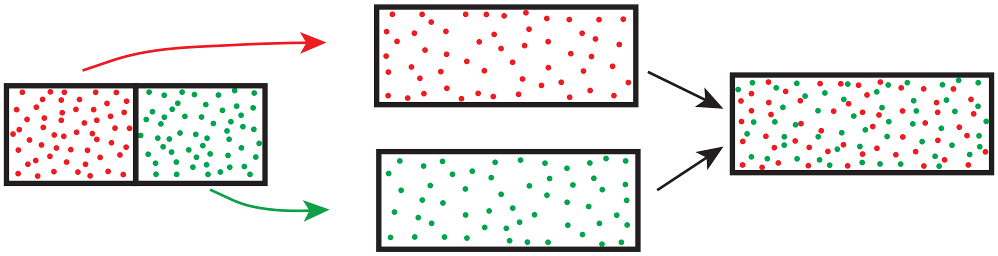


Figure 11.15: The mixing process may be considered as two expansions and subsequent superposition of the expanded gases; the last superposition step does not cause any thermodynamic change, because these gas particles do not interact. Entropy changes only during expansion processes. The expanded states must have the final temperature T_F

Superposition of the expanded states is adiabatic and reversible, so there is no entropy change in the final step. All the changes are during expansions.

For the red arrow the volume of the red gas is changed from V to $2V$ and the temperature T to $T_F = 13T/8$, that is, the internal energy is from $(3/2)RT$ to $(3/2)R \times 13T/8$. Therefore,

$$\Delta S_{\mathrm{red}} = \frac{3}{2} R \log \frac{13}{8} + R \log 2. \tag{11.91}$$

For the green arrow the volume of the green gas is changed from V to $2V$ and the temperature $2T$ to $13T/8$, that is, the internal energy is from $(5/2)R(2T)$ to $(5/2)R \times 13T/8$. Therefore,

$$\Delta S_{\mathrm{green}} = \frac{5}{2} R \log \frac{13}{16} + R \log 2. \tag{11.92}$$

The total entropy change is thus

$$\Delta S = \frac{3}{2} R \log \frac{13}{8} + \frac{5}{2} R \log \frac{13}{16} + R \log 4. \tag{11.93}$$

12 Introduction to statistical mechanics

Summary
$*$ If we have a translation table between mechanical and thermodynamic quantities, we can calculate thermodynamic quantities with the aid of mechanics.
$*$ The table must include not only mechanical (i.e., thermodynamic coordinates) but thermal quantities. The latter is supplied by Boltzmann's principle: $S = k_B \log w(E, X)$.
$*$ With very natural observations as to thermodynamics and mechanics, we can understand this principle from $dS = d'Q/T$ [as Einstein did].

Key words
phase space, microstate (classical and quantum), microcanonical ensemble, microcanonical partition function, Boltzmann's principle

What you should be able to do
$*$ Tell what thermodynamics can and cannot do.
$*$ Clearly explain the meaning of the quantities appearing in Boltzmann's principle.
$*$ Be able to use Boltzmann's principle for simple examples.
$*$ Explain why the conventional justification of statistical mechanics in terms of ergodic theory is totally absurd.

12.1 Power and limitation of thermodynamics
We have learned rudiments of thermodynamics. As you have realized, thermodynamics is very powerful when right inputs are introduced, but it cannot tell you anything specific to a particular system. For example, the equation of state or the functional form of $S = S(E, V)$ cannot be supplied by thermodynamics; when we computed this, even for an ideal gas, we relied on $E = C_V T$ and $PV = RT$, neither of which is thermodynamically obtained.

You must clearly know what thermodynamics can do and what not. Thermodynamics can compute the changes of state functions (state variables) between two equilibrium states irrespective of the actual processes that have happened, IF the equation of state of the system is known. Thermodynamics cannot calculate materials-specific (or system-specific) properties, which must be supplied extra-thermodynamically.

12.2 Why statistical mechanics?

We believe that the microscopic world underlies the world we experience daily (= the macroscopic world), and their descriptions in terms of mechanics is much more detailed than what the macroscopic phenomenology can offer. Then, we can have hope that looking at the microscopic details, we may be able to obtain the information thermodynamics needs but cannot provide.

Since the microscopic world is described by mechanics governing numerous particles, we should try to compute thermodynamic quantities in terms of mechanics. To describe a macrosystem in terms of particle mechanics, we must expect that we need numerous variables far more than the dimension of the thermodynamic space (recall scooping out water on the earth by a tablespoon!). Thus, it is a natural guess that we need some statistical means: *statistical mechanics*.

12.3 What do we really need?

However, as is emphasized repeatedly, the macroscopic world is the world governed by the law of large numbers, so if you know how to get the expectation values, we do not need statistics explicitly. We need only the *translation table* of thermodynamic quantities in terms of mechanical quantities.

We have learned that the most fundamental description of any equilibrium state is in terms of thermodynamic coordinates (E, X), where E is the internal energy and X (collectively) are the work coordinates. We know E is the system mechanical energy. X may be the volume V, magnetization M, etc., and can be described in terms of microscopic mechanical variables easily and/or naturally; we only need their expectation values (no distribution needed). Thus, we can write down the translation table for thermodynamic coordinates relatively easily.

12.4 Boltzmann's principle

However, thermodynamics is 'thermo'dynamics. Indeed, we have learned that entropy $S = S(E, X)$ is the fundamental quantity we need in order to use thermodynamics. Therefore, the translation table must include S.

The translation table was completed by Boltzmann in the following form, the *Boltzmann principle*:[243]

$$S = k_B \log w(E, X), \tag{12.1}$$

where k_B is the Boltzmann constant (see **D3.3**), and $w(E, X)$ is the 'number' of 'microscopic states (= microstates)' compatible with the macrostate (E, X) (hence-

[243]Some authors define entropy by this formula. However, S is thermodynamically defined, and we know how to measure ΔS (entropy change). The definition of entropy not referring to thermodynamics is empty as a physical concept, because we cannot measure it. The correctness of the translation table is only guaranteed by the fact the it gives correct thermodynamics.

forth, the same symbol $w(E, X)$ will be used to denote the collection of microstates compatible with (E, X) as well). To understand this statement precisely, we must clarify what 'microstate' means.[244]

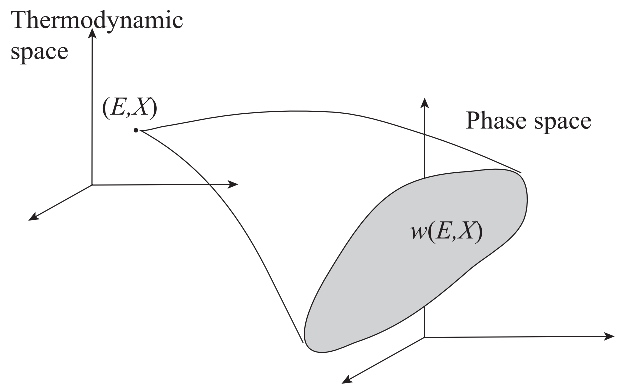


Figure 12.1: For each equilibrium state (E, X) in the thermodynamic space, we can imagine a subset $w(E, X)$ of the phase space consisting of microstates that give the same thermodynamic coordinates.

12.5 Classical microstates

Classical-mechanically,[245] the most detailed description of a system is in terms of a set of the canonical variables. The most popular canonical variables are the position and momentum vectors. For an N-point-mass system, the $6N$-dimensional vector $(\boldsymbol{r}_1, \cdots, \boldsymbol{r}_N, \boldsymbol{p}_1, \cdots, \boldsymbol{p}_N)$, where $\boldsymbol{r}_i$ is the position vector of the ith particle and $\boldsymbol{p}_i$ the momentum vector of the ith particle, gives the ultimately detailed description of the system. The space spanned by these $6N$ coordinates (the totality of these $6N$-dimensional vectors) is called the *phase space* of the system, and a point in this space is classically the elementary event = microstate.

12.6 Quantum microstates

Quantum-mechanically,[246] an elementary state is (roughly speaking) a state ket, but physically $|\cdot\rangle$ and $c|\cdot\rangle$ for any complex number c are indistinguishable, so actually, an elementary state is a *ray* (= 1D subspace spanned by a ket). We may take a convenient orthonormal basis of the vector space spanned by all the state kets and

[244] You may understand that a 'microstate' corresponds to an 'elementary event' in probability.

[245] The Feynman Lectures I is a good classical mechanics introduction. Then, read the first volume of the Landau-Lifshitz series.

[246] The Feynman lectures III is a good quantum mechanics introduction. However, if you wish to finish the rudiments as quickly as possible, read Griffiths. At a more leisurely pace, if you are interested in a more historical development, see the beginning part (Part I) of my lecture notes `https://www.dropbox.com/home/IntroQM/contents_files`.

interpret any vector in this basis set as a microstate. In particular, normalized eigenkets of the system Hamiltonian may be interpreted as microstates.[247]

12.7 How to obtain microcanonical partition function

Thus, to obtain $w(E, X)$, for classical cases, we calculate the volume of the subset of the phase space compatible with the thermodynamic coordinates (E, X). Recall that for any phase point we can compute (E, X) (at least in principle). If the computed E' and X' nearly agree with (that is, are macroscopically indistinguishable from) the thermodynamic coordinates of a macrostate (E, X), we say that the microstate is compatible with this macrostate (see Fig. 12.1). Thus, we can find the subset $w(E, X)$ of the phase space consisting of such microstates.

Quantum-mechanically, we make observables corresponding to E (that is, the system Hamiltonian) and X (we may write such an operator as $\hat{X}$), and then collect eigenkets $|\cdot\rangle$ of the Hamiltonian whose eigenvalues are close to E and also $\langle\cdot|\hat{X}|\cdot\rangle \simeq X$.

The set $w(E, X)$ is called a *microcanonical ensemble*, and the numerical value $w(E, X)$ (phase volume or number of states) is called a *microcanonical partition function*.

12.8 Statistical Mechanics is completed!

We have completely specified the statistical mechanical rule to compute thermodynamics. The rest is taken care of by the Gibbs relation

$$dS = \frac{1}{T}dE + \frac{P}{T}dV - \frac{\mu}{T}dN - \frac{x}{T}dX + \cdots. \tag{12.2}$$

In practice, use statistical mechanics sparingly, and use thermodynamics whenever you can.

Of course, there are two problems remaining: How to use Boltzmann's principle and how to understand the principle. First, let us use the principle a bit.

12.9 Let us study an ideal gas (classically)

We can use the completed translation table to compute S from mechanics. Let us study a classical ideal gas. It consists of N non-interacting mass points of mass m

[247] Any unitary transformation of the basis set is again a basis set, so in quantum mechanics the choice of the microstates is not unique. The situation is not different for classical cases; we may apply any canonical transformation to the phase space coordinates.

in a volume V. The system Hamiltonian is the pure kinetic energy:

$$H = \sum_i \frac{\boldsymbol{p}_i^2}{2m}. \tag{12.3}$$

Precisely speaking, $w(E, V)$ collects all the microstates in the volume V with energy in $(E - \Delta E, E]$, where ΔE is a (macroscopically small) leeway. What we should do first is to formally write down $w(E, V)$.

$$w(E, V) = \int_{\boldsymbol{r}_i \in V,\, E-\Delta E < \sum \boldsymbol{p}_i^2/2m \le E} d\Gamma, \tag{12.4}$$

where $d\Gamma = d\boldsymbol{r}_1 \cdots d\boldsymbol{r}_N d\boldsymbol{p}_1 \cdots d\boldsymbol{p}_N$ is the volume element of the $6N$-dimensional phase space. The space and momentum integrals can be totally decoupled, so

$$\begin{aligned} w(E, V) &= \int_{\boldsymbol{r}_i \in V,\, \sum \boldsymbol{p}_i^2/2m \in (E-\Delta E, E]} d\Gamma & (12.5)\\ &= \int_V d\boldsymbol{r}_1 \cdots \int_V d\boldsymbol{r}_N \int_{\sum \boldsymbol{p}_i^2/2m \in (E-\Delta E, E]} d\boldsymbol{p}_1 \cdots d\boldsymbol{p}_N & (12.6)\\ &= V^N \int_{\sum \boldsymbol{p}_i^2/2m \in (E-\Delta E, E]} d\boldsymbol{p}_1 \cdots d\boldsymbol{p}_N. & (12.7) \end{aligned}$$

The last integral is the volume of the skin of thickness $\propto \Delta E$ of a $3N$ dimensional ball ($3N - 1$-sphere[248]) of radius $\sqrt{2mE}$, which must be proportional to $E^{(3N-1)/2}(\sqrt{E + \Delta E} - \sqrt{E}) \propto E^{3N/2-1}\Delta E$,[249] so

$$w(E, V) \propto V^N E^{3N/2} \Delta E. \tag{12.8}$$

Here, $N \gg 1$, so 1 is ignored. Therefore, Boltzmann tells us that

$$S = k_B \log w(E, V) = N k_B \log V + \frac{3}{2} N k_B \log E + k_B \log \Delta E + \cdots, \tag{12.9}$$

where the remaining terms are $N\times$ a constant.[250] Using thermodynamic relations,

$$\frac{1}{T} = \left.\frac{\partial S}{\partial E}\right|_V = \frac{3}{2}\frac{N k_B}{E} \tag{12.10}$$

or $E = (3/2) N k_B T$. Also

$$\frac{P}{T} = \left.\frac{\partial S}{\partial V}\right|_E = \frac{N k_B}{V}, \tag{12.11}$$

[248] Notice that in mathematics, 1-sphere is the edge of a disk, 2-sphere is the skin of a 3D ball (= the ordinary sphere), etc.

[249] Dimensional analysis can give you this answer as well.

[250] By the way, ΔE can be pretty much anything, if not too small (as $\Delta E = O[E/e^{\alpha N}]$ for some $a > 0$).

which is the equation of state. It works!

Incidentally, (12.9) does not satisfy the fourth law **9.14**: if you double extensive quantities (experimentally, we have only to join two identical systems to make a compound system): $N \to 2N$, $E \to 2E$, $V \to 2V$, then we must also have $S \to 2S$, but this does not hold. When you use statistical mechanics, a wise practice is to make a shortcut with the aid of thermodynamics. We demand that the fourth law holds. Then, we are forced to accept the following form:

$$S = k_B \log w = N k_B \log \frac{V}{N} + \frac{3}{2} N k_B \log \frac{E}{N} + k_B \log \Delta E + \cdots . \tag{12.12}$$

This corresponds to replacing w with $w/N!$. Boltzmann also noted in his original paper that the latter choice is convenient, because the extensivity of entropy is satisfied. We will come back to this problem in Section 14.

12.10 Basis of Boltzmann's formula: key observations

Boltzmann's formula works, so don't ask any question and get good grades and publish papers. Wise professors may well preach like this. Well, science should not tolerate incantations. Every black box must be opened.

Let us go to a derivation(!) of Boltzmann's principle starting from empirical facts and some general observations about mechanics. Since we are physicists, and not metaphysicists, let us be as empirical as possible.

The facts we wish to rely on are:
[O] If we (in a constant environment thermally) isolate a system, it will eventually arrive at a system that does not depend on time macroscopically (actually this must be the main part of the zeroth law).
[X] The needed observation time for thermodynamic coordinates is very short (say, 1 μs or much less if the system is large enough).

A general picture of microscopic dynamics is that the instantaneous microstate wanders around the phase space; in particular, if the macrostate is in (E, X), it wanders around in $w(E, X)$. Traditionally, 'statistics' of 'statistical mechanics' was understood as taking statistics over all the microstates in $w(E, X)$. Consequently, a misconception was spread that the key to statistical mechanics was the even mechanical sampling over $w(E, X)$ (the ergodic theoretical justification of statistical mechanics).

For the ordinary macro object containing $N \sim 10^{23}$ particles, what is the time scale required to sample w evenly? It is roughly the time scale of the Poincaré cycle $\sim e^N$.[251] [X] implies that during one thermodynamic observation, only an extremely tiny fraction of w is sampled. However, [O] implies that if you repeat this experiment

[251] The time scale of the Poincaré cycle is roughly the time scale required for a given closed

after 1 billion years later, we get the same thermodynamic result. A 1 μs observation in 10^9 CE will cover again only very tiny portion of w (Fig. 12.2).

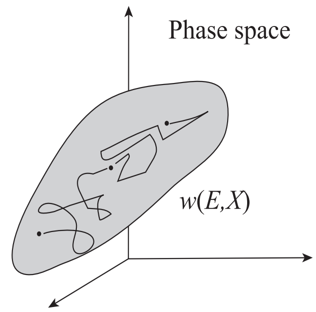


Figure 12.2: Repeating thermodynamic observation samples extremely tiny subsets (black dots) of w, but they all give the same thermodynamic results.

What is the most natural conclusion? Suppose we prepare an isolated macrosystem reaching an equilibrium state (E, X). Since it is isolated, we may interpret it as a mechanical system as well. If you sample a microstate (mechanically instantaneous state), and compute the thermodynamic coordinates, almost surely they agree with (E, X) and give the correct thermodynamic relation. That is, if you wish to know thermodynamics, you have only to sample a single microstate; *almost every microstate gives the same thermodynamics. This is the secret of equilibrium statistical mechanics.*

Remark As we will learn later (Section 14) the identical particles are indistinguishable, so the two phase points that are indistinguishable under particle permutation must be counted as a single microstate. Then, $w/N!$ must be the number of states, which is vastly smaller than w itself. Therefore, one might expect that 'ergodicity' holds for this true phase space. Suppose we have N particles packed loosely in the space. Due to the indistinguishability we can largely ignore the exchange of particles, so the number of microstates is determined by the local configuration of each particle (e.g., the location of the particle in a local cell just as in the cell model of liquids). Even if there are only two local states, we have total more than $2^N \sim 10^{N/3}$ microstates, so the estimate of the needed Poincarë time is 'not much different' from e^N.

12.11 Derivation of Boltzmann's formula

Let us derive Boltzmann's principle from thermodynamics (and mechanics). For simplicity, only E is written explicitly; you can repeat the following argument with X restored. The phase volume $w(E)$ compatible with the microstates

dynamical system to return to its intial condition. Poincar'e's recurrence theorem guarantees that any state can return to its any neighborhood whose energy is in $(E - \Delta E, E]$ may be written as

$$w = \int d\Gamma\, \chi_{\Delta E}(H - E), \tag{12.13}$$

where $\chi_{\Delta E}$ is the indicator of the leeway set, $(-\Delta E, 0]$, and $d\Gamma$ is the phase volume element.[252] Here, the integration is over all the phase space of the system. Let us assume that the Hamiltonian contains a parameter λ that can be controlled externally (to do macroscopic work, or to regulate work coordinates; λ is something like a handle). The change of the Hamiltonian due to the change of the parameter $\lambda \to \lambda + \delta\lambda$ (averaged over the original equilibrium distribution) is identified with work $\delta' W$ by Einstein. We can also change E by δE. Thus, notice that

$$\langle H(\lambda + \delta\lambda) - H(\lambda)\rangle - \delta E = \delta' W - \delta E, \tag{12.14}$$

where $\langle\ \rangle$ is the equilibrium average. In terms of this variation, we have

$$\delta w = \int \chi'_{\Delta E}(H - E)(H(\lambda + \delta\lambda) - H(\lambda) - \delta E)\, d\Gamma. \tag{12.15}$$

Since almost all the microstates give the same thermodynamic results as already argued, $\delta' W - \delta E$ is almost always the same for any microstate compatible with a given thermodynamic state. Therefore, we obtain

$$\delta w = (\delta' W - \delta E) \int \chi'_{\Delta E}(H - E)\, d\Gamma, \tag{12.16}$$

or with the aid of the first law $\delta' W - \delta E = -\delta' Q$, after dividing with w,

$$\delta \log w = -\delta' Q \frac{\int d\Gamma\, \chi'_{\Delta E}(H - E)}{\int d\Gamma\, \chi_{\Delta E}(H - E)}. \tag{12.17}$$

Defining

$$\eta \equiv \left.\frac{\partial \log w}{\partial E}\right|_X = -\frac{\int d\Gamma\, \chi'_{\Delta E}(H - E)}{\int d\Gamma\, \chi_{\Delta E}(H - E)}, \tag{12.18}$$

we get (under constant X)

$$d \log w = \eta d' Q. \tag{12.19}$$

What is η? Let us compute this quantity for an ideal gas. Actually, we have already done that in (12.10):

$$k_B \frac{\partial \log w(E, V)}{\partial E} = \frac{3 k_B N}{2E}. \tag{12.20}$$

[252] A quantum version is in PST **17.12**.

We know this is $1/T$ even before thermodynamics was established (recall the Maxwell distribution). Now we can use thermodynamics $\delta S = \delta' Q/T$, (and adjusting the units, if needed), we conclude

$$dS = k_B d \log w. \tag{12.21}$$

Integrating this, we obtain Boltzmann's principle.[253]

12.12 Derivation of Boltzmann's formula: quick way

If we accept that entropy is a functional of w, then (12.21) is an inescapable conclusion.

A crucial observation is that entropy is an extensive quantity. If we form a compound system by combining two systems I and II already in thermal equilibrium with each other, the entropy of the compound system is the sum of that of each component (the fourth law).

The interaction introduced by the contact of the two systems is, for macroscopic systems, a very weak one. In any case, the effect is confined to the boundary layer whose thickness is microscopic. Thus, the two subsystems may be regarded statistically independent. Therefore, the total number of microstates of the compound system must be very close to the product of the total numbers of microstates for I and II: $w = w_{\mathrm{I}}\, w_{\mathrm{II}}$.

Combining the above considerations, we have arrived at the following functional relation:

$$S(w_{\mathrm{I}}\, w_{\mathrm{II}}) = S(w_{\mathrm{I}}) + S(w_{\mathrm{II}}), \tag{12.22}$$

where suffixes denote subsystems.

Assuming that S is an increasing function of w, we may conclude from the relation that S is proportional to $\log w$. Therefore, we have arrived at (12.21). The proportionality coefficient k_B must be positive, because entropy should be larger with larger E that corresponds to larger w.

12.13 Entropy and information

We have already discussed the meaning of entropy in terms of the number of yes-no questions to specify the molecular state. From this idea, notice that $S \propto \log w$ is quite natural. S in bits is the number of YN questions you must ask to pinpoint the microstate when you know the system is in a particular macrostate.

12.14 Why traditional justification is meaningless

[253] How can we choose the integration constant? It is an excellent question. Also look at the factor $N!$ we discussed briefly above.

When Boltzmann arrived at his statistical mechanics framework, he initially thought that thermodynamic observables were the average value over w. To average, the trajectory of the system as a mechanical system should sample the subset w evenly, so he conceived the so-called *ergodicity*: the trajectory can visit in any neighborhood of any point in w. Almost all the currently popular textbooks explain this totally wrong idea. You should have already realized this.

As we have seen in Lecture 7, every ambitious young man attempted to derive the irreversibility from mechanics. Boltzmann studied the gas dynamic in detailed and 'demonstrated' irreversibility. His colleague Loschmidt questioned why time-reversal symmetric mechanics could give rise to a system losing this symmetry. Boltzmann realized that there is an approximation to discard memory. Then came Zermelo who pointed a logical error out: even if memory is discarded, still any trajectory can return in any neighborhood of the starting point (Poincaré's recurrence theorem), so irreversibility cannot be concluded. Boltzmann countered that the young man (= Zermelo) should know physics; can you wait for that long time of order 10^N? Thus, in practice, irreversibility is real, even if the system is finite.

However, you must have quickly realized that this counterargument backfires. For an even sampling of the phase space, you must observe the system for an extremely long time. That is, ergodicity cannot justify statistical mechanics! Actually, Boltzmann seems to have realized that there was a serious problem with the ergodicity argument to found statistical mechanics long before Zermelo's criticism. He even realized the secret of equilibrium statistical mechanics: every microstate gives the same thermodynamic observables!

Boltzmann's followers all ignored (or could not understand) this insight. The total absurdity of the ergodicity argument should be obvious from the fact that larger systems require shorter observation times for accurate determination of thermodynamic observables. This is basically the law of large numbers.

Although the theoretical system we have arrived at is called 'statistical mechanics', we need only the law of large numbers as Khinchin realized long ago.

Q12.1 [How Boltzmann introduced his principle].
Let us taste the original paper.[254] Main steps are stated as questions (and answers to them). Let us consider a gas consisting of N particles in a container with volume V. Let w_n be the number of particles with the (one-particle) energy between $(n-1)\varepsilon$ and $n\varepsilon$ ($\varepsilon > 0$). Thus, the set $\{w_n\}$ specifies a collection of microstates of the system with w_n particles in the one particle energy bin with the energy in $((n-1)\varepsilon, n\varepsilon]$.
(1) Show that maximizing the number of ways ('Komplexionszahl') to realize a collection of microstates ('Komplexion') specified by $\{w_n\}$ is equivalent to the minimization condition for

$$M = \sum w_n \log w_n. \tag{12.23}$$

(2) Write $w_i = w(x)\epsilon$ and simultaneously take the $n \to \infty$ and $\varepsilon \to 0$ limits, maintaining $x = n\varepsilon$ finite. Show that minimizing M is equivalent to minimizing

$$M' = \int w(x) \log w(x) dx. \tag{12.24}$$

(3) We should not ignore the constraints that the total number of particles is N and the total energy is E. Under this condition, derive Maxwell's distribution in 3-space by minimizing M'.
(4) Now, Boltzmann realized that $\log Z_K = \log N! - M'$ gives the entropy of the ideal gas. Based on this finding, he proposed

$$S \propto \log(\text{Number of 'Komplexions'}). \tag{12.25}$$

Compare this and the formula for S obtained thermodynamically, as Boltzmann did, to confirm his proposal.

Remark. Usually, the story ends here (so did Boltzmann's original paper). However, being a much deeper thinker than is usually regarded, Boltzmann later confirmed for macrosystems described by E and V that his formula of entropy (12.1) satisfied the Gibbs relation for general classical many-body systems; in particular, $(dE + PdV)/T$ is a complete differential.[255]

Solution.
(1) The Komplexionszahl reads

$$Z_K = \frac{N!}{w_1!w_2!\cdots w_n!\cdots}, \tag{12.26}$$

[254] L. Boltzmann, "Über die Beziehung zwischen dem zweiten Hauptsatze der mechanischen Wärmetheorie und der Wahrscheinlichkeitsrechinung respective den Sätzen über Wärmegleichgewicht," Wiener Berichte **76**, 373 (1877) ("On the relation between the second law of thermodynamics and probability calculation concerning theorems of thermal equilibrium")
[1877: Accession of Queen Victoria to 'Empress of India'; Tchaikovsky *Swan Lake* debuts; Crazy Horse was killed; Lewis H. Morgan, *Ancient Society*; Shen Fu: *Six Records of a Floating Life*; G. Caillebotte *Paris Street; Rainy Day* (Art Institute, Chicago)]
[255] For a detail, see **Q17.3** in PST.

so maximizing this is equivalent to minimizing the denominator or its logarithm (here Stirling's formula (13.6) is used):

$$\log(w_1!w_2!\cdots w_n!\cdots) = \sum_n \log w_n! = \sum (w_n \log w_n - w_n) = M - N. \qquad (12.27)$$

The original paper kindly discusses that we can discard numerical factors, etc., in Stirling's formula, which we will derive in the next lecture.
(2) Substituting the quantities in M as indicated, we have

$$\sum_n w_n \log w_n = \sum_n w(x)\varepsilon \log[w(x)\varepsilon] = \sum_n w(x)\varepsilon \log w(x) + \sum_n w(x)\varepsilon \log \varepsilon \quad (12.28)$$

The first term is a Riemann sum, so we obtain (12.24). The second term is $N \log \varepsilon$ and is unrelated to the number of complexions, so we may ignore it.
(3) In the original paper Boltzmann regarded the variable x as the three components of velocity vector v_x, v_y, v_z. Here, we take the momentum $\boldsymbol{p}$ and the position $\boldsymbol{r}$ as x: $w(x) = w(\boldsymbol{r}, \boldsymbol{p})$. The constraints are

$$N = \int d\boldsymbol{r}d\boldsymbol{p}\, w(\boldsymbol{r}, \boldsymbol{p}), \quad E = \int d\boldsymbol{r}d\boldsymbol{p}\, w(\boldsymbol{r}, \boldsymbol{p})E(\boldsymbol{p}), \qquad (12.29)$$

where $E(\boldsymbol{p}) = \boldsymbol{p}^2/2m$ is the energy of a single particle state $\boldsymbol{p}$ with m being the mass of a gas particle. Using Lagrange's technique, we should maximize (α and β are multipliers)

$$\int d\boldsymbol{r}d\boldsymbol{p}\, w(\boldsymbol{r}, \boldsymbol{p})[\log w(\boldsymbol{r}, \boldsymbol{p}) + \alpha + \beta E(\boldsymbol{p})]. \qquad (12.30)$$

Hence, ($E = (3/2)Nk_BT$ is used to fix β)

$$w(\boldsymbol{r}, \boldsymbol{p}) = \frac{N}{V}\frac{1}{(2\pi m k_B T)^{3/2}} e^{-p^2/2k_BTm}. \qquad (12.31)$$

Thus, we have obtained the Maxwell distribution.
(4) If we compute (12.25) (i.e., $N \log N - M'$) with the aid of w in (12.31)

$$S = N \log V + N\left(\frac{3}{2} + \frac{3}{2}\log(2\pi k_B T m)\right) = N \log VT^{3/2} + \text{ const.} \qquad (12.32)$$

This agrees with the entropy obtained thermodynamically (apart from $\log N!$; the formula is not extensive). Indeed, the Gibbs relation is

$$dS = \frac{1}{T}dE + \frac{P}{T}dV, \qquad (12.33)$$

so with the aid of the internal energy $E = (3/2)Nk_BT$ and the equation of state, we have

$$S = Nk_B \log T^{3/2} + Nk_B \log(V/N) + \text{ const.} \qquad (12.34)$$

Discussion 7

We review intuitive understanding of entropy, various thermodynamic potentials and Boltzmann's principle.

D7.1 [Legendre transformation]
Let $f(x)$ be a convex function. Then, Legendre transformation $f \to f^*$ is defined as[256]

$$f^*(y) = \max_x [xy - f(x)]. \tag{12.35}$$

We know $(f^*)^* \equiv f^{**} = f$, so Legendre transformation perfectly preserves the functional information. Notice that no differentiability is required for f; only its convexity is required.[257] We know internal energy E is a convex function of S. Therefore, $E^* = -A$ is well-defined:

$$-A(T) = \max_S [ST - E(S)], \tag{12.36}$$

so $-A$ is again convex: that is, $A(T)$ is a concave function of T. We can recover E from A by Legendre transformation

$$E(S) = \max_T [TS - (-A)]. \tag{12.37}$$

All the thermodynamic potentials are connected with each other by a certain Legendre transformation, so if you know one of them, you can know all the rest. Notice that no differentiability of thermodynamic potentials is required; this is quite important, because, if there are phase transitions, thermodynamic potentials often lose differentiability.

Find the Legendre transform of $f(x) = 5|x|$.

Solution.
See Fig. 12.3:

For the red line with slope y less than -5 the vertical distance (red arrow: upward positive) $yx - 5|x|$ is indefinitely large, since we can make x as small (far left) as possible (i.e., as $x \to -\infty$). Thus $f^*(y) = +\infty$ for $y < -5$. For green line with the slope $y > -5$, since the line is below f the (signed) distance $xy - f(x)$ is maximum when the line touches $f(x)$. Thus, $f^*(y) = 0$ for $5 > y > -5$.

However, if the slope y becomes larger than 5 (blue line) the situation similar to

[256]This convention is at variance with the thermodynamic tradition, but I strongly recommend you to get rid of the old irrational convention and adopt the mathematically rational definition given here, because you will learn this is indeed natural for statistical mechanics.

[257]Convex functions are inevitably continuous.

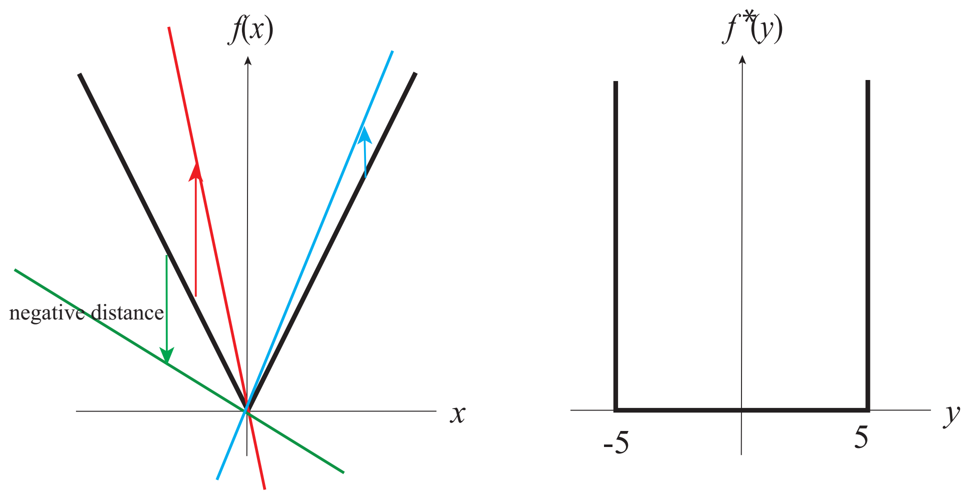


Figure 12.3: $f(x) = 5|x|$. Red line is with slope $y < -5$ and green with slope in $[-5, 5]$.

the red line occurs (look at the blue arrow). Thus $f^*(y) = +\infty$, Thus, we can draw a symmetric $f^*(y)$ as in Fig. 12.3 Right; formally,

$$f^*(y) = \begin{cases} +\infty & \text{for } y < -5, \\ 0 & \text{for } y \in [-5, 5], \\ +\infty & \text{for } 5 < y. \end{cases} \tag{12.38}$$

This is indeed convex.

Can you show $f = f^{**}$?

D7.2. [Elementary questions about various thermodynamic potentials]
(1) Which change is zero for the following processes, ΔE, ΔH, ΔA, or ΔG? If not zero, think whether we can fix their signs.

(i) In Fig. 12.4 adiabatically a gas on the left side of a plug is pushed with a constant pressure P_1 into a chamber with another constant pressure P_2 (you can interpret this as a throttle experiment)

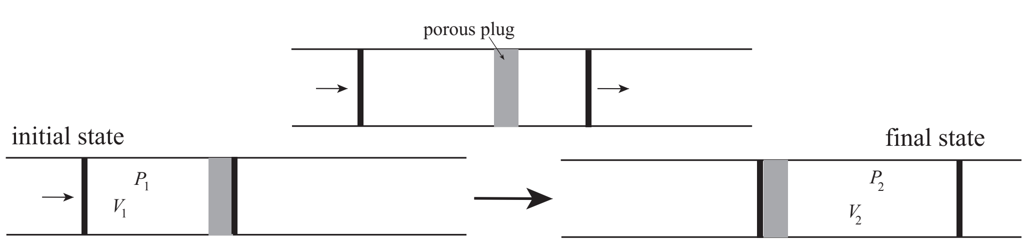


Figure 12.4: Throttle experiment

(ii) In an adiabatic cylinder sulfur is burnt.

(iii) Ethanol boils at its equilibrium boiling temperature (78 °C) under 1 atm (of its own gas).

Solution.
(i) Thanks to the plug, there is no systematic flow with appreciable macroscopic kinetic energy. The change of the internal energy is solely due to the volume work: P_1V_1 is added to the system and P_2V_2 is done to the external world by the system. Thus, the first law says

$$E_2 = E_1 + P_1V_1 - P_2V_2 \tag{12.39}$$

Thus, $E + PV$, that is, enthalpy H is conserve: $\Delta H = 0$. Certainly, $\Delta E \neq 0$. Since it is an adiabatic irreversible change, $\Delta S > 0$. Therefore, generally, $\Delta G = \Delta H - \Delta(TS) \neq 0$; I do not think its sign can be fixed without any further information. Since there is no particular relation between PV and TS, generally $\Delta A \neq 0$.

This is the setup of Joule-Thomson experiment, disproving Newton's repulsive interaction theory of the gas pressure.

$$\left.\frac{\partial T}{\partial P}\right|_H \tag{12.40}$$

is called the Joule-Thomson coefficient.

(ii) The reaction has no exchange of energy with its environment, so $\Delta E = 0$. $\Delta H = \Delta E + V\Delta P$, because V is constant. The reaction $\mathrm{S} + \mathrm{O_2} \to \mathrm{SO_2}$ does not change the number of particles in the gas phase, but the temperature of the system should have increased, so $\Delta H > 0$ is expected. This is irreversible, so $\Delta S > 0$. $\Delta T > 0$, so $\Delta A = \Delta E - \Delta(TS) < 0$. To understand ΔG we must compare $\Delta(ST)$ and $V\Delta P$, so we need more information about the reaction, but there is no particular relation between these changes, so, generally, $\Delta G \neq 0$. I do not think a definite sign can be claimed without any further details.

(iii) This is an equilibrium process under constant T and P, so $\Delta G = 0$. Ethanol absorbs its boiling heat, so $\Delta H > 0$. $\Delta A = \Delta G - P\Delta V < 0$. $\Delta E = \Delta H - P\Delta V$ has no reason to vanish; I do not think we can tell its sign without further details.

(2) Initially, we have one mole of a monatomic ideal gas at 273 K at 1 atm (thus, its volume is 22.4 l). Find the changes of ΔE, ΔH, ΔA and ΔG for adiabatic free expansion to the final volume 300 l.

Solution.
We know $\Delta E = 0$ (no work, no heat).
The final temperature is 273 K (unchanged) and the final volume is 300 l. Therefore,

$$\Delta S = R \log \frac{V_\mathrm{F}}{V_\mathrm{I}} = 8.3 \log \frac{300}{22.4} = 8.3 \times 2.59 = 21.6 \text{ J/K}. \tag{12.41}$$

This means

$$\Delta A = \Delta E - T\Delta S = -273 \times 21.6 = -5897 \text{ J}. \tag{12.42}$$

Notice that the temperature does not change so $P_F V_F = P_I V_I$. Therefore,

$$\Delta H = \Delta E + \Delta(PV) = 0. \tag{12.43}$$

From this

$$\Delta G = \Delta A. \tag{12.44}$$

(3) 100 g of ice at 250 K is thrown into 100 g of boiling water under 1 atm. Assume the whole system is under adiabatic condition and the pressure is maintained at 1 atm. What is the total entropy change? You may assume that the specific heat of ice is 2 J/g·K, that for water 4.2 J/g·K and the equilibrium melting enthalpy change is 333 J/g.

Solution.
The process is patently irreversible, so in order to use thermodynamics
(i) Identify the initial and the final equilibrium states.
(ii) Invent a convenient quasistatic process connecting these two states.

Initially, the state is ice at 250 K + water at 373 K (under 1 atm) (in equilibrium as a compound system).

To determine the final state, we use the first law. First, 100 g ice must be brought to ice at 273 K. This requires $100 \times 2 \times (273 - 250) = 4600$ J. To make 0°C water we need $100 \times 333 = 33,300$ J. Mixing 100 g of 100°C water and 100 g of 0°C water makes 200 g of 50°C water. Now, we must supply 4,600 +33,300 = 37,900 J from the 'warmth' this water has. Then, it is cooled by ΔT:

$$200 \times 4.2 \times \Delta T = 37,900 \tag{12.45}$$

or $\Delta T = 45.1$ K. Thus, the finial state is 200 g of water with $T_{\mathrm{F}} = 277.9$ K.

The next task is to invent a convenient quasistatic path connecting the initial and the final states. Perhaps, the easiest way is to bring 100 g of cold ice to 100 g of water at $T = 277.9$ K. On the other hand, 100 g water at 373 K is cooled to 277.9 K. Then, simply join these two waters.

Heat the ice to its equilibrium melting temperature, and then melt it at its equilibrium temperature. Then, the resultant water is heated up to the final temperature. Thus,

$$\begin{aligned}\Delta S &= \int_{250}^{273} \frac{200}{T} dT + \frac{33,300}{273} + \int_{273}^{278} \frac{420}{T} dT = 200 \log \frac{273}{250} + 122 + 420 \log \frac{278}{273} \\ &= 17.6 + 122 + 7.6 = 147 \text{ J/K}.\end{aligned} \tag{12.46}$$

On the other hand cooling the other 100 g water requires

$$\Delta S = \int_{373}^{278} \frac{420}{T} dT = -420 \log \frac{373}{278} = -123 \text{ J/K}. \tag{12.47}$$

Therefore, $147 - 123 = 24$ J/K is the overall entropy change.

D7.3 [Einstein model with microcanonical formalism]
The total energy of the system is $E = M\varepsilon$, where ε is the size of the energy quantum and M is the number of energy quanta (phonons originally). There are N lattice sites and each lattice site can accommodate some energy quanta.[258] Each microstate is distinguished by the distribution of energy quanta over the lattice sites.
(1) Obtain the entropy S as a function of E (or M).
(2) Obtain the average number M/N of energy quanta (phonons) for each lattice site ($M\varepsilon/N$ is the average energy per lattice site) as a function of T.
(3)* Prepare two identical such systems, 1 and 2, and put them into thermal contact. Suppose the total energy is $2M\varepsilon$. How sharp is the most likely energy partition (i.e., an even partition of energy between the two identical systems) in equilibrium?

Solution.
Notice that the system has only one thermodynamic coordinate E.
(1) The problem is equivalent to distributing M indistinguishable objects into N distinguishable bins. See Appendix 3A. Hence,

$$w(E) = \binom{M+N-1}{M}. \tag{12.48}$$

We may ignore 1, since M and N are both macroscopic. Boltzmann's principle tells us that

$$S(E)/k_B = \log w(E) = (N+M)\log(N+M) - M\log M - N\log N, \tag{12.49}$$

where we have used Stirling's approximation with $M = E/\varepsilon$.

(2) To introduce T we use the Gibbs relation:

$$\frac{1}{T} = \frac{dS}{dE} = \frac{1}{\varepsilon}\frac{dS}{dM} = \frac{k_B}{\varepsilon}\log\frac{N+M}{M}. \tag{12.50}$$

From this, we get the average number of energy quanta per site:

$$\frac{M}{N} = \frac{1}{e^{\beta\varepsilon} - 1}. \tag{12.51}$$

The distribution is called the Bose-Einstein distribution.

(3) To study the probability of deviation from the even partition of energy, let us

[258]The model is equivalent to the Einstein model of insulating solids. Einstein introduced a collection of N quantized harmonic oscillators to explain the low temperature behavior of the specific heat of solids. Each oscillator localized at a lattice point is understood as a container of phonons (energy quanta) of energy $\varepsilon = \hbar\omega$. [We ignore the zero-point energy.]

define $M_1 = M+x$ (resp., $M_2 = M-x$). Then, the microcanonical partition function (= the number of all the microstates compatible with the constraints) of the whole system $w(x) = w(M_1, M_2)$ is given by

$$w(x) = \binom{N+M+x}{N}\binom{N+M-x}{N}. \tag{12.52}$$

Let us compute $\log[w(x)/w(0)]$ with the aid of the following Taylor expansion:

$$(A+x)\log(A+x) = A\log A + (\log A + 1)x + x^2/2A + o[x^2]. \tag{12.53}$$

$$\begin{aligned}\log\binom{N+M\pm x}{N} &= (N+M\pm x)\log(N+M\pm x) - (M\pm x)\log(M\pm x) - N\log N \\ &= \log\binom{N+M}{N} \pm (\log(N+M)+1)x \mp (\log M + 1)x \\ &\qquad + \frac{x^2}{2}\left[\frac{1}{N+M} - \frac{1}{M}\right].\end{aligned} \tag{12.54}$$

Therefore,

$$\log[w(x)/w(0)] = -x^2\left[\frac{1}{M} - \frac{1}{N+M}\right] = -\frac{N}{M(N+M)}x^2. \tag{12.55}$$

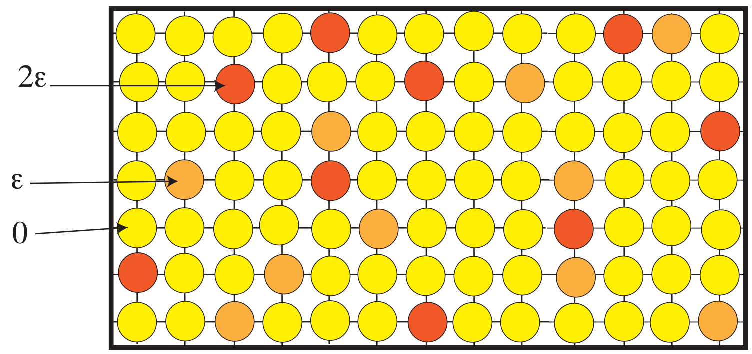
This implies that $w(x)$ obeys a Gaussian distribution of mean 0 and variance $M(N+M)/2N$. You might think the variance is very large, but we must compare it with the equilibrium expectation (= the most probable) M. The ratio

$$\frac{\sqrt{\langle x^2\rangle}}{M} = \frac{1}{\sqrt{2N}}\sqrt{1+N/M} \tag{12.56}$$

implies, as long as T is not extremely small, the width of the central peak scales as $1/\sqrt{\text{system size}}$. That is, the internal energy is evenly partitioned very sharply between the two macrosystems.

D7.4 [Ensemble equivalence and max term approximation].

A lattice consists of a spatially fixed N identical (indistinguishable) particles each of which can assume three energy states: the ground state 0, and the two excited states of energy ε and 2ε, respectively.



(1) Find the microcanonical partition function (= the total number of microstates) $W(E)$, where E is the (internal) energy of the system. I am pretty sure you cannot sum the formula, so you have only to write down the definition of $W(E)$ in the following form

$$W(E) = \sum_{n_1+2n_2=E/\varepsilon} w(n_1, n_2), \tag{12.57}$$

where n_1 (resp., n_2) is the number of particles with energy ε (resp. 2ε). You must write down $w(n_1, n_2)$ explicitly. Use n_0 to denote the number of ground state particles ($n_0 + n_1 + n_2 = N$). [Almost trivial.]

Solution.

Let n_0 be the number of particles in the ground state and n_1 (resp., n_2) that in the first (resp., second) excited state. $n_0 + n_1 + n_2 = N$, and $E = (n_1 + 2n_2)\varepsilon$. Therefore,

$$W(E) = \sum_{n_1+2n_2=E/\varepsilon} \frac{N!}{n_0!n_1!n_2!}. \tag{12.58}$$

That is,

$$w(n_1, n_2) = \frac{N!}{n_0!n_1!n_2!}. \tag{12.59}$$

(2)* [**Max term approximation works: quite important**] Let w_M be the largest value of $w(n_1, n_2)$ under the condition that $E = (n_1 + 2n_2)\varepsilon$. Show that $S = k_B \log w_M$ is an extremely good approximation formula (the relative error is of order $\log N/N$) for $S = k_B \log W(E)$.

Solution.

Since all the summands are positive, obviously,

$$w_M \le \sum_{n_1+2n_2=E/\varepsilon} w(n_1, n_2) \le \text{the number of terms} \times w_M. \tag{12.60}$$

The number of the terms in the summation cannot be larger than N^2 (actually $N+1$, since if you fix n_1, n_2 is fixed as well, but any fairly crude estimate will do; thermodynamics is very robust), so we have

$$w_M \le W(E) \le N^2 w_M. \tag{12.61}$$

Therefore,

$$k_B \log w_M \le S \le k_B \log w_M + 2k_B \log N. \tag{12.62}$$

Notice that S is extensive (of order N), so $\log N$ should be ignorable. Thus,

$$S = k_B \log w_M \tag{12.63}$$

is very accurate, if $N > 10^3$.

(3) Let us compute w_M with the aid of the Lagrange multiplier β. That is, maximize

$$\log w(n_1, n_2) - \beta(n_1 + 2n_2)\varepsilon \tag{12.64}$$

with respect to n_1 and n_2 (do not forget that $n_0 = N - n_1 - n_2$), and find n_1/n_0 and n_2/n_0, using β (do not try to determine β).

Solution.

Let us find the maximum value of $w(n_1, n_2)$ under the given E (and N). With the aid of Stirling's formula, we obtain

$$\log w(n_1, n_2) = -N \left[\sum_{i=0,1,2} \frac{n_i}{N} \log \frac{n_i}{N} \right]. \tag{12.65}$$

Let us use Lagrange's multiplier: we maximize ($n_0 = N - n_1 - n_2$ is used)

$$\log w(n_1, n_2) - \beta(n_1 + 2n_2)\varepsilon. \tag{12.66}$$

Therefore,

$$\log \frac{N - n_1 - n_2}{n_1} - \beta\varepsilon = 0, \quad \log \frac{N - n_1 - n_2}{n_2} - 2\beta\varepsilon = 0. \tag{12.67}$$

This means

$$n_1 = n_0 e^{-\beta\varepsilon}, \; n_2 = n_0 e^{-2\beta\varepsilon}, \tag{12.68}$$

so

$$n_0 e^{-\beta\varepsilon} + 2n_0 e^{-2\beta\varepsilon} = E/\varepsilon \tag{12.69}$$

and

$$n_0 + n_0 e^{-\beta\varepsilon} + n_0 e^{-2\beta\varepsilon} = N. \tag{12.70}$$

These two equations fix β and n_0 implicitly (I cannot solve them in a neat form).

(4) Using the obtained n_1 and n_2 in (3) we can write entropy $S = k_B \log w_M$ in the following form:

$$S = n_0(e^{-\beta\varepsilon} + 2e^{-2\beta\varepsilon})k_B\beta\varepsilon + Nk_B \log \Phi. \tag{12.71}$$

Find Φ in terms of N and n_0.

Solution.

$$\begin{aligned}
S &= -Nk_B \left[\frac{n_0}{N}\log\frac{n_0}{N} + \frac{n_1}{N}\log\frac{n_1}{N} + \frac{n_2}{N}\log\frac{n_2}{N}\right] \\
&= -Nk_B \left[\frac{n_0}{N}\log n_0 + \frac{n_1}{N}\log n_1 + \frac{n_2}{N}\log n_2\right] + Nk_B \log N. \\
&= -Nk_B \left[\log n_0 + \frac{n_1}{N}\log\frac{n_1}{n_0} + \frac{n_2}{N}\log\frac{n_2}{n_0}\right] + Nk_B \log N. \\
&= -Nk_B \left[\frac{n_1}{N}\log\frac{n_1}{n_0} + \frac{n_2}{N}\log\frac{n_2}{n_0}\right] + Nk_B \log\frac{N}{n_0}.
\end{aligned}$$

Using the above results, we get

$$S = n_0(e^{-\beta\varepsilon} + 2e^{-2\beta\varepsilon})k_B\beta\varepsilon + Nk_B \log\frac{N}{n_0}. \tag{12.72}$$

That is, $\Phi = N/n_0$.

The following two subquestions should be considered after Section 13.

(5) Find the canonical partition function $Z(T)$ for this system at temperature T and explicitly calculate the Helmholtz free energy.

Solution.

$$Z(T) = (1 + e^{-\beta\varepsilon} + e^{-2\beta\varepsilon})^N, \tag{12.73}$$

so

$$A = -Nk_BT\log(1 + e^{-\beta\varepsilon} + e^{-2\beta\varepsilon}). \tag{12.74}$$

(6) [**Ensemble equivalence**] Show that the entropy obtained from A in (5) and the formula in (4) are consistent.

Solution.

$$E = N\frac{e^{-\beta\varepsilon} + 2e^{-2\beta\varepsilon}}{1 + e^{-\beta\varepsilon} + e^{-2\beta\varepsilon}}\varepsilon, \tag{12.75}$$

so

$$S = N\frac{e^{-\beta\varepsilon} + 2e^{-2\beta\varepsilon}}{1 + e^{-\beta\varepsilon} + e^{-2\beta\varepsilon}}\frac{\varepsilon}{T} + Nk_B\log(1 + e^{-\beta\varepsilon} + e^{-2\beta\varepsilon}). \tag{12.76}$$

Thus, with an identification $\beta = 1/k_B T$, we see these two results agree, if we notice

$$1 + e^{-\beta\varepsilon} + 2e^{-2\beta\varepsilon} = N/n_0. \tag{12.77}$$

Exercise 7

E7.1 [Intuitive entropy]
There is a solid made of fairly spherical molecules. They freely tumble in the liquid phase, but cannot rotate in the solid phase. With a small chemical modification the steric hindrance against molecular rotation in the solid phase can be removed with almost no altering of molecular interaction energies. Thanks to this modification, now the new molecules can rotate fairly freely even in the solid phase below the melting temperature of the solid of the unmodified molecules.

What can you guess about the melting point of the new chemical substance relative to that of the unmodified substance?

Solution.
Any answer is OK, if your answer is consistent with your physically plausible explanation. However, probably the most natural answer would be as follows.

Since molecular interaction energies do not change, the latent heat should not be very different with and without the chemical modification. However, the melting entropy change must be reduced due to the chemical modification, because molecules already tumbles in the solid, increasing its entropy (you must ask more questions to determine what a molecule is doing). $\Delta S = \Delta H/T_m$, where ΔH is the heat of melting. To reduce ΔS without changing ΔH, the only way is to increase T_m. That is, the melting temperature should go up (in actual examples this can be considerable, a few tens of K).

E7.2 [Elementary calculation of thermodynamic changes]
Initially, we have one mole of a monatomic ideal gas at 273 K at 1 atm (thus, its volume is 22.4 l). Find the changes of ΔE, ΔH, ΔA and ΔG for reversible isothermal expansion to the final volume 300 l.

Solution.
This is reversible isothermal expansion, so $\Delta E = 0$. $PV = RT$ does not change: $\Delta(PV) = 0$. Therefore, $\Delta H = 0$ as well.

$$\Delta S = R \log \frac{300}{22.4} = 21.6 \text{ J/K}. \tag{12.78}$$

T does not change, so

$$\Delta A = \Delta E - T\Delta S = -273 \times 21.6 = -5889 \text{ J}. \tag{12.79}$$

That is, $\Delta A = -5.9$ kJ. Notice that 5.9 kJ is the work done by the system. It absorbed this much of heat from the environment, and converted it into work (of course, this does not mean the violation of Thomson's law. Why?). $\Delta G = \Delta A$.

E7.3 [Independent spin in magnetic field with microcanonical formalism] The total energy of the system is $E = M\varepsilon$, where ε is the size of the energy quantum and M is the total number of energy quanta. There are N lattice sites and each lattice site can accommodate at most one energy quanta.[259] Each microstate is distinguished by the distribution of energy quanta over the lattice sites.
(1) Obtain the entropy S as a function of E (or M).
(2) Obtain the average number M/N of energy quanta for each lattice site ($M\varepsilon/N$ is the average energy per lattice site) as a function of T.
(3) Prepare two identical such systems, 1 and 2, and put them into thermal contact. Suppose the total energy is $2M\varepsilon$. How sharp is the most likely energy partition (i.e., an even partition of energy between the two identical systems) in equilibrium? [As in Discussion **4** study the distribution of the deviation x from M.]

Solution.
Notice that the system has only one thermodynamic coordinate E.
(1) The problem is equivalent to choosing M lattice sites to place the energy quanta from N distinguishable lattice sites. Hence,

$$w(E) = \binom{N}{M}. \tag{12.80}$$

Boltzmann's principle tells us that

$$S(E)/k_B = \log w(E) = N \log N - M \log M - (N - M) \log(N - M), \tag{12.81}$$

where we have used Stirling's approximation with $M = E/\varepsilon$.
(2) To introduce T we use the Gibbs relation or:

$$\frac{1}{T} = \frac{dS}{dE} = \frac{1}{\varepsilon}\frac{dS}{dM} = \frac{k_B}{\varepsilon} \log \frac{N - M}{M}. \tag{12.82}$$

From this, we get the average energy of the site:

$$\frac{M}{N} = \frac{1}{e^{\beta\varepsilon} + 1}. \tag{12.83}$$

This is called the Fermi-Dirac distribution. Notice that this cannot be larger than $\varepsilon/2$, if $\beta > 0$.[260]

(3) To study the probability of deviation from the even partition of energy, let us

[259] The model is equivalent to a lattice of non-interacting two state spins in an external magnetic field that makes the 'up' and 'down' states have energy difference ε.
[260] For this system the so-called negative temperature state is possible, for which the above formula gives the value larger than $\varepsilon/2$.

define $M_1 = M+x$ (resp., $M_2 = M-x$). Then, the microcanonical partition function of the whole system $w(x) = w(M_1, M_2)$ is given by

$$w(x) = \binom{N}{M+x}\binom{N}{M-x} \tag{12.84}$$

Let us compute $\log[w(x)/w(0)]$ with the aid of the following Taylor expansion:

$$(A+x)\log(A+x) = A\log A + (\log A + 1)x + x^2/2A + o[x^2]. \tag{12.85}$$

$$\begin{aligned}\log\binom{N}{M\pm x} &= N\log N - (N-M\mp x)\log(N-M\mp x) - (M\pm x)\log(M\pm x) \\ &= \log\binom{N}{M} \pm (\log(N-M)+1)x \mp (\log M + 1)x \\ &\qquad\qquad - \frac{x^2}{2}\left[\frac{1}{N-M}+\frac{1}{M}\right]\end{aligned} \tag{12.86}$$

Therefore,

$$\log[w(x)/w(0)] = -x^2\left[\frac{1}{M}+\frac{1}{N-M}\right] = -\frac{N}{M(N-M)}x^2. \tag{12.87}$$

This implies that $w(x)$ obeys a Gaussian distribution of mean 0 and variance $M(N-M)/2N$. you might think the variance is very large, but if M is macroscopic as N. The ratio

$$\frac{\sqrt{\langle x^2\rangle}}{M} = \frac{1}{\sqrt{2N}}\sqrt{1-N/M} \tag{12.88}$$

is $1/\sqrt{\text{system size}}$. That is, the internal energy is evenly partitioned very sharply between the two macrosystems.

13 Statistical mechanics of isothermal systems

Summary
* Isothermal systems are handled by the canonical formalism: $A = -k_BT \log Z$.
* Microcanonical and canonical formalisms give identical results if the system is large (if $\log N/N \ll 1$) [Ensemble equivalence].
* The principle of equal probability allows us to estimate the probabilities of a collection of microstates.

Key words
canonical partition function, microcanonical partition function, Gibbs-Helmholtz formula, ensemble equivalence, Stirling's formula, Schottky defect, Schottky type specific heat.

What you should be able to do
* You must be able to compute the microcanonical partition functions and canonical partition functions for simple systems.
* You must remember the Gibbs formula for S (i.e., $dS = \cdots$).
* Understand the significance of the ensemble equivalence.

13.1 What we have now

We have constructed the statistical mechanics for isolated systems = the translation table between mechanical and thermodynamic quantities: for the thermodynamic coordinates the correspondence is straightforward. To utilize the Gibbs relation

$$dE = TdS - PdV + \mu dN + xdX + \cdots, \tag{13.1}$$

we need the interpretation of S in terms of mechanics. We have derived Boltzmann's principle:

$$S = k_B \log w(E, X). \tag{13.2}$$

w is not very easy to compute, so we will not discuss how to use this formula very much, but let us look at a simple example.

13.2 Another practice: Schottky defects

Let us consider an isolated crystal with point defects (vacancies) on the lattice sites (*Schottky defects*). To create one such defect we must move an atom from a lattice point to the surface of the crystal. The energy cost for this is assumed to be ε.

Although the number n of vacancies are macroscopic, we may still assume it to be very small compared to the number N of all lattice sites. Hence, we may assume that the volume of the system is constant. Therefore for this example, the (internal) energy E of the system is a macroscopic (thermodynamic) variable which completely specifies macrostates.

We must compute w as a function of the total energy E, which is given by

$$E = n\varepsilon. \tag{13.3}$$

We may interpret this as the internal energy. We may consider w as a function of n. A microstate of this system is specified by the locations to place n vacancies. Since all the lattice points can be distinguished, the number of placing n vacancies is obviously

$$w(n) = \binom{N}{n}. \tag{13.4}$$

13.3 Approximate evaluation of $\log N!$ (Stirling's formula)

To compute the entropy with the aid of Boltzmann's principle, we use *Stirling's formula* to evaluate $\log N!$ asymptotically for large N:

$$N! \approx \left(\frac{N}{e}\right)^N, \tag{13.5}$$

or

$$\log N! \approx N \log N - N, \tag{13.6}$$

which may be understood as follows:

$$\log N! = \sum_{k=1}^{N} \log k \simeq \int_0^N dx\, \log x = (x \log x - x)_{x=0}^N = N \log N - N. \tag{13.7}$$

13.4 Entropy of Schottky defect system

Boltzmann's principle with the use of 13.3 gives us

$$S = k_B \log w \simeq k_B[N \log N - n \log n - (N-n)\log(N-n)]. \tag{13.8}$$

Incidentally, the following formula is useful (and easy to remember):

$$\log \binom{A}{B} = -A\left[\frac{B}{A}\log\frac{B}{A} + \left(1 - \frac{B}{A}\right)\log\left(1 - \frac{B}{A}\right)\right]. \tag{13.9}$$

This gives

$$S = -Nk_B \left[\frac{n}{N} \log \frac{n}{N} + \left(1 - \frac{n}{N}\right) \log \left(1 - \frac{n}{N}\right) \right], \tag{13.10}$$

which is the same as (13.8). Using the Gibbs relation, we get (notice that $dE = \varepsilon dn$)

$$\frac{1}{T} = \left.\frac{\partial S}{\partial E}\right|_V = \frac{1}{\varepsilon}\frac{dS}{dn} = \frac{k_B}{\varepsilon} \log \frac{N-n}{n}. \tag{13.11}$$

When you differentiate (13.10), the derivatives of the logarithmic terms cancel each other, so essentially, you have only to differentiate the prefactors in front of the logarithms. This is very easy, and you immediately get (13.11).

If the temperature is sufficiently low or ε is sufficiently large so that $\varepsilon/k_BT \gg 1$, the above formula reduces to

$$\frac{\varepsilon}{k_BT} \simeq \log \frac{N}{n}, \tag{13.12}$$

because $N \gg n$. Hence, under this low temperature condition, the internal energy E reads

$$E = \varepsilon N e^{-\varepsilon/k_BT}, \tag{13.13}$$

which may be guessed from the Boltzmann factor.

13.5 Schottky type specific heat

The constant volume specific heat C_V of the system can be obtained as

$$C_V = \frac{dE}{dT} = Nk_B \left(\frac{\varepsilon}{k_BT}\right)^2 e^{-\varepsilon/k_BT}. \tag{13.14}$$

Notice that C_V has a peak at a certain temperature (Fig. 13.1). This type of specific heat is called the *Schottky type specific heat*, which tells you the energy gap for an elementary excitation in the system. What can you say from the dimensional analytical point of view about the same problem?

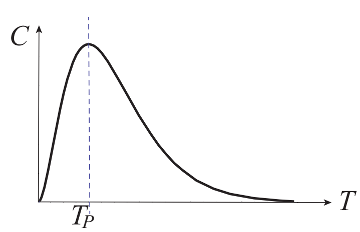


Figure 13.1: The Schottky type specific heat, which has a peak indicating the energy gap of the order $k_BT_P = \varepsilon/2$.

13.6 Thermostat

Isolated systems are not so easy to handle, compared with thermostatted systems. We have introduced the Helmholtz free energy A to study thermostatted systems. We have learned that the information as to thermodynamic potentials can be completely obtained from A (the equivalence of thermodynamic potentials thanks to the Legendre transformation).

13.7 Relation between microcanonical partition function and $\boldsymbol{A}$

We wish to make a translation rule for the Helmholtz free energy A in terms of microstates. Our starting point is thermodynamics, or the definition of A:

$$-A = \max_S [ST - E]. \tag{13.15}$$

Notice that S is a monotone increasing function of E, so we may rewrite this as

$$-A = \max_{E>0} [ST - E]. \tag{13.16}$$

Here we have assume that there is a lower bound for the internal energy.

We must relate this to Boltzmann's principle: $S = k_B \log w(E)$:

$$e^{-\beta A} = \max_E \exp[S/k_B - \beta E] = \max_E \left[w(E) e^{-\beta E} \right]. \tag{13.17}$$

13.8 Canonical partition function

Let us consider

$$Z(T) = \sum_E w(E) e^{-\beta E}. \tag{13.18}$$

Here the summation is over all the energy shells. If the system is thermodynamically normal, $\exp[S - \beta E]$ decays exponentially for sufficiently large E as we see below. Notice that

$$\left. \frac{\partial S}{\partial E} \right|_V = \frac{1}{T(E)}. \tag{13.19}$$

As E increases, $T(E)$ increases indefinitely. Therefore at some large E, $T(E) > 2T$ and for such E $E \to E + \Delta E$ implies

$$w(E) e^{-\beta E} \to w(E) e^{-\beta E} e^{\Delta E (1/k_B T(E) - 1/k_B T)} = w(E) e^{-\beta E} \times e^{-\beta \Delta E / 2}. \tag{13.20}$$

Thus, the summand decays exponentially, so Z is well-defined.

As we see in **??** for sufficiently large systems

$$\log Z \sim \log \max_E \left[w(E)e^{-\beta E}\right] = -\beta A. \tag{13.21}$$

Thus, we have devised a statistical mechanically convenient way to compute the Helmholtz free energy. The resutl

$$A = -k_B T \log Z \tag{13.22}$$

with Z defined as (13.18) is called the canonical formalism.

13.9 Canonical formalism; error estimate

Since Z is a convergent sum

$$Z(T) = \sum_{0<E<cE_{\text{eq}}} w(E)e^{-\beta E} + \text{ small error} \tag{13.23}$$

must hold for some positive c, where E_{eq} is the E realizing max in (13.17). How large c do we need for this to happen? The specific heat is bounded, so (13.20) suggests that $c \simeq 2$ should already be good enough. To be safe let us choose c as some large (but system-size-independent) number. Thus, we can write

$$Z(T) = \sum_{0<E<cE_{\text{eq}}} w(E)e^{-\beta E} + \text{ small error.} \tag{13.24}$$

Here, the small error may be written, accroding to (13.20), as max $\left[w(E)e^{\beta E}\right]$ times some intensive number at the worst (largest). Therefore, we have the following trivial bounds:

$$\max_E w(E)e^{-\beta E} \le Z(T) \le \left[\frac{cE_{\text{eq}}}{\Delta E} + c'\right] \max_E w(E)e^{-\beta E}, \tag{13.25}$$

where c' is a system-size independent number. Notice that $E_{\text{eq}} = O[N]$ (extensivity), so

$$\log \frac{cE_{\text{eq}}}{\Delta E} = O[\log N] \tag{13.26}$$

Thus for $O[N]$ quantities

$$-\beta A = \log Z(T). \tag{13.27}$$

As you have seen, we have ignored the error of order $\log N/N$, which is very small for macroscopic systems.

13.10 Standard (textbook) 'derivation' of canonical formalism

The logic conventioanlly used to study isothermal systems is a familiar one: we regard the system as a small portion I of a big isolated system I+II, and assume that the system can freely exchange heat with its surroundings II.

The total energy E_0 of the compound system is given by

$$E_0 = E_{\rm I} + E_{\rm II}. \tag{13.28}$$

The number of microstates for system I (resp., II) with energy $E_{\rm I}$ (resp., $E_{\rm II}$) is denoted by $w_{\rm I}(E_{\rm I})$ (resp., $w_{\rm II}(E_{\rm II})$). Thermal contact is a very weak interaction, so the two systems are statistically independent. Hence, the number of microstates for the compound system with the energies $E_{\rm I}$ in I and $E_{\rm II}$ in II is given by

$$w_{\rm I}(E_{\rm I})w_{\rm II}(E_{\rm II}). \tag{13.29}$$

The total number $w(E_0)$ of microstates for the compound system must be the sum of this product over all the ways to partition energy between I and II. Therefore, we get

$$w_{\rm I+II}(E_0) = \sum_{0 \le E_{\rm I} \le E_0} w_{\rm I}(E_{\rm I})w_{\rm II}(E_0 - E_{\rm I}). \tag{13.30}$$

The system II is huge compared with I. Expand the entropy as follows:

$$S_{\rm II}(E_0 - \mathcal{E}) = S_{\rm II}(E_0) - \mathcal{E}\frac{\partial S_{\rm II}}{\partial E_{\rm II}} + \frac{1}{2}\mathcal{E}^2\frac{\partial^2 S_{\rm II}}{\partial E_{\rm II}^2} + \cdots \tag{13.31}$$

and denote the temperature of the heat bath (i.e., system II) by T:

$$\frac{\partial S_{\rm II}}{\partial E_{\rm II}} = \frac{1}{T}. \tag{13.32}$$

We wish to use this formula in equilibrium, so $\mathcal{E}$ should be close to the internal energy of system I. Therefore, due to the extensivity of internal energy this should be of order $N_{\rm I}$, the total number of particles in system I. Therefore,

$$\mathcal{E}\frac{\partial S_{\rm II}}{\partial E_{\rm II}} = O[N_{\rm I}]. \tag{13.33}$$

The second derivative in (13.31) is proportional to $1/\frac{\partial E}{\partial T} = 1/C_{V{\rm II}}$, where $C_{V{\rm II}}$ is the specific heat of II, which is $O[N_{\rm II}]$:

$$\mathcal{E}^2\frac{\partial^2 S_{\rm II}}{\partial E_{\rm II}^2} = -\frac{\mathcal{E}^2}{T^2 C_{V{\rm II}}} = \frac{O[N_{\rm I}]^2}{O[N_{\rm II}]} = O[N_{\rm I}]\frac{O[N_{\rm I}]}{O[N_{\rm II}]} \ll O[N_{\rm I}]. \tag{13.34}$$

Therefore, the ratio of the second term and the third term in (13.31) is of order $N_{\rm I}/N_{\rm II}$, which is negligibly small. Thus, (13.30) reads

$$w_{\rm I+II}(E_0) \simeq e^{S_{\rm II}(E_0)/k_B}\sum_{\mathcal{E}} w_{\rm I}(\mathcal{E})\mathrm{e}^{-\beta\mathcal{E}}, \tag{13.35}$$

or

$$w_{\rm I+II}(E_0)e^{-S_{\rm II}(E_0)/k_B} \simeq \sum_{\mathcal{E}} w_{\rm I}(\mathcal{E})\mathrm{e}^{-\beta\mathcal{E}}, \tag{13.36}$$

where a standard notation

$$\beta = 1/k_BT \tag{13.37}$$

is used.

With the aid of Boltzmann's principle, we have, with E being the equilibrium internal energy of system I,

$$k_B \log w_{\mathrm{I+II}}(E_0) = S_{\mathrm{I}}(E) + S_{\mathrm{II}}(E_0 - E), \tag{13.38}$$

so (from now on let's drop the suffix I to denote the system)

$$k_B \log[w_{\mathrm{I+II}}(E_0)e^{-S_{\mathrm{II}}(E_0)/k_B}] = S(E) + S_{\mathrm{II}}(E_0 - E) - S_{\mathrm{II}}(E_0) = S(E) - E/T = -A/T. \tag{13.39}$$

That is, (28.27) reads (suffix I dropped from w_{I})

$$e^{-\beta A} = \sum_{\mathcal{E}} w(\mathcal{E})\mathrm{e}^{-\beta\mathcal{E}}. \tag{13.40}$$

13.11 Difficulty of 'standard textbook approach' 13.10

The conventional argument that is adopted by almost all the textbooks has two flaws.
(1) The resultant canonical formalism are not legitimately used to understand phase transitions. The twice differentiability of S as a function of E is required to justify the use of the Taylor expansion, but this excludes many phase transitions.
(2) The outer thermostat is used in order to save the description of the whole system as an isolated mechanical system, but the larger is the system, the harder becomes the pure mechanics.

Thus, I recommend the approach explained in **13.7**-**13.9**. As you will see quite parallel formalisms work for any ensembles we will encounter later. Besides, the appraoch tells us how big the system should be for us to use statistical mechanics freely.

M0re fundamentally, it is unscientific to base a theory on the metaphysics based on mechanics (that Helmoholtz adopted at least when he was active in thermodynamics).

13.12 Canonical formalism: summary

Thus, we have arrived at our desired formalism, the *canonical formalism* that gives A directly: Let

$$Z = \sum_{\mathcal{E}} w(\mathcal{E})e^{-\beta\mathcal{E}}. \tag{13.41}$$

Then,

$$A = -k_BT \log Z. \tag{13.42}$$

Z is called the *canonical partition function*, and this method to compute the free energy is called the *canonical formalism*.

A more microscopic expression is possible:

$$Z = \sum_{\text{all microstates}} \mathrm{e}^{-\beta\mathcal{E}} = \mathrm{Tr}\, \mathrm{e}^{-\beta\mathcal{H}}. \tag{13.43}$$

Here, the sum over all the microstates is, in the quantum mechanical cases, the summation over all the eigenvalues of the Hamiltonian, so quantum mechanically, we may use the trace to compute the partition function. If we decompose the sum as follows, we can easily understand this formula:

$$\sum_{\text{all microstates}} = \sum_{\mathcal{E}} \sum_{\text{all microstates with energy} \sim \mathcal{E}}, \tag{13.44}$$

but

$$\sum_{\text{all microstates with energy} \sim \mathcal{E}} \mathrm{e}^{-\beta\mathcal{E}} = w(\mathcal{E})\mathrm{e}^{-\beta\mathcal{E}}. \tag{13.45}$$

13.13 Ensemble equivalence

We can compute S directly from $w(E, X)$ using Boltzmann's principle (the microcanonical formalism). E may be solved from this. Then, using thermodynamics (Legendre transformation **11.12**), we can compute A. On the other hand we can use the canonical formalism to compute A directly from Z. Then, using thermodynamics (Legendre transromation) we can compute E. The relative error is of order $\log N/N$.

Thus, rthe microcanonical and the canonical formalisms give consistent thermodynamics if the system size is large enough. This i an example of a general proposition called the ensemble equivalence

13.14 Principle of equal probability

The conventional more or less standard statistical mechanics assumes a principle called the *principle of equal probability*: if we sample a microstate from $w(E, X)$ every microstate is equally probable. Why this principle may be used to understand thermodynamic quantities is explained in Appendix 13A. If we accept this principle, then in each $w(E, X)$ the probability to sample any subset $u \in w(E, X)$ is proportional to its phase volume (classically) or number of states in it (quantum-mechanically). Thus, we can interpret that the probability for a microstate γ is

$$P(\gamma) = \frac{1}{Z} e^{-\beta H(\gamma)}. \tag{13.46}$$

This is called the *canonical distribution*.

13.15 Warning about the canonical distribution

(13.46) may look as if it gives the probability for individual microstates. However, for a macroscopic system there is no way to single out individual microstates, so there is no direct way to verify (13.46) experimentally. Thus, the expression itself is only formal and no physical meaning as it is. A thermodynamic justification of the principle of equal probability (see Appendix 13A) corroborates this warning.

(13.46) is legitimate only when we compute expectation values of macro or mesoscopic observables or probabiliities of macro or mesoscopic events.

13.16 The Gibbs-Helmholtz formula

Once the canonical partition function is known, the internal energy of the system can be obtained easily:

$$E = \langle \mathcal{E} \rangle = \sum_{\mathcal{E}} P(\mathcal{E})\mathcal{E} = \frac{1}{Z}\sum_{\mathcal{E}} \mathcal{E} w_{\mathrm{I}}(\mathcal{E})\mathrm{e}^{-\beta\mathcal{E}} = -\frac{\partial \log Z(\beta)}{\partial \beta}, \tag{13.47}$$

where Z (cf. (13.43)) is explicitly written as a function of β. (13.47) is a thermodynamically well-known formula:

$$\left.\frac{\partial (A/T)}{\partial (1/T)}\right|_V = E, \text{ or } \left.\frac{\partial \beta A}{\partial \beta}\right|_V = E, \tag{13.48}$$

the *Gibbs-Helmholtz formula*. Do not forget that this is a purely thermodynamic relation.

13.17 Schottky defects revisited

Let's revisit the Schottky defects. With $w(n)$ known (see (13.4)), it is easy to compute Z:

$$Z = \sum_n w(n)e^{-\beta n\varepsilon} = (1 + e^{-\beta\varepsilon})^N, \tag{13.49}$$

where we have used the *binomial theorem*:

$$(x+y)^N = \sum_{n=0}^{N} \binom{N}{n} x^n y^{N-n}. \tag{13.50}$$

If you are uncomfortable, review Appendix 2A after Lecture 2. Thus,

$$\sum_{n=0}^{N} w(n)e^{-\beta n\varepsilon} = \sum_n \binom{N}{n} \left(e^{-\beta\varepsilon}\right)^n 1^{N-n} = (1 + e^{-\beta\varepsilon})^N. \tag{13.51}$$

However, you can probably write down the right-most formula directly: the canonical partition function is a sum over all the possible microstates

$$Z = \sum_{\varepsilon(1)\in\{0,\varepsilon\},\cdots,\varepsilon(N)\in\{0,\varepsilon\}} e^{-\beta\sum_{i=1}^{N}\varepsilon(i)}, \tag{13.52}$$

where $\varepsilon(i)$ is the energy of the ith lattice point (occupied 0 or empty ε). Here, do not forget that a 'microstate' is a microscopically described state of the whole macro system; in our case $(\varepsilon(1), \varepsilon(2), \cdots, \varepsilon(N))$ is a microstate, where each $\varepsilon(i)$ is 0 or ε. Do not confuse the microstate and the elementary states of individual microscopic entities. Notice that all the combinations of the lattice states show up, so

$$Z = \left(\sum_{\varepsilon(1)\in\{0,\varepsilon\}} e^{-\beta\varepsilon(1)}\right)\cdots\left(\sum_{\varepsilon(N)\in\{0,\varepsilon\}} e^{-\beta\varepsilon(N)}\right) = (1+e^{-\beta\varepsilon})^N. \tag{13.53}$$

Since this transformation is the key that makes the canonical formalism often easier than the microcanonical formalism, a more detailed explanation is in the following small lettered portion.

Suppose there are N lattice points. Each lattice point has several states $a, b, c, \cdots$ with the corresponding 'excitation energies' $\varepsilon(a), \varepsilon(b)$, etc. Since the total energy of the system, that is, the energy of the microstate, reads

$$\mathcal{H} = \varepsilon(a_1) + \varepsilon(a_2) + \cdots + \varepsilon(a_N), \tag{13.54}$$

the canonical partition function is computed as

$$Z = \sum_{a_1,a_2,\cdots,a_N\in\{a,b,c,\cdots\}} e^{-\beta[\varepsilon(a_1)+\varepsilon(a_2)+\cdots]}. \tag{13.55}$$

Here, the summation is over all the possible combinations of the states of individual particles.

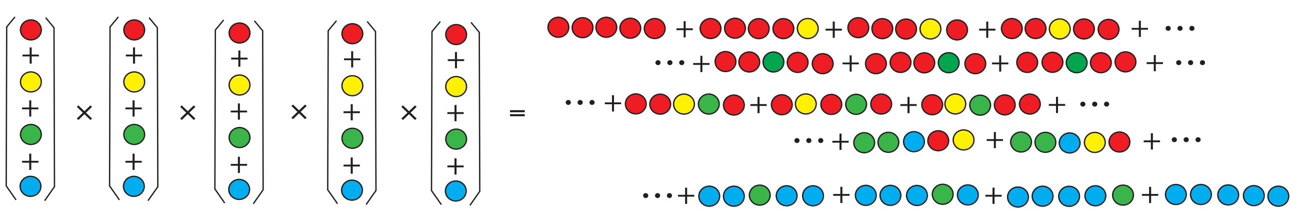


Figure 13.2: Illustration using a 5 lattice point toy model. Each column on the LHS corresponds to the sum over all states at each lattice point (i.e., Z_1 in (13.57)). The RHS illustrates the partition function Z of the system; 5-color-ball strings correspond to microstates. All the possible microstates appear once and only once on the RHS.

Since all the combinations appear once and only once, we can rewrite this as (see Fig. 13.2)

$$Z = \left(\sum_{a_1\in\{a,b,c,\cdots\}} e^{-\beta\varepsilon(a_1)}\right)\left(\sum_{a_2\in\{a,b,c,\cdots\}} e^{-\beta\varepsilon(a_2)}\right)\cdots\left(\sum_{a_N\in\{a,b,c,\cdots\}} e^{-\beta\varepsilon(a_N)}\right) = Z_1^N, \tag{13.56}$$

where

$$Z_1 = \sum_{a_1 \in \{a,b,c,\cdots\}} e^{-\beta\varepsilon(a_1)} \tag{13.57}$$

is the 'canonical partition function' of a single lattice point about its (internal) states. Notice that you cannot usually do this for the microcanonical approach, because not all the microstates appear in the computation of the microcanonical partition function w.

Thus, if 'particles' or 'lattice points' do not interact with each other, we can guess

$$\sum_{\text{microstates}} = \left(\sum_{\text{one particle states}} \right)^N \tag{13.58}$$

From this the Helmholtz free energy of the lattice with Schottky defects immediately follows:

$$A = -Nk_BT\log(1+e^{-\beta\varepsilon}). \tag{13.59}$$

We can get entropy by differentiation:

$$S = -\frac{\partial A}{\partial T} = Nk_B\log(1+e^{-\beta\varepsilon}) + N\frac{\varepsilon}{T}\frac{e^{-\beta\varepsilon}}{(1+\mathrm{e}^{-\beta\varepsilon})}. \tag{13.60}$$

Various other partition functions will be introduced in these lectures. As you will learn later, if you wish to study the thermodynamics of a system, any formalism will be OK, as long as the system is large enough (roughly speaking, if $\log N/N \ll 1$). We have so far discussed the microcanonical and the canonical formalism. Let us check that the canonical result for S agrees with the microcanonical result for this simple example. The microcanonical approach gives us

$$S = -Nk_B\left[\frac{n}{N}\log\frac{n}{N} + \left(1-\frac{n}{N}\right)\log\left(1-\frac{n}{N}\right)\right], \tag{13.61}$$

and

$$\frac{n}{N} = \frac{1}{1+e^{\beta\varepsilon}}. \tag{13.62}$$

Combining both, we get

$$S = -Nk_B\left[\frac{1}{1+e^{\beta\varepsilon}}\log\frac{1}{1+e^{\beta\varepsilon}} + \frac{e^{\beta\varepsilon}}{1+e^{\beta\varepsilon}}\log\frac{e^{\beta\varepsilon}}{1+e^{\beta\varepsilon}}\right]. \tag{13.63}$$

This indeed agrees with (13.60).

13.18 Another example: Dipoles on the honeycomb lattice with an easy direction

Consider a honeycomb lattice with N lattice points. At each lattice point is a dipole that can point in one of the three bond directions. If a dipole is along the easy direction, its energy is zero. If it points in other directions, its energy is ε (> 0). We assume dipoles do not interact.

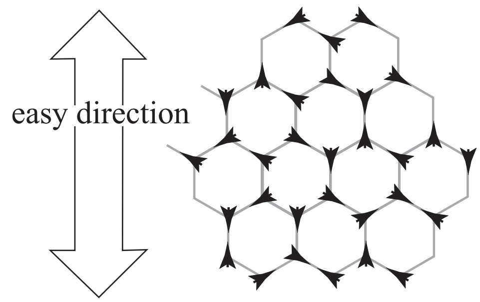


Figure 13.3: If a dipole is along the easy direction, it is energetically stabilized (by ε).

The canonical ensemble approach is easy. Using the idea explained around (13.53), we get

$$Z(T) = (1 + 2e^{-\beta\varepsilon})^N, \tag{13.64}$$

because at each lattice point one direction is an easy direction, and the other two have the energy penalty of ε. The internal energy is

$$E = -\frac{\partial \log Z}{\partial \beta} = N\varepsilon \frac{2e^{-\beta\varepsilon}}{1 + 2e^{-\beta\varepsilon}}. \tag{13.65}$$

With the aid of the principle of equal probability, we can ask the probability for a dipole to be in the leftward tilt:

$$P(\text{left}) = \frac{e^{-\beta\varepsilon}}{1 + 2e^{-\beta\varepsilon}}. \tag{13.66}$$

The probability to point in the easy direction is

$$P(\text{easy}) = \frac{1}{1 + 2e^{-\beta\varepsilon}}. \tag{13.67}$$

⟪Dipole example with the microcanonical formalism⟫

It is rather stupid to study this system with the microcanonical approach, but let us check that we can obtain the same result. Let A be the state of dipole tilting to the left, B to the right and C in the easy direction. Let n_X ($X = A, B$ or C) be the number of dipoles in state X. $N = n_A + n_B + n_C$. The number of microstates with definite n_A and n_B (n_C is determined) is (cf. the multinomial coefficients, see Appendix 2A)

$$\frac{N!}{n_A! n_B! n_C!}. \tag{13.68}$$

To obtain the microstates with $E = \varepsilon(N - n_C) = \varepsilon(n_A + n_B)$, we must collect all possible n_A and n_B compatible with the energy condition:

$$\begin{aligned} w(\varepsilon(N - n_C)) &= \sum_{n_A + n_B = N - n_C} \frac{N!}{n_A! n_B! n_C!} = \sum_{n_A + n_B = N - n_C} \frac{N!}{(N - n_C)! n_C!} \frac{(N - n_C)!}{n_A! n_B!}. \\ &= \binom{N}{n_C} \sum_{n_A = 0}^{N - n_C} \frac{(N - n_C)!}{n_A! n_B!} = \binom{N}{n_C} 2^{N - n_C}. \end{aligned}$$

You should have realized that this is easily obtained as follows. First we choose n_C sites to place easy-direction dipoles. There are $\binom{N}{n_C}$ ways. Then, choose the remaining dipoles to tilt leftward or rightward. There are 2^{N-n_C} ways. Hence, we obtain the above result.

Thus, the entropy is

$$S = k_B \log w(\varepsilon(N - n_C)) = -Nk_B \left[\frac{n_C}{N} \log \frac{n_C}{N} + \left(1 - \frac{n_C}{N}\right) \log \left(1 - \frac{n_C}{N}\right)\right] + (N - n_C)k_B \log 2. \tag{13.69}$$

With the aid of the Gibbs relation (notice that $dE = -\varepsilon dn_C$)

$$\frac{1}{T} = \frac{\partial S}{\partial E} = -\frac{1}{\varepsilon}\frac{\partial S}{\partial n_C} = \frac{k_B}{\varepsilon} \log \frac{n_C}{N - n_C} + \frac{k_B}{\varepsilon} \log 2. \tag{13.70}$$

That is,

$$e^{-\beta\varepsilon} = \frac{N - n_C}{2n_C} \tag{13.71}$$

From this we obtain

$$n_C = \frac{N}{1 + 2e^{-\beta\varepsilon}}. \tag{13.72}$$

The internal energy is

$$E = \varepsilon(N - n_C) = N\varepsilon\frac{2e^{-\beta\varepsilon}}{1 + 2e^{-\beta\varepsilon}}, \tag{13.73}$$

which is identical to (13.65).

Appendix 13A. How to derive the principle of equal probability

You will see how important the law of large numbers is to establish statistical mechanics.

We first summarize fundamental properties of thermodynamic equilibrium states. We have already noted:
(O') If the equilibrium system is partitioned into two (approximately equal[261]) parts (by a plane), then
(i) each piece in isolation is in equilibrium, and
(ii) if these pieces are joined as before the partition, the joined result is in equilibrium as a whole, and its state cannot be (thermodynamically) distinguished from the state before the partition (Fig. 13.4).
We further know the fourth law or its direct consequence: Thermodynamic observables are obtainable from the partitioned system.

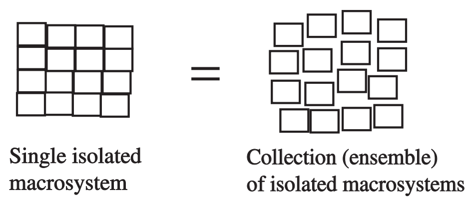


Figure 13.4: Thermodynamic quantities can be obtained from 'pieces' obtained by partitioning of an equilibrium state.

Thus, we may conclude that thermodynamic equilibrium states are partitioning-rejoining invariant.

Although usually not stated clearly, we know one more fact:
(Y) *Invariance under thermal contact* of equilibrium states: Any equilibrium state of a thermally isolated system has a heat bath (*individual heat bath*) such that thermal contact with it does not alter its thermodynamic state (Fig. 13.5).

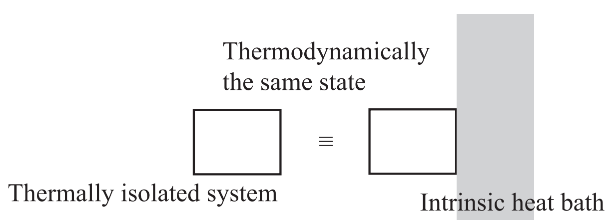


Figure 13.5: There is a heat bath that does not destroy a given equilibrium system upon thermal contact.

(O') and (Y) imply that the following procedure keeps thermal equilibrium intact

[261] This requirement is only to avoid extreme cases in which one part contains not macroscopic number of particles.

(Fig. 13.6).
(i) Partition a thermally isolated equilibrium system into (macroscopic) pieces.
(ii) Attach each piece to its private individual heat bath for a while, and then again thermally isolate it.
(iii) Re-join all the pieces as before to reconstruct the whole piece.

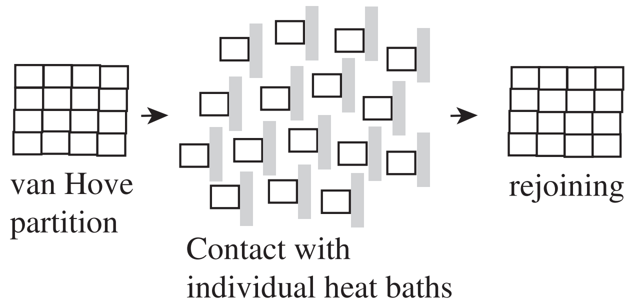


Figure 13.6: An equilibriums system may be replaced by statistically independent pieces to obtain thermodynamic quantities.

The above procedure does not alter thermodynamic observables of the system. Thus, a macroscopic system in thermal equilibrium may be replaced with a collection of many statistically independent mechanical systems, if we are interested in thermodynamic quantities. In other words, thermodynamics observables are such physical quantities that are quite insensitive to subtle correlations (as quantum mechanics implies) among portions of a system. Therefore, we may use a brutal procedure to compute them.

How many such independent pieces can we find in an ordinary macroobject? 1 mm^3 is big enough from the molecules' point of view, so in a cube with 10 cm edge, we can easily expect more than 10^6 macroscopic subsystems; we may safely use the law of large numbers, so thermodynamic quantities obtained from the partitioned system and the actual values are quite close.

You may even expect that to compute thermodynamic quantities, we may use the principle of equal probability = all the microstates compatible with a given thermodynamic state are equally probably sampled.

The logic to demonstrate this statement is as follows:
(i) The direct product model may be used as a micro-model of a thermodynamic system.
(ii) Then, the asymptotic equipartition (see below) implies that the correct expectation values are obtained, even if we assume all the energy states are equally probably distributed.
(iii) Thus, to obtain thermodynamics, we may assume that all the compatible microstates are equally probable. This is called the *principle of equal probability* traditionally assumed to obtain statistical mechanics.

The *asymptotic equipartition* is nothing but the law of large numbers.

$$\frac{1}{n}\log P(x_1,\cdots,x_n) = \frac{1}{n}\sum_i \log P(x_i) \;\; \text{converges to } -s \tag{13.74}$$

in the large n limit. Here s is the entropy per piece. That is, the asymptotic equipartition law:

$$P(x_1,\cdots,x_n) = e^{-ns\pm o[n]} \tag{13.75}$$

holds independent of the actual microstate $\{x_1,\cdots,x_n\}$.

Q13.1 [Noninteracting magnetic moments with easy directions]
There is a 2D square lattice with M lattice points. On each lattice point is a magnetic moment that can point only in the lattice bond directions (4 directions as illustrated), but the $\pm y$ directions are the easy directions: if the dipole is along the y-axis, it is stable, that is, the energy of the dipole along the x-axis is ε (> 0 more energy) and that along the y-axis is zero. We do not pay attention to the kinetic energy of the system. You may ignore the interactions among dipoles.

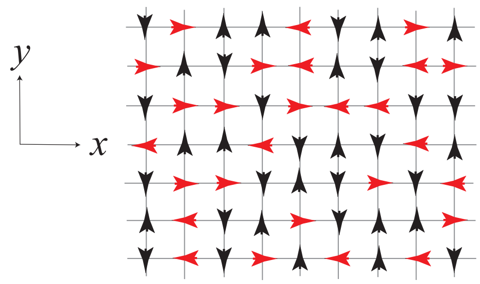


Figure 13.7: Each dipole can point only 4 direction along the lattice bonds.

(1) What is the canonical partition function of the system (the temperature is T)?
(2) What is the average energy per dipole?
(3) Compute the entropy $S(T)$ per dipole. What is the difference $S(\infty) - S(0)$? How many bits is this? Is this consistent with the intuitive interpretation of entropy per molecule as the number of YES-NO questions?
(4) Compute the 'microcanonical partition function' $w(N\varepsilon)$ ($0 \le N \le M$).
(5) Show that the entropy you computed from the microcanonical scheme (Boltzmann's principle) and the result (3) agree. [Compute N/M as a function of T (use $1/T = \partial S/\partial E$) and get rid of N/M from the formula to obtain the result of (3).]

Solution. (1) Needless to say, you can start from the very definition of the canonical partition function, BUT notice that if you collect all the microstates (= microscopic states = mechanically describable whole-system states), all the states of microscopic entities (molecules, etc., in our case dipoles sitting on the lattice points) appear once and only once (recall Fig. 13.2). Therefore, to construct the partition function for the whole lattice, we study all the states of each microscopic entity to make their individual canonical partition functions (in our case $1+1+e^{-\beta\varepsilon}+e^{-\beta\varepsilon}$) and multiply them over the whole lattice:

$$Z(T) = (2 + 2e^{-\beta\varepsilon})^M. \tag{13.76}$$

(2) Using the Gibbs relation, we get

$$\frac{E}{M} = -\frac{1}{M}\frac{\partial \log Z}{\partial \beta} = \frac{\varepsilon e^{-\beta\varepsilon}}{1 + e^{-\beta\varepsilon}}. \tag{13.77}$$

(3) Since $A = E - TS$, $S = (E - A)/T$

$$\frac{S}{M} = k_B \log(2 + 2e^{-\beta\varepsilon}) + \frac{\varepsilon}{T}\frac{e^{-\beta\varepsilon}}{1 + e^{-\beta\varepsilon}}. \tag{13.78}$$

$S(0) = k_B \log 2$ (notice that for any n, $x^n e^{-x} \to 0$ in the $x \to \infty$ limit) and $S(\infty) = k_B \log 4$, so ΔS is just 1bit. At $T = 0$ the dipoles are always along y (2 directions), but at $T = \infty$ they can evenly assume 4 directions (i.e., along x and y directions). Thus, if we ask one yes-no question ("Is it along y?") we can reduce the uncertainty in the equilibrium state at $T = \infty$ to that at $T = 0$. In other words, to identify the state of a dipole in the $T \to \infty$ limit we need 2 bits (2 questions), because we must find 1 particular state out of 4 possibilities. In the $T \to 0$ limit all the dipoles are along the easy direction, so there are only 2 choices for each dipole. Therefore, we need only one question to pinpoint the state of a dipole. ΔS just corresponds to the difference in the numbers of questions we must ask.

(4) You can immediately obtain

$$w(N\varepsilon) = \binom{M}{N} 2^M, \tag{13.79}$$

because 2 choices along x and along y can be selected without affecting the system energy.

A more pedestrian way (which I do not recommend) is to introduce n_1, n_2, n_3 and n_4 pointing respectively $+x$, $-x$, $+y$ and $-y$. $N = n_1 + n_2$ (x-direction) and $M - N = n_3 + n_4$ (y-direction):

$$w(N\varepsilon) = \sum_{n_1=0}^{N} \sum_{n_3=0}^{M-N} \frac{M!}{n_1!(N-n_1)!n_3!(M-N-n_3)!}, \tag{13.80}$$

but an easy reorganization is: (i) choose N parallel x dipoles, and then (ii) count the number of ways to point $+$ and $-$ directions:

$$w(N\varepsilon) = \binom{M}{N} \sum_{n_1=0}^{N} \sum_{n_3=0}^{M-N} \binom{N}{n_1} \binom{M-N}{n_3} = \binom{M}{N} 2^N 2^{M-N}. \tag{13.81}$$

This is just the answer above.

(5) Thanks to Boltzmann

$$\frac{S}{M} = -k_B \left[\frac{N}{M} \log \frac{N}{M} + \left(1 - \frac{N}{M}\right) \log \left(1 - \frac{N}{M}\right) \right] + k_B \log 2. \tag{13.82}$$

I strongly urge you to learn the following by heart:

$$\log \binom{M}{N} = -M \left[\frac{N}{M} \log \frac{N}{M} + \left(1 - \frac{N}{M}\right) \log \left(1 - \frac{N}{M}\right) \right]. \tag{13.83}$$

Since

$$\frac{1}{T} = \frac{k_B}{\varepsilon} \frac{\partial S}{\partial N} = -\frac{k_B}{\varepsilon} \log \frac{N}{M-N}, \tag{13.84}$$

we have

$$N = \frac{M}{1 + e^{-\beta\varepsilon}}. \tag{13.85}$$

Computing N/M and using it in the entropy formula above, we get

$$\begin{aligned}
\frac{S}{M} &= -k_B \left[\frac{N}{M}\log\frac{1}{1+e^{-\beta\varepsilon}} + \left(1 - \frac{N}{M}\right)\log\left(\frac{e^{-\beta\varepsilon}}{1+e^{-\beta\varepsilon}}\right)\right] \\
&= k_B \left[\frac{N}{M}\log(1+e^{-\beta\varepsilon}) + \left(1-\frac{N}{M}\right)\log(1+e^{-\beta\varepsilon})\right] + k_B \log 2 - k_B \frac{e^{-\beta\varepsilon}}{1+e^{-\beta\varepsilon}}\log\left(e^{-\beta\varepsilon}\right) \\
&= k_B \log(2 + 2e^{-\beta\varepsilon}) + \frac{\varepsilon}{T}\frac{e^{-\beta\varepsilon}}{1+e^{-\beta\varepsilon}}.
\end{aligned}$$

Q13.2 [Magnet under constant magentic field]
It is convenient to study a magnet under constant magnetic field B rather than under constant magnetization M. Then, the thermodynamic independent variables should be T, B rather than E, M. Therefore, we should use the 'magnetic-counterpart' of the Gibbs free energy $\tilde{G} = A - BM$ rather than the Helmholtz free energy A itself.[262] Notice that $d\tilde{G} = -SdT - MdB$.
(1) Let H_0 be the Hamiltonian (energy) of the magnetic system. Define an appropriate partition function Q that directly gives

$$\tilde{G} = -k_B T \log Q(T, B). \tag{13.86}$$

You must define Q in terms of $Z(T, M)$. [Needless to say, **Q12.2** is a hint, but be careful about the sign.]
(2) Consider a collection of N magnetic dipoles μ_i whose magnetization can be written as $M = \sum \mu_i$. The magnetic moments can point only up or down state (of value $\pm\mu$) aligned to the magnetic field direction (say, along the z-axis; its potential energy is $\mp B\mu$). If we ignore the kinetic energy of the magnetic moments, the system Hamiltonian of the noninteracting magnetic moments is just 0 (no energy associated).[263] Compute Q and obtain the magnetization as a function of T and B.
(3) Show that M obtained from the microcanonical approach agrees with the result of (2).

Solution
(1)

$$-\frac{\tilde{G}}{T} = -\frac{A}{T} - \frac{BM}{T} = k_B \log \sum_M Z(T, M) e^{\beta BM} \tag{13.87}$$

[262] Recall $G = A + PV$. Compare $dE = TdS + BdM$ and $dE = TdS - PdV$. YOU MUST MEMORIZE THE BASIC GIBBS RELATION.

[263] $-B\sum \mu_i$ is the potential energy stored in the relation between the system and the device generating the magnetic field B as we have already seen in **Q8.2**. Many books confuse this point, so be careful.

That is,

$$\tilde{G} = -k_B T \log Q \tag{13.88}$$

with

$$Q = \sum_M e^{-\beta(H_0 - BM)}. \tag{13.89}$$

However, in our case the system energy is zero ($H_0 = 0$), so $Z(T, M) = w(0, M)$ or

$$Q = \sum e^{\beta BM} = \sum_{\mu_i \in \{\mu, -\mu\}} e^{\beta B \sum_i \mu_i}, \tag{13.90}$$

where the summation is over all the microstates.
(2)

$$Q = \sum_M e^{\beta HM} = \left(2 \cosh \frac{B\mu}{k_B T}\right)^N. \tag{13.91}$$

Hence,

$$\tilde{G} = -N k_B T \log \left(2 \cosh \frac{B\mu}{k_B T}\right). \tag{13.92}$$

From this

$$M = -\left.\frac{\partial \tilde{G}}{\partial B}\right|_T = N\mu \tanh \frac{B\mu}{k_B T}. \tag{13.93}$$

(3) The microcanonical partition function we need is $w(0, M)$. Let N_+ be the number of up-spins. Then,

$$w = \binom{N}{N_+}, \tag{13.94}$$

so

$$S = -k_B N \left[\frac{N_+}{N} \log \frac{N_+}{N} + \left(1 - \frac{N_+}{N}\right) \log \left(1 - \frac{N_+}{N}\right)\right]. \tag{13.95}$$

The number of down-spins is $N - N_+$, so $M = \mu(2N_+ - N)$. Therefore, $N_+ = (M + \mu N)/2\mu$. From $dS = -(B/T)dM$ for our system (recall we cannot change $E \equiv 0$),

$$\frac{B}{T} = -\left.\frac{\partial S}{\partial M}\right|_E = -\frac{1}{2\mu} \left.\frac{\partial S}{\partial N_+}\right|_E = \frac{k_B}{2\mu} \log \frac{N_+/N}{1 - (N_+/N)}, \tag{13.96}$$

that is,

$$N_+ = \frac{e^{2\beta\mu B}}{1 + e^{2\beta\mu B}} = \frac{N}{1 + e^{-2\beta\mu B}}. \tag{13.97}$$

From this, we get the same result:

$$M = N\mu \frac{1 - e^{2\beta\mu B}}{1 + e^{2\beta\mu B}} = N\mu \tanh \frac{\mu B}{k_B T}. \tag{13.98}$$

Which do you think is easier?

14 Classical ideal gas and quantum-classical correspondence

Summary
$*$ All ensembles are equivalent. You can use any that you can compute most easily.
$*$ We compute the classical ideal gas partition function. We must treat all gas particles indistinguishable.
$*$ The canonical partition function of a classical fluid system reads

$$Z = \frac{1}{N!h^{3N}} \int d\Gamma\, e^{-\beta H}.$$

$*$ The classical-quantum partition function relation may be understood as the requirement that the partition function must be dimensionless.
$*$ Equipartition of energy and classical specific heat is studied with the aid of the canonical formalism. Quantization turns out to be mandatory.

Key words
ensembles, ensemble equivalence, Gibbs paradox, indistinguishability, Frenkel defect, equipartition of energy

What you should be able to do
$*$ Get the canonical partition function of a classical gas with dimensional analysis.
$*$ Be able to explain what the ensemble equivalence means, and the condition that we can use any ensemble.
$*$ Be able to use the equipartition formula to compute simple averages.
$*$ Be able to explain why the specific heat of a diatomic gas is not as big as expected classically.

14.1 Review: ensemble equivalence

We have learned two formalisms to do equilibrium statistical mechanics:

$$S = k_B \log w(E,X) \quad \text{microcanonical formalism,} \tag{14.1}$$

$$A = -k_B T \log Z(T,X) \quad \text{canonical formalism.} \tag{14.2}$$

These formalisms are equivalent if $\log N/N \ll 1$. The meaning of 'equivalence' is: The free energy computed from S according to (14.1) agrees with that computed directly from statistical mechanics according to (14.2); The entropy computed from A according to (14.2) agrees with S directly computed statistical mechanically from (14.1).

Here, we discuss only the equivalence of the microcanonical and canonical ensembles, but we will encounter many other ensembles and they are equivalent in the sense that any of them can be used to obtain the full thermodynamic potential of the system. In short, you may use any 'ensemble.' This is called the ensemble equivalence. Here, '*ensemble*' means the collection of microscopic states with a definite summation rule (or probability assignment, if we use the principle of equal probability).

14.2 Derivation of Maxwell's distribution

The principle of equal probability implies that the probability for a particular particle, called 0 here, to have energy ε in a macrosystem is given by

$$P(\varepsilon) = \sum_{\gamma \in \Gamma_\varepsilon} \frac{1}{Z} e^{-\beta H(\gamma)}, \tag{14.3}$$

where Γ_ε is the totality of microstates compatible with particle 0 to have energy around ε. The summation is an informal expression of summing or integration over all the appropriate microstates.[264]

For an ideal gas, $H(\gamma)$ consists of a sum of the form $\sum_i \varepsilon_i$, where ε_i is the energy for i-th particle. The variables are statistically independent; this is the meaning of the ideality. Therefore, obviously,

$$P(\varepsilon) \propto e^{-\beta\varepsilon}. \tag{14.4}$$

Thus, we recover Maxwell's distribution function, because $\varepsilon = m\boldsymbol{v}^2/2$:

$$P(\boldsymbol{v}) \propto e^{-m\boldsymbol{v}^2/2k_BT}. \tag{14.5}$$

14.3 Frenkel defect

Let us study an example: the *Frenkel defects*. As illustrated in Fig. 14.1 particles leave their original lattice points and wander into non-lattice positions (interstitial positions). There are N lattice points and M interstitial points. There are total N particles and n particles leave their lattice points and move into interstitial sites. There is an energy cost of ε to leave a lattice point to move to an interstitial site.

[264]Clearly notice that we are not dealing with individual microstates of a macrosystem, because Γ_ε contains macroscopically many microstates.

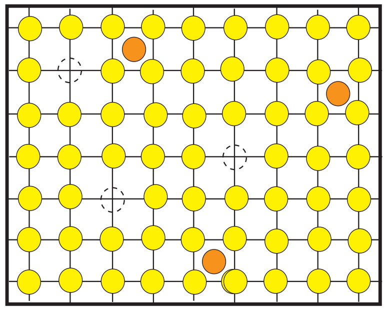


Figure 14.1: Particles with darker color are interstitial particles (excited particles), which leave vacancies (dotted circles).

The system energy is $E = n\varepsilon$. Thus, (we write $w(E)$ as $w(n)$)

$$w(n) = \binom{N}{n}\binom{M}{n}, \tag{14.6}$$

and the canonical partition function reads

$$Z(T) = \sum_{n=0}^{N} w(n)e^{-\beta n\varepsilon} = \sum_{n=0}^{N} \binom{N}{n}\binom{M}{n} e^{-\beta n\varepsilon}. \tag{14.7}$$

Unfortunately, this cannot be summed in a closed form. However, in this case, it is very easy to prove the ensemble equivalence as follows.

14.4 Equivalence of microcanonical and canonical ensembles

In this lecture notes, the canonical ensemble was introduced with the logic expecting the ensemble equivalence **13.8**, but this concept is of superb importance for statistical thermodynamics, let us repeat the error analysis.

Since all the summands are positive, the following inequalities are obvious:

$$\max_n \left[w(n)e^{-\beta n\varepsilon}\right] \le Z(T) \le N \max_n \left[w(n)e^{-\beta n\varepsilon}\right]. \tag{14.8}$$

On the other hand, we have

$$\max_n \left[w(n)e^{-\beta n\varepsilon}\right] = \exp\left[\frac{1}{k_B}\max_E (S - E/T)\right], \tag{14.9}$$

but the 'honest' definition of the Helmholtz free energy is

$$-A = \max_E [TS - E]. \tag{14.10}$$

Therefore, (14.8) reads

$$-A/k_BT \le \log Z(T) \le -A/k_BT + \log N. \tag{14.11}$$

A is an extensive quantity, so it is of order N. Therefore, if you can ignore $\log N/N$ as very small, $-k_BT\log Z(T)$ (the free energy directly obtained by the canonical formalism of statistical mechanics) and the free energy obtained (using thermodynamics, i.e., (14.10)) from entropy (which is computed statistical-mechanically with the aid of the microcanonical approach) are indistinguishable.

14.5 Why the theroetical structure of statistical thermodynam is very stable and reliable

Although our demonstration of the ensemble equivalence **14.4**, in the present case the equivalence of the canonical and microcanonical formalisms, relies on a particular example, the logic we have employed is identical to the key logic to demonstrate the ensemble equivalence generally and rigorously: Z is sandwiched between the maximum term in the sum and the maximum term $\times$ something proportional to N.

You must clearly recognize that the estimations (bounds) required by the proof above are very obvious (not at all delicate). That is why the results are general and very stable.

Also you must clearly recognize that to compute Z is equivalent to estimating its maximum summand.

14.6 Frenkel defect, microcanonical approach

Let us continue the Frenkel defect problem. Let us compute entropy using Boltzmann's principle.

$$S = k_B \log \binom{N}{n}\binom{M}{n}. \tag{14.12}$$

We use Stirling's approximation, or

$$\log \binom{A}{B} = -A\left[\frac{B}{A}\log\frac{B}{A} + \left(1-\frac{B}{A}\right)\log\left(1-\frac{B}{A}\right)\right]. \tag{14.13}$$

We obtain

$$S/k_B = -N\left[\frac{n}{N}\log\frac{n}{N} + \left(1-\frac{n}{N}\right)\log\left(1-\frac{n}{N}\right)\right] - M\left[\frac{n}{M}\log\frac{n}{M} + \left(1-\frac{n}{M}\right)\log\left(1-\frac{n}{M}\right)\right]. \tag{14.14}$$

We need temperature, so we use the Gibbs relation $dS = (1/T)dE + (P/T)dV + \cdots$:

$$\frac{1}{T} = \left.\frac{\partial S}{\partial E}\right|_V, \tag{14.15}$$

but $dE = \varepsilon dn$,[265] so

$$\frac{\varepsilon}{k_B T} = \frac{1}{k_B}\frac{dS}{dn} = \log\frac{1-\frac{n}{N}}{\frac{n}{N}} + \log\frac{1-\frac{n}{M}}{\frac{n}{M}} = \log\frac{(N-n)(M-n)}{n^2}. \tag{14.16}$$

Here, notice that when you differentiate $\log\binom{N}{n}$ wrt n, virtually you have only to differentiate the factors outside log. Usually n is small, so we obtain

$$e^{-\beta\varepsilon} = \frac{n^2}{NM}. \tag{14.17}$$

From this we can write S in terms of T.

14.7 Classical ideal gas and de Broglie wavelength

The classical ideal gas is characterized by the total absence of quantum effect: here, quantum effect means that the particles can delocalize. Consider a gas consisting of N identical noninteracting particles. To ignore all quantum effects, the average de Broglie wave length of each particle must be much smaller than the average interparticle distance. The de Broglie wave length λ may be estimated as

$$\lambda \sim h/\sqrt{mk_BT}, \tag{14.18}$$

where m is the mass of the particle, and h is Planck's constant. This estimate is due to $\lambda = h/p = h/\sqrt{2mK}$ and $K \sim k_BT$, where p is the representative value of the magnitude of the momentum of a particle, and K is the representative value of the one-particle kinetic energy. The mean particle distance is $\sqrt[3]{V/N}$, so the condition we want is $\sqrt[3]{V/N} \gg \lambda$, or

$$\frac{N}{V} \ll \left(\frac{mk_BT}{h^2}\right)^{3/2}. \tag{14.19}$$

When this inequality is satisfied, we say the gas is classical.[266]

Since there are no interactions among particles, each particle cannot sense the density. Consequently, the internal energy of the system must be a function of T only: $E = E(T)$. This is a good characterization of ideal gases.

14.8 Single particle states

Let us first compute the number of microscopic states allowed to a single particle

[265] S is now a function of E, but we do not write it explicitly.

[266] Notice that the dynamics of internal degrees of freedom such as vibration and rotation need not be classical as we will see in Section 23.

(called one-particle states) in a box of volume V. To this end we solve the Schrödinger equation in a cube with edges of length L:

$$-\frac{\hbar^2}{2m}\Delta\psi = E\psi; \tag{14.20}$$

Δ is the Laplacian, and a homogeneous Dirichlet boundary condition $\psi = 0$ at the wall is imposed. As is well-known, the eigenfunctions are:

$$\psi_{\boldsymbol{k}} \propto \sin k_x x \sin k_y y \sin k_z z \tag{14.21}$$

with the following quantization condition due to the boundary condition:

$$\boldsymbol{k} \equiv (k_x, k_y, k_z) = \frac{\pi}{L}(n_x, n_y, n_z) \equiv \frac{\pi}{L}\boldsymbol{n}. \tag{14.22}$$

Here, $n_x, \cdots$ are positive integers, $1, 2, \cdots$. The eigenfunction $\psi_{\boldsymbol{k}}$ belongs to the eigenvalue (energy) $\hbar^2 k^2/2m$.

The number of states with wave number vectors $\boldsymbol{k}$ in the range k to $k + dk$ is

$$\begin{aligned}\#\{\boldsymbol{k} \mid k < |\boldsymbol{k}| < k + dk\} &= \#\left\{\boldsymbol{n} \,\middle|\, \frac{L}{\pi}k < |\boldsymbol{n}| < \frac{L}{\pi}(k + dk)\right\} \\ &= \left(\frac{1}{8}4\pi n^2 dn =\right)\ \frac{1}{8}\frac{L^3}{\pi^3}4\pi k^2 dk = \frac{1}{2\pi^2}V k^2 dk. \end{aligned} \tag{14.23}$$

The factor 1/8 is required because the relevant $\boldsymbol{k}$ are only in the first octant (all the components must be positive).

14.9 Classical ideal gas: single particle canonical partition function

Now we can compute the canonical partition function for a single particle using its definition:

$$\begin{aligned} Z_1 &= \sum_{n_x>0, n_y>0, n_z>0} \exp(-\beta E) && (14.24)\\ &= \int_k \#\left\{\boldsymbol{n} \,\middle|\, \frac{L}{\pi}k < |\boldsymbol{n}| < \frac{L}{\pi}(k + dk)\right\} \exp(-\beta k^2\hbar^2/2m) && (14.25)\\ &\simeq \frac{1}{8}\frac{V}{\pi^3}\int_0^\infty 4\pi k^2 dk \exp(-\beta k^2 \hbar^2/2m). && (14.26)\end{aligned}$$

The integration is readily performed. (14.26) is

$$Z_1(V) = V\frac{1}{8\pi^3}\int_{-\infty}^{\infty} dk_x\, e^{-k_x^2\hbar^2/2mk_BT}\int_{-\infty}^{\infty} dk_y\, e^{-k_y^2\hbar^2/2mk_BT}\int_{-\infty}^{\infty} dk_z\, e^{-k_z^2\hbar^2/2mk_BT}, \tag{14.27}$$

and we know

$$\int_{-\infty}^{\infty} dx\, e^{-ax^2} = \sqrt{\frac{\pi}{a}}. \tag{14.28}$$

Therefore,

$$Z_1(V) = V\frac{1}{8\pi^3}\left(\frac{2\pi m k_B T}{\hbar^2}\right)^{3/2} = V\left(\frac{1}{4\pi^2}\right)^{3/2}\left(\frac{8\pi^3 m k_B T}{h^2}\right)^{3/2}. \tag{14.29}$$

That is,

$$Z_1(V) = V\left(\frac{2\pi m k_B T}{h^2}\right)^{3/2}. \tag{14.30}$$

The important point of this result is that $Z_1 \propto V$.

14.10 Classical ideal gas: Gibbs paradox

According to our preliminary discussion around (13.58) the partition function Z of the whole ideal gas system consisting of N identical particles should read

$$\text{“}Z = Z_1^N\text{”}. \tag{14.31}$$

This implies

$$A(N, V) = -Nk_BT \log Z_1(V). \tag{14.32}$$

Now, prepare two identical systems each of volume V with N particles. The free energy of each system is given by $A(N, V)$. Next, combine these two systems to make a single system. The resultant system has $2N$ particles and volume $2V$, so its free energy should be $A(2N, 2V)$. The fourth law of thermodynamics **9.14** requires that

$$A(2N, 2V) = 2A(N, V). \tag{14.33}$$

Unfortunately, as you can easily check, this is not satisfied by (14.32). $Z_1 \propto V$ is the key feature, so let us write $Z_1 = cV$ with a positive constant c. Then, $Z = (cV)^N$, so indeed

$$\log(c2V)^{2N} = 2\log(cV)^N + \log 2^{2N} \neq 2\log(cV)^N. \tag{14.34}$$

Thus we must conclude (14.31) is wrong. This is the famous *Gibbs paradox*.

14.11 Correct canonical partition function

Since the fourth law is an empirical fact, we must correct (14.31) as

$$Z = f(N)Z_1^N = f(N)(cV)^N, \tag{14.35}$$

where $f(N)$ is as yet an unspecified function of N. The fourth law demands (14.33):

$$\log f(2N) + 2N\log(c2V) = 2\log f(N) + 2N\log(cV). \tag{14.36}$$

That is,

$$\log f(2N) + 2N\log 2 = 2\log f(N) \tag{14.37}$$

or

$$f(N)^2 = 2^{2N} f(2N) \text{ (more generally, } f(N)^\alpha = \alpha^{\alpha N} f(\alpha N)). \tag{14.38}$$

The general solution to this functional equation is (set $\alpha = 1/N$; recall Stirling's formula $(N/e)^N \approx N!$)

$$f(N) = \left(\frac{f(1)}{N}\right)^N \propto (N!)^{-1}. \tag{14.39}$$

Thus, thermodynamics forces us to write

$$Z = \frac{1}{N!} Z_1^N, \tag{14.40}$$

where we have discarded the unimportant multiplicative factor.

Therefore, the canonical partition function for a classical ideal gas reads

$$Z_{ideal} = \frac{V^N}{N!}\left(\frac{2\pi m k_B T}{h^2}\right)^{3N/2} = \left[\frac{Ve}{N}\left(\frac{2\pi m k_B T}{h^2}\right)^{3/2}\right]^N. \tag{14.41}$$

14.12 Why does a gas require $1/N!$, but does a lattice system not?

For a lattice system we considered in the preceding lecture, a spatial pattern consisting of states at individual lattice points is identified as a microstate (see Fig. 14.2 (1) and (2)). In this case, the particles sitting at the lattice points are identical chemical species (atom or molecule) and we never pay any attention to the arrangement of particles on the lattice. If these particles are marbles, then their arrangements on the lattice can distinguish microstates, but since we do not do that, we have already assumed that all the particles are (combinatorially) indistinguishable.

Even for a gas system a microstate corresponds to a pattern of particle positions and momentum vectors (see Fig. 14.2 (3) or (4)), since as we will learn later, quantum-mechanically identical particles are indistinguishable combinatorially in contrast to marbles. However, if you use classical mechanics to describe a gas we must name particles to describe them separately. Consequently, the identical patterns with differently named particles look as if they are distinct microstates. In Fig. 14.2 (5) and (6) are with an identical pattern (3) so they must represent an identical microstate, but due to different namings they are handled as distinct microstates. If

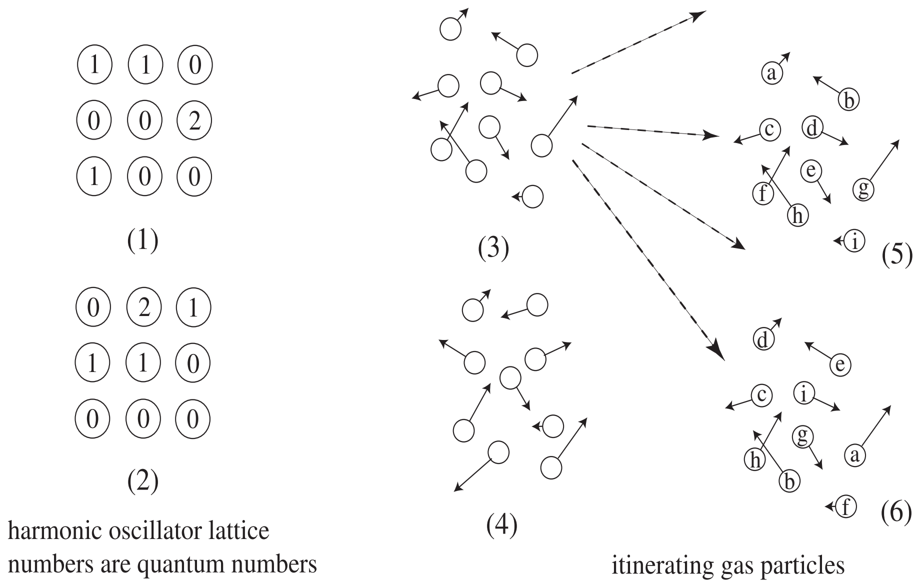


Figure 14.2: Left: A lattice system we studied in the preceding lecture; Right: a particle system. For the lattice system, a microstate is identified with a pattern on the whole lattice that is an arrangement of states at all lattice points. Thus, (1) and (2) are distinct microstates since they have distinct spatial patterns. Notice that the particles sitting at lattice points are already indistinguishable. The situation does not vary very much for gasses. A pattern consisting of positions and momentum vectors of the particles corresponds to a single microstate. Thus, (3) and (4) are distinct microstates. Here, what particle is assigned to what position does not matter. In contrast to the lattice system, however, when the partition function is written down, particles have definite names as a, $\cdots$, i and are distinguishable. Consequently, a certain single microstate of N (= 9 in the figure) particles are distinguished into $N!$ apparently distinct microstates due only to the naming of the particles. For example, due to distinct names of the particle variables required in the classical description, the microstate (3) may be written as (5), (6) or other $N!$ distinct configurations.

there are N gas particles, the number of microstates are multiplied with $N!$ due to namings of particles, so to correct this overcounting $1/N!$ must be multiplied.

14.13 Classical canonical partition function of particle system

Let's recap. If we 'honestly count' the number of quantum states to obtain the microcanonical partition function (i.e., $w(E, X)$), we see ($\to$(14.30))

$$Z_1 = \frac{1}{h^3}\int d\boldsymbol{r}\int \boldsymbol{p}\, e^{-p^2/2mk_BT}. \tag{14.42}$$

Therefore, the canonical partition function in terms of the phase integral reads

$$Z = \frac{1}{h^{3N}N!}\int d\Gamma e^{-\beta\sum_i \boldsymbol{p}_i^2/2m}, \tag{14.43}$$

where $d\Gamma = d\boldsymbol{q}_1 d\boldsymbol{q}_2\cdots d\boldsymbol{q}_N d\boldsymbol{p}_1 d\boldsymbol{p}_2\cdots d\boldsymbol{p}_N$ is the phase volume element.

The prefactors in front of the phase integral are determined while considering a particular system (the classical ideal gas), so you may think they are rather ad hoc. However, the factor $1/N!$ comes from the indistinguishability of the particles, so as long as particles are distinguished in the description of the system, this should not be peculiar to ideal gases. How about h^{3N}?

Z appears in log, so it must be dimensionless (if not, the free energy shifts according to the choice of units, for example). Therefore, in front of the integral whose dimension is $(\text{action})^{3N}$ ($[pq] = M(L/T)L = M(L/T)^2 \times T$[267]), we must have a factor killing this dimension. The most fundamental quantity in physics that has the dimension of action is h. Since we do not expect that the factor is idiosyncratic to the ideal gas, it is natural to expect $1/h^{3N}$ to appear. Therefore, we define the canonical partition function in terms of the phase integral as follows:

$$Z = \frac{1}{h^{3N}N!}\int d\Gamma\, \mathrm{e}^{-\beta\mathcal{H}}. \tag{14.44}$$

This relation can be rigorously demonstrated by semi-classical analysis.

14.14 Dimensional analysis of ideal gases

We did a lot of calculation to get Z_1 quantum mechanically. However, dimensional analysis almost gives you the same result, or, actually, since we may ignore any constant factor, we get the correct result by dimensional analysis alone.

Our starting point is $Z_1 \propto V$. This is very natural. To make a dimensionless quantity, we need another quantity with the dimension of volume, or rather, if we can find a quantity with the dimension of length, we can use it to make Z dimensionless. What length scales do we have in this problem? The system size (the box size L) is certainly relevant, but we have already used it $V = L^3$. There is one more length scale, which we have already discussed: the de Broglie wave length $\lambda \sim \sqrt{mk_BT/h^2}$. Therefore,

$$Z_1 \propto V/\lambda^3 = V\left(\frac{mk_BT}{h^2}\right)^{3/2}. \tag{14.45}$$

Compare this with (14.30). Needless to say, $1/h^3$ appears naturally.

14.15 Generalization of equipartition of kinetic energy

We already know the equipartition of kinetic energy for an ideal gas with the aid of the kinetic theory of gases, e.g.,

$$\left\langle \frac{1}{2}mv_x^2 \right\rangle = \frac{1}{2}k_BT. \tag{14.46}$$

[267] Action is energy times time. Recall $h\nu$ is energy.

Let us demonstrate, with the aid of the canonical formalism, a general theorem that implies the above formula and that is applicable to any classical systems.

Let x_i and x_j be two components of canonical coordinates (say, the x-component of the spatial coordinate of particle 1 and z-component of the momentum of particle 2). Then, for classical systems we have

$$\left\langle x_i \frac{\partial H}{\partial x_j} \right\rangle = k_B T \delta_{ij}, \tag{14.47}$$

where the average is over the canonical distribution. Indeed,

$$\begin{aligned} \left\langle x_i \frac{\partial H}{\partial x_j} \right\rangle &= \frac{1}{Z} \int d\Gamma\, x_i \left[-k_B T \frac{\partial}{\partial x_j} e^{-\beta H} \right], & (14.48) \\ &= -\frac{1}{Z} k_B T x_i e^{-\beta H} \Big|_{|x| \to \infty} + \frac{1}{Z} k_B T \int d\Gamma\, \frac{\partial x_i}{\partial x_j} e^{-\beta H}. & (14.49) \end{aligned}$$

Here, the first term due to an integration by parts must vanish, so H must increase sufficiently fast in the large variable limit. For example, if a system is spatially confined (by a potential well), certainly this is true for the spatial coordinates.

14.16 Equipartition of kinetic energy again

From (14.47) we obtain the *law of equipartition of energy* for classical kinetic energy such as (no summation convention implied)

$$\left\langle \frac{p_i^2}{2m} \right\rangle = \frac{1}{2} k_B T, \tag{14.50}$$

or

$$\left\langle \frac{L_i^2}{2I_i} \right\rangle = \frac{1}{2} k_B T, \tag{14.51}$$

where m is the mass, I_i is the i-th principal moment of inertia (i-th eigenvalue of the inertial moment tensor) and L_i is the corresponding component of the angular momentum.

If the spatial position of a particle is governed by a harmonic potential with a spring constant k (i.e., the harmonic potential energy $U = kx^2/2$), we obtain, with the same logic,

$$\left\langle \frac{kx^2}{2} \right\rangle = \frac{1}{2} k_B T. \tag{14.52}$$

14.17 Application to homogeneous energy functions

Suppose the spatial position of a particle is governed by an anharmonic potential $U = kx^4$, where k is a positive constant, then we can compute the equilibrium average of this potential energy as

$$\left\langle x\frac{\partial U}{\partial x}\right\rangle = 4\langle U\rangle = k_BT. \tag{14.53}$$

Since the classical kinetic energy k is quadratic in (angular) momenta,[268]

$$\sum_i p_i\frac{\partial K}{\partial p_i} = 2K. \tag{14.54}$$

Thus, if there are N particles, then there are $3N$ variables, so

$$\langle K\rangle = \frac{3N}{2}k_BT. \tag{14.55}$$

If a system is described as coupled harmonic oscillators, then the potential energy U is a quadratic function of the position (displacement) coordinates. Therefore, quite analogously the average total potential energy is

$$\langle U\rangle = \frac{n_v}{2}k_BT, \tag{14.56}$$

if there are n_v modes.

14.18 Specific heat of gases, computed classically

A direct application of the equipartition of energy is the high temperature (constant volume) specific heat per particle of a multiatomic molecular ideal gas. Let us assume that each molecule contains M atoms. The Hamiltonian of each molecule can be written as

$$H = K_{CM} + K_{rot} + K_{vib} + U_{vib}, \tag{14.57}$$

where K_X is the kinetic energy associated with the motion X: CM denotes the center of mass translational motion; rot implies rotational motion around its center of mass; vib means the vibrational motion. U_{vib} is the potential energy for the vibrational

[268]If $K = \sum_{i,j} A_{ij}p_ip_j$, where A_{ij} is a constant, then

$$\sum_k p_k\frac{\partial}{\partial p_k}K = \sum_k p_k\sum_{i,j}A_{ij}(\delta_{ik}p_j + p_i\delta_{kj}) = \sum_k p_k\left(\sum_j A_{kj}p_j + \sum_i A_{ik}p_i\right) = 2K.$$

This is an example of Euler's theorem about homogeneous functions.

motion. We may assume that the molecular internal vibrations are harmonic, so all these terms are quadratic terms. Therefore, the internal energy can be obtained only by counting the number of degrees of freedom. Notice that the total number of (angular) momenta is always $3M$ for a M-atomic molecule, so, obviously

$$\langle K_{CM} + K_{rot} + K_{vib} \rangle = \frac{3}{2} M k_B T. \tag{14.58}$$

Thus, we have only to count the number of vibrational modes.

For a not-linear molecule there are 3 translational degrees, and 3 rotational degrees, so there are $3M - 6$ harmonic modes. Thus, $\langle U_{vib} \rangle = (3M - 6)k_B T/2$. That is, the internal energy is $E = (3M - 3)k_B T$ per molecule, so $C_V = (3M - 3)R$ per mole, where R is the gas constant.

For a molecule whose shape is linear there are 3 translational degrees, and 2 rotational degrees, so there are $3M - 5$ harmonic modes.[269] Thus, $\langle U_{vib} \rangle = (3M - 5)k_B T/2$. That is, $E = (3M - 5/2)k_B T$ per molecule, so $C_V = (3M - 5/2)R$ per mole.

It is a well-known fact that these specific heat values grossly overestimate the actual specific heats of molecular gases and were regarded as a paradox before the advent of quantum mechanics.

For a diatomic gas $M = 2$, so $C_V = (7/2)R$ according to our formula just derived, but actually around the room temperature it is usually $(5/2)R$. That is, it is less by R. This is because the vibrational mode is frozen and its contribution to kinetic and potential energies $R/2 + R/2$ does not show up. To excite vibration the heat bath must pay a big sum of energy (= vibrational energy quantum) at once to the molecule, so if its temperature is low, the heat bath cannot afford it. In classical mechanics the environment is allowed to pay the big sum by 'monthly installment,' so vibration could be excited, but in the real quantized world, this is impossible. Thus, the specific heat becomes small.

[269] When a molecule is straight, the reader must be able to explain into what modes the rotational degree is converted, comparing, e.g., water and carbon dioxide.

Q14.1 [Cyclohexane ring packering]
There is a 1 mole of ideal gas consisting of molecules with one internal degree of freedom.[270] The internal motion of an individual molecule is described by the following Hamiltonian

$$H_{int} = \frac{1}{2}\mu p^2 + \frac{1}{4}\alpha q^4, \tag{14.59}$$

where μ and α are positive constants, and p and q are canonical coordinates describing the internal motion. The total Hamiltonian of the whole gas must be the sum of the Hamiltonian governing the center of mass translational motions of individual molecules and the Hamiltonians describing their internal motions (i.e., (14.59) for each molecule).
(1) Let z_i be

$$z_i = \frac{1}{h}\int dp \int dq\, e^{-\beta H_{int}}. \tag{14.60}$$

Write down (you can copy anything usable from the lecture notes) the canonical partition function Z for this ideal gas utilizing z_i. Let us assume the temperature of the gas to be T, its volume V and the mass of each particle m.
(2) What is the constant volume specific heat of this system? [Hint: try to calculate the average of the total Hamiltonian to obtain the internal energy E.]
(3) Although it is possible to analytically evaluate (14.60), since we take the logarithm of z_i, we have only to obtain the exponent θ in $z_i \propto T^\theta$. Get θ dimensional analytically, and confirm that your result agrees with (or is consistent with) (2). [Hint. Find the dimension of $\beta\mu$, etc.]
(4) What is the constant pressure specific heat C_P of the system?
(5) Classically C_V does not depend on α, but quantum mechanically it is not the case. Suppose the temperature goes very close to $T = 0$ (or α becomes extremely large), what do you expect to happen to C_V?

Soln.
(1) $Z = Z_{ideal} z_j^N$. That is,

$$Z = \frac{1}{N!}\left(\frac{2\pi m k_B T}{h^2}\right)^{3N/2} z_j^N.$$

(2) The contribution of the translational motion is $3RT/2$. The contribution of p is just another kinetic energy , so $RT/2$. The contribution of q can be obtained with the aid of the equipartition of energy:

$$\left\langle \alpha q \frac{\partial H}{\partial q} \right\rangle = \langle \alpha q^4 \rangle = k_B T,$$

so $RT/4$ is its contribution. Combining all of them, we get

$$\langle H \rangle = \frac{3}{2}RT + \frac{1}{2}RT + \frac{1}{4}RT = \frac{9}{4}RT.$$

[270] The shallow potential may be an approximaodel of ring packering of cyclohexanes.

Hence, $C_V = 9R/4$.
(3) The integral wrt p has the dimension of p, and must be a function of $\beta\mu$. $[\beta\mu p^2] = 1$, so $[p] = [\beta\mu]^{-1/2}$. Analogously, $[q] = [\beta\alpha]^{-1/4}$. Therefore,

$$[hz_i] = [\beta\mu]^{-1/2}[\beta\alpha]^{-1/4}, \Rightarrow \quad z_i \propto T^{3/4}.$$

Therefore, $3R/4$ is the contribution of the internal degree of freedom. Consistent.
(4) Use Mayer's relation. $C_P = C_V + R = 13R/4$.
(5) The internal motion is a kind of oscillation, and obviously there is a finite energy gap. Therefore, at lower temperatures, energy quantization makes excitation harder. Eventually, C_V goes to the value without the contribution of the internal degree of freedom. That is, $3R/2$.

15 Information and entropy

Summary
∗ The Gibbs-Shannon formula for entropy/information is explained.
∗ Entropy quantifies how much amount of knowledge (information, measured in terms of the number of Yes-No questions) you need to specify an individual elementary event (= microstate) of a system.

Key words
(Gibbs-)Shannon formula, information, bit, surprisal

What you should be able to do
∗ Explain why the Shannon formula is plausible (perhaps in terms of surprisal).
∗ For simple examples, you should be able to estimate entropy change in terms of information (or by the number of needed extra questions).

15.1 Gibbs-Shannon formula of entropy

Using the canonical formalism, let us compute entropy explicitly:

$$
\begin{aligned}
TS &= E - A & (15.1)\\
&= k_BT \log Z - k_BT\, Tr\, \frac{e^{-\beta H}}{Z} \log e^{-\beta H} & (15.2)\\
&= -k_BT\, Tr\, \frac{e^{-\beta H}}{Z} \log \frac{e^{-\beta H}}{Z}. & (15.3)
\end{aligned}
$$

That is,

$$
S = -k_B Tr\, \rho \log \rho, \tag{15.4}
$$

where $\rho = e^{-\beta H}/Z$ is the canonical density operator, or, similarly, classically

$$
S = -k_B \int d\Gamma\, p \log p, \tag{15.5}
$$

where p is the canonical distribution function. This is the formula first given by Gibbs in his famous book on the foundation of statistical mechanics.

The same formula was proposed by Shannon to quantify information, so (15.5) is often called *Shannon's formula*. It is a convenient occasion to see why such a formula is a good measure of information. Shannon did *not* ask what information was, but tried to quantify it.[271]

[271] ⟪**Textbook of information theory**⟫ The best textbook of information theory (in English) is T. M. Cover and J. A. Thomas, *Elements of Information Theory* (Wiley, 1991).

15.2 How to quantify information: equal probability case

Let $\eta(m)$ be the 'information' per letter we can send with a message (letter sequence) that is composed of m distinct symbols. Here, the word 'information' should be understood intuitively. Let us assume that all the symbols are used evenly. Then, $\eta(m)$ must be an increasing function of m; if you are allowed to use only two symbols, we can send, per letter, the information telling whether $\{1, 2, 3\}$ or $\{4, 5, 6\}$ as to the outcome of a single casting of a dice, but if you can use three, then more detailed information: $\{1, 2\}$, $\{3, 4\}$ or $\{5, 6\}$ may be sent per single letter.

Now, let us use simultaneously the second set of symbols consisting of n symbols. We could make compound symbols by juxtaposing them as ab (just as in many Chinese characters). The information carried by each compound symbol should be $\eta(mn)$, because there are mn symbols. We could send the same message by sending all the left half symbols first and then the right half symbols later. The amount of information sent by these methods must be equal, so we must conclude that[272]

$$\eta(mn) = \eta(m) + \eta(n). \tag{15.6}$$

Since η is an increasing function, we conclude

$$\eta(n) = c \log n, \tag{15.7}$$

where $c > 0$ is a constant. Its choice is equivalent to the choice of unit of information per letter and corresponds to the choice of the base of the logarithm in the formula.

If $c = 1$, we measure information in *nat*; if we choose $c = 1/\log 2$ (i.e., $\eta(n) = \log_2 n$), in *bit*. 1 bit is an amount of information one can obtain from an answer to a single yes-no question.

15.3 How to quantify information: general case

We have so far assumed that all the symbols are used evenly, but such uniformity is not usual. What is the most sensible generalization of (15.7)? We can write $\eta(n) = -\log_2(1/n)$ bits; $1/n$ is the probability for a particular symbol. $-\log_2(1/n)$ may be interpreted as the expectation value of $-\log_2$(probability of a symbol). This suggests that for the case with not-equal-probability occurrence of n symbols with probabilities $\{p_1, \cdots, p_n\}$, the expectation value of the information carried by the

[272] We must send a message explaining how to combine the transferred symbols as a part of the message, but the length of the needed message is finite and independent of the length of the actual message we wish to send, so in the long message limit we may ignore this overhead.

i-th symbol should be defined as $-\log_2 p_i$ bits. Then, the average information in bits carried by a single symbol should be defined by

$$H(\{p_i\}) = -\sum_{i=1}^{n} p_i \log_2 p_i. \tag{15.8}$$

This is called the *Shannon information formula*.[273] When Shannon arrived at (15.8), he asked von Neumann what it should be called. It is told that von Neumann suggested the name 'entropy,' adding that it was a good name because no one understood it.

15.4 Average surprisal

The quantity $-\log_2 p_i$ that appears in the above is sometimes called the *surprisal* of symbol i, because it measures how much we are surprised by encountering this symbol (smaller p should give more surprise). It may be easier to use the axioms for *surprisal* to understand the Shannon formula (15.8). The 'extent of surprise' $f(p)$ we get, spotting a symbol that occurs with probability p or knowing that an event actually happens whose expected probability is p, should be
(1) A monotone decreasing function of p (smaller p should give us bigger surprise).
(2) Nonnegative.
(3) Additive: $f(pq) = f(p) + f(q)$.[274]
Therefore, $f(p) = -c \log p$ ($c > 0$) is the only choice. The additivity should be natural, if we consider our surprise when something rare occurs successively.

15.5 Entropy vs Information

Now, we have learned two pieces as to the relation between entropy and information:
(i) ΔS due to a process in a macrosystem is related to (when $\Delta S > 0$) the number of extra YES-NO questions we need to determine the microstate of the macrosystem as accurately as before the process. For an ideal gas all the molecules are independent, so we must determine all the states of particles individually.[275] Therefore, we must multiply the number of particles to get the number of questions to pinpoint a particular microstate of the gas.
(ii) The Gibbs-Shannon formula: the expression of entropy of a system and the expression of the information carried by a collection of letters are identical.

Combining these two, we may conclude that entropy is the amount of knowledge/information required to pinpoint the (micro)state (= elementary event) of a

[273]for an uncorrelated (or Bernoulli) information source. About Shannon himself, see S. W. Golomb et al., "Claude Elwood Shannon (1916-2002)," Notices AMS **49**, 8 (2002).

[274]We could invoke the Weber-Fechner law.

[275]Let us not consider the indistinguishability here, for simplicity.

system. If the volume of an ideal gas is doubled, then $\Delta S = R \log 2$ per mole. Suppose we can know the state of each molecule (within a specified error) before doubling the volume. After doubling, if we know whether each molecule is in the left or in the right half (i.e., a 1 bit/molecule information), then we can know the state of each molecule even after the volume doubling (within the same specified error). The extra knowledge per molecule required is one bit. This must correspond to the entropy increase just mentioned. Therefore, $R \log 2$ of entropy should be identical to the N_A bits of information: $R \log 2 = N_A$ bits. This was already alluded in Lecture 10.

15.6 Order-disorder and information

Let us look at particle configurations (maybe spin configurations) on a lattice in Fig. 15.1.

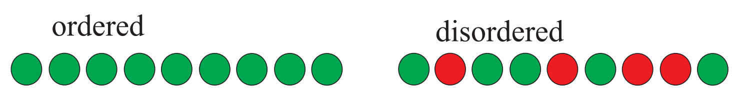


Figure 15.1: Left: ordered; Right: a representative of a collection of disordered microstates with N $(= 9)$ microscopic entities.

If a microstate is ordered (Fig. 15.1 Left), since in this idealized example, there is only two microstates, to pinpoint a microstate, we need one question: Are all particles green? How about the disordered state on the Right? In this case a macrostate corresponds to many distinct microstates. To single-out any particular microstate, we need N YES-NO questions. That is, we need N $(= 9$ in this example) bits of information to describe it.[276]

As discussed S may be understood as the required (expectation) amount of information we need to pinpoint any microstate in the macrostate. Therefore, we can interpret S as the measure of disorder of the macrostate seen microscopically.

15.7 'Thermodynamic unit' of information

In chemical physics entropy is often measured in eu (entropy unit = cal/mol·K). It may be useful to remember that 1 eu = 0.726... bits/molecule. Some people say that

[276] Even if the pattern is disordred, if a macrostate corresponds to one of the disordered configurations such as the one in the figure, then there is one YES-NO question to determine its microstate: Is the configuration such as: the first red, the second green, the third green, etc.? You may well say that no one can conceive such a question. You are very likely to be correct, but our question is whether there is such a question or not; notice that if you did not know the state is ordered, you could not make a single question even in the Left case of Fig. 15.1.

However, your objection highlights the distinction between the disordered states and the disordered systems (such as glasses).

the unit of entropy (e.g., J/K) and unit of information (bit) are disparate. This is simply because they do not think things microscopically. If one wishes to tell each molecule to turn 'to the right', the number of required messages is comparable to the number of molecules, so it is huge, but for each molecule it is about a few bits. For example, the entropy change due to a reaction involving small molecules is usually the order of a few eu. This is a reasonable value.

15.8 How to quantify the amount of knowledge (gained)

How much information do we need to know the outcome of a fair dice? We guess it is $\log_2 6$ bits. This is the entropy of a state of a dice. Suppose you are told that the face value is larger than or equal to 3. How much information does this statement carry? Information is something that can reduce our extent of ignorance. After hearing this message, we know 4 faces are still possible, so we need 2 more YN questions to remove uncertainty completely (i.e., to get a particular elementary event). Therefore, $\log_2 6 - \log_2 4 = \log_2(3/2) > 0$ must be the information carried by the message.

Example [Information carried by messages]
(1) Suppose a positive integer is given. It must begin with one of 1, 2, $\cdots$, and 9. If all the non-zero digits are likely to appear evenly, what is the information carried by the message that the first digit was actually 6?

Since all 9 non-zero digits are likely to appear, the initial uncertainty (entropy) is $\log_2 9 = 3.17$ bits. No uncertainty remains after receiving the message (i.e., entropy is zero), so the message must have provided the information of 3.17 bits. This is exactly the surprisal of '6' itself.
(2) In reality, it is known that the first digit does not distribute evenly. Approximately the probability that digit D appears as the first digit is $P_D = \log_{10}(1+1/D)$. What is the information carried by this empirical law?

After knowing the law, the remaining uncertainty (entropy) is $-\sum_D P_D \log P_D =$ 2.88 bits. Therefore $3.17 - 2.88 = 0.29$ bits is the information provided by this empirical law.
(3) Now, after knowing the empirical law what is the information carried by the message that the first digit was actually 6?

With this information no uncertainty remains, so 2.88 bits must be the answer.

15.9 Statistical mechanics from information theory?

Maximizing Shannon's entropy is to find the least biased distribution, so we may expect that the resultant distribution is the most probable distribution. We should be able to obtain the 'true distribution' p by maximizing the Gibbs-Shannon formula under the condition that we know the expectation value of energy (internal energy). This is equivalent to maximizing the following variational functional with Lagrange's multipliers β and λ (the latter for the normalization condition):

$$-k_B \int p \log p \, d\Gamma - \beta \int pH d\Gamma - \lambda \int p \, d\Gamma. \tag{15.9}$$

This indeed gives

$$p \propto e^{-\beta H}. \tag{15.10}$$

The Shannon formula is derived logically from almost inescapable requirements about 'knowing something.' Therefore, the above line of argument seems to indicate that the principle of statistical mechanics can be derived directly from this fundamental conceptual basis. Thus, some brave people concluded that this was the true basis of statistical mechanics; forget about mechanics.[277] This is the so-called information-theoretical derivation of statistical mechanics.

15.10 Don't be fooled by Jaynes

Don't be fooled by such a logic. Even if we admit that the result that maximizes the information entropy is the maximally likely result from our point of view, why does Nature have to accept it as the most 'natural' outcome? There is a logical gap here. The most natural argument to fill this gap is that we (or our brains) have evolved (or have been selected) to feel that the most natural things in the actual world are the most probable. In short, our brains have evolved in the world following the principle of equal probability. That is, the logic of information maximization is circular; implicitly, the principle of equal probability is incorporated.

Furthermore, if we look at (15.5), we should realize that something is wrong. p there is not probability but probability density, so it is not invariant under coordinate transformation. The description, for example, in the Cartesian coordinates and that in the equivalent polar coordinates should not give different entropies. Therefore, $\log p$ must be $\log(p/q)$ for some density distribution q. That is, if entropy is free from the choice of the coordinate system to describe distribution functions, the 'true' Gibbs entropy formula must read as[278]

$$S = -k_B \int d\Gamma \, p \log \frac{p}{q}. \tag{15.11}$$

We cannot do anything without fixing q. To determine it, we need a certain statistical principle.[279]

[277]The originator seems to be E. T. Jaynes, "Information theory and statistical mechanics," Phys. Rev. **106**, 620-630 (1959).

[278]This is the (negative) *Kullback-Leibler entropy*, whose natural implication is supplied by large deviation theory.

[279]It cannot be overemphasized that even for discrete states the use of information tacitly presupposes the principle of equal probability. Think of surprisal, for example. Why is it simply a

15.11 What is 1/2 question?

You might wonder what 0.5 yes-no questions imply. How can we ask such a question? Suppose there are 1 red ball and 999 white balls. How many questions do you need to determine the colors of all the balls? The total entropy is in this case 11.4 bits. That is, you need 0.01 Yes-No questions to determine the color of a single ball. Let us assume that initially you only know that there are red and white balls only. First, we divide the balls into two 500 ball sets and ask if one set you choose is with all the same color or not. If the answer is yes, this single bit question determines the color of 500 balls at once. Thus, it should not be so difficult to understand what a fraction of a question means.

15.12 Summary of information vs entropy

We may safely conclude that the amount of (the average) information required to pinpoint an elementary event in the sample set Ω is proportional to

$$\eta = -\sum_{\omega \in \Omega} p(\omega) \log p(\omega). \tag{15.12}$$

If you use $\log_2$ (i.e., $(1/\log 2)\log$), this is the information in bits (# of average YES-NO questions you must ask). If you use $k_B \log$, you measure information in energy unit (per molecule). The entropy S in bits is, according to Boltzmann's principle, given by $\log_2 w(E, X)$. This is the number of yes-no questions you must ask to single out a microstate that is consistent with the macrostate (E, X). Increasing entropy ($\Delta S > 0$) implies that to pinpoint a microstate you must ask extra questions corresponding to ΔS; you need ΔS extra information. This implies that the randomness of the system has increased.

Information, addendum

15.13 Mixing entropy and information

We know if we mix 1 mole each of two chemically distinct ideal gas in the same state (P and T), the mixing entropy per particle is 1 bit or $1 k_B \log 2 = 9.57 \times 10^{-24}$ J/(K·molecule). This is intuitively understandable, because you ask one question to clarify the situation.

If you mix 1 mole each of three chemically distinct ideal gas in the same state, the mixing entropy per molecule should be $k_B \log 3$ J/(K·molecule) so it should be

$$\frac{k_B \log 3}{k_B \log 2} = \log_2 3 = 1.58 \text{ bits.} \tag{15.13}$$

---

function of the probability without depending on any other contexts? It is because the world is uniform. However, this uniformity is not a consequence of any logic, but an empirical fact; we feel it natural thanks to phylogenetic learning.

15.14 Mixing entropy, the most general case

Let us have n chemically distinct ideal gases in the same TP state. The total number of particles is N and the total volumes is V. Thus, $PV = Nk_BT$. The number of particles of chemical species i is $N_i = Np_i$. Here, $p_i \in [0,1]$ and $\sum_i p_i = 1$. Initially all the chemicals are separate. Let us mix them by removing the separations (see Fig.15.2).

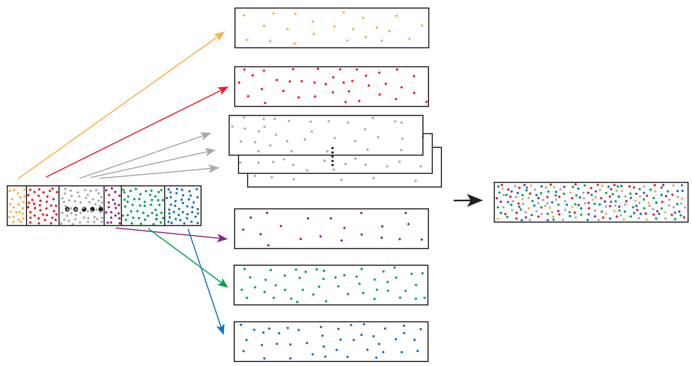


Figure 15.2: General case of mixing process

The mixing entropy must be

$$\Delta S = k_B \sum_i N_i \log \frac{V}{V_i} = Nk_B \sum_i p_i \log \frac{1}{p_i}. \tag{15.14}$$

Thus, mixing entropy per particle is

$$\Delta S/N = -k_B \sum p_i \log p_i \tag{15.15}$$

or in bits

$$\Delta S/N = -\sum p_i \log_2 p_i. \tag{15.16}$$

Therefore, this must be the information we need to guess the 'color' of the particle, when your probability of hitting color i is p_i.

15.15 Gibbs paradox and mixing entropy

An astute reader should have realized that the Gibbs paradox **14.10** is due to the wrong entropy calculation: if two gases are not identical, the discrepancy $2N \log 2$ is exactly the mixing entropy contribution. There should not be any mixing entropy for identical gases, but the 'classical calculation without the $1/N!$ factor concludes there is. This is the core of the Gibbs paradox.

15.16 Maxwell's demon

Suppose in the separating wall in Fig. 15.3 is a small gate with a gate keeper. The system is thermally insulated and initially the gas inside is at T. The gate keeper watches the left-hand side and if the incoming particle has kinetic energy larger than $3k_BT$, the keeper allow the particle to go to the right-hand side.

The keeper then allows any particle coming from the right-hand side go to the other side. Then, we expect the RHS would be warmer than the LHS. Thus, Clausius' principle is violated. We could run an engine between the RHS and LHS. If this could be realized in reality,

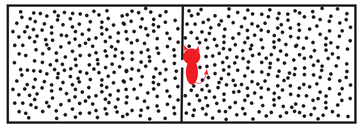


Figure 15.3: Demon selecting kinetic energy

probably biological systems should have exploited the mechanism to win the evolution game.

Why is this mechanism not possible? Notice that (at least ideally) 'thinking' or computation can be done without any dissipation. We can select fast particles with the aid of a potential barrier; the demon has only to observe whether the particle come from the RHS or not. Such observations can be realized without dissipation (ideally).

Obtaining this 1 bit information (that is, writing it into its 'brain'), the demon controls the gate.

15.17 Szilard engine

Szilard proposed the engine illustrated as follows (Fig. 15.4)

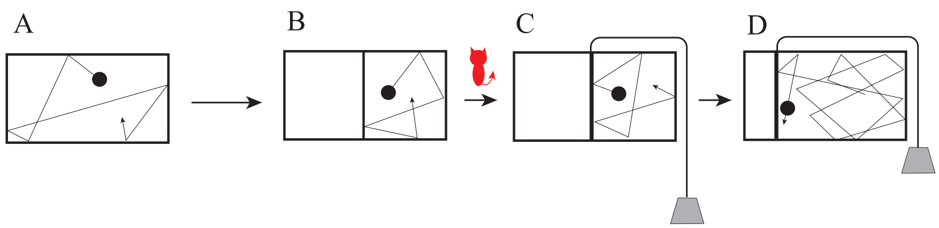


Figure 15.4: Szilard's engine

We can illustrate its process in more detail as follows (Fig. 15.5).

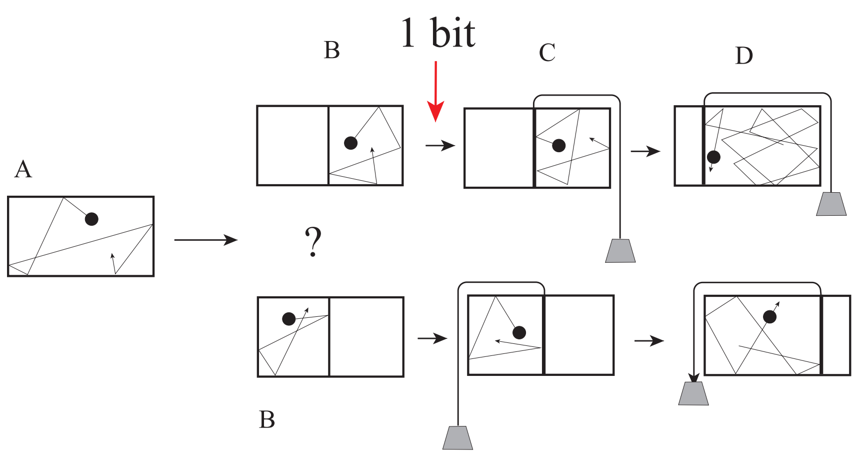


Figure 15.5: How Szilard's engine works

Using the 1 bit information obtained from the observation at the B stage, the direction to move the piston is chosen. In a certain sense, this information is used to 'cool' the system.

The head of the demon mst be finite, so its memory capacity cannot be infinite. Therefore, for this engine to work forever, the memory stored in the head of the demon must be erased. Thus, 1 bit is lost by erasure. This erasure is costly, paying back totally the gain through observation. Thus, the engine actually does not work.

15.18 Is information engine totally useless?

Thus, we have learned that even if we take information into account, the engine efficiency cannot be improved beyond the Carnot limit. Then, use of information totally useless?

You could use a temporary memory to store used information and can temporarily increase the efficiency of information. Then, later, if you need not have high efficiency, you could erase the memory. In the long run there is no gain, but perhaps you could outrun your predator.

Q15.1[Boiling of acetic acid]
The boiling temperature of acetic acid under 1 atm is 391 K, and the evaporation heat (= latent heat of evaporation) is about 23.7 kJ/mol.
(1) What is the entropy increase due to evaporation?
(2) Roughly, how many yes-no questions do you have to ask to specify the (single) molecular state in the gas phase as accurately as in the liquid phase?
(3) The evaporation entropy of ethanol is about 110 J/K·mol. You should have realized a big difference between this value and the value you obtained in (1). This is said to be due to dimerization: acetic acid gas (around the boiling point) consists of dimers $(CH_3COOH)_2$ (due to strong hydrogen bonding, but ethanol does not make dimers in the gas phase).[280] Is the entropy difference roughly consistent with this explanation (or not)? Give your opinion with your supporting argument.

Solution.
(1) The entropy change due to evaporation is $\Delta S = 23700/391 = 60.1$ J/K·mol.
(2) This corresponds to 60.6 $\times 0.17 = 10.3$ bits/molecule. That is, we need about 10 Yes-No questions to determine the state of each molecule as precisely as we can do so in the liquid phase. The volume of the gas (under the condition we are interested in) is about 200 times as large as that of the liquid. This explains about 7 to 8 bits. Not very bad.
(3) Ethanol evaporation corresponds to almost 19 bits/molecule increase of entropy, so we may say that the number of questions required for ethanol is almost doubled. If we assume that roughly two molecules behave together, then the knowledge about one molecule tells us about one more molecule, so this is reasonable.

[280] Precisely speaking, there are also tetramers, and the average acetic acid molecules in a single gas particle seems about $105/60 \simeq 1.75$.

Discussion 8

We will discuss generalized cannonical formalisms and information.

D8.1 [Pressure ensemble]

Starting from the microcanonical approach, we go to the canonical formalism that allows exchange of energy between the system and the environment (thermostat). Compare the following formulas:

$$S = k_B \log W(E,V), \tag{15.17}$$

$$-\frac{A}{T} = \max_E \left[S - \frac{E}{T}\right] = k_B \log Z(T,V). \tag{15.18}$$

The first equality in (21.5) is due to the standard Legendre transformation applied to E: $-A = \max_S[ST - E] = \max_E[ST - E]$ (T is a constant).[281] Boltzmann's principle (15.17) means that the first equality (which is a thermodynamic relation) in (21.5) is equivalent to(recall $1/k_BT = \beta$)

$$e^{-\beta A} = \max_E e^{S/k_B - \beta E} = \max_E \left[W(E,V)e^{-E/k_BT}\right]. \tag{15.21}$$

The key to the 'general' ensemble method is the 'max-sum' correspondence:[282]

$$\max_E \left[W(E,V)e^{-E/k_BT}\right] = \sum_E W(E,V)e^{-E/k_BT} = Z(T,V) \tag{15.22}$$

with a relative error of order $\log N/N$.[283]

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[281]If you wish to use the Legendre transformation applied to entropy (or $-S$, which is convex), we first look at the Gibbs relation

$$d(-S) = \left(-\frac{1}{T}\right)dE + \left(-\frac{P}{T}\right)dV. \tag{15.19}$$

so a Legendre transformation applied to the convex function $-S$ can be written as

$$\max_E \left[\left(-\frac{1}{T}\right)dE - (-S)\right] = \max_E [S - E/T] = -A/T, \tag{15.20}$$

which is (21.5).

[282]The E integral may be understood as summation over energy shells.

[283]As you see, for statistical mechanics S, $-A/T$, etc. (the so-called Massieu functions), are much more natural than the energies (thermodynamic potentials). Also look at the Gibbs relations to see what really the independent variables are for statistical mechanics:

$$d\left(S - \frac{E}{T}\right) = -d\frac{A}{T} = -Ed\frac{1}{T} + \frac{P}{T}dV + \cdots. \tag{15.23}$$

Note that this immediately gives us the Gibbs-Helmholtz formula.

(1) Let us consider an ideal gas under constant temperature and pressure. What is the most convenient thermodynamic potential?
(2) Write down the partition function Y that directly gives the thermodynamic potential in (1) as $-k_BT\log Y$.
(3) Compute Y for a monatomic ideal gas. You may use its canonical partition function

$$Z(T,V) = \frac{1}{N!}\left(\frac{2\pi m k_B T}{h^2}\right)^{3N/2} V^N. \tag{15.24}$$

(4) Recover the ideal gas law.

Solution
(1) We know the answer is $G = E - ST + PV$, the Gibbs free energy. If you wish to retrace all the argument to derive the 'generalized' canonical formalism for the present case, read the following.

To maintain the temperature and pressure of the system, heat and volume work should be freely exchanged with its environment. Therefore, we pay attention to the energy change

$$\Delta E - \Delta Q + \Delta(PV) = \Delta E - T\Delta S + \Delta(PV) = \Delta G, \tag{15.25}$$

where G is the Gibbs free energy as we already know. The Legendre transformation we use is

$$-G = \max_{S,V}[ST + (-P)V - E] \tag{15.26}$$

or

$$-\frac{G}{T} = \max_{S,V}\left[S - \frac{P}{T}V - \frac{E}{T}\right]. \tag{15.27}$$

This is directly related to the Legendre transformation of entropy (recall that $-S$ is convex; see Footnote 1):

$$-\frac{G}{T} = \max_{E,V}\left[-\frac{P}{T}V - \frac{E}{T} - (-S)\right], \tag{15.28}$$

because, for each V, S and E are one-to-one correspondent.

(2) Therefore, we obtain

$$e^{-\beta G} = \max_{E,V} e^{S/k_B - \beta(E+PV)}. \tag{15.29}$$

Using Boltzmann's principle, we get

$$e^{-\beta G} = \max_{E,V}\left[W(E,V)e^{-\beta(E+PV)}\right], \tag{15.30}$$

where $W(E,V)$ is the total 'number' of microstates compatible with the thermodynamic state (E,V); W is often called the microcanonical partition function. We can also write the above formula as

$$e^{-\beta G} = \max_V \left[Z(T,V)e^{-\beta PV}\right], \tag{15.31}$$

because (15.26) implies $-G = \max_V[(-P)V + \max_S[ST-E]] = \max_V[(-P)V - A]$[284] and because we know

$$e^{-\beta A} = \max_E \left[W(E,V)e^{-\beta E}\right] = Z(T,V). \tag{15.32}$$

Needless to say, we always ignore the relative errors of $O[\log N/N]$, which is very small already for $N \sim 1000$.

(15.31) implies ('max-sum' correspondence, although the sum here is written as an integral)

$$e^{-\beta G} = \int dV Z(T,V,X)e^{-\beta PV} = Y(T,P), \tag{15.33}$$

or you may use, shortcutting the intermediate 'max-sum' correspondence,

$$e^{-\beta G} = e^{-\beta(A+PV)} \;\Rightarrow\; e^{-\beta G} = \sum_V Z(T,V)e^{-\beta PV} = Y(T,P) \tag{15.34}$$

to memorize the practical rule.

(3) The canonical partition function is given as

$$Z(T,V) = \frac{1}{N!}\left[\left(\frac{2\pi m k_B T}{h^2}\right)^{3/2}\right]^N V^N, \tag{15.35}$$

so we need the following integral:

$$\int dV \frac{1}{N!}V^N e^{-\beta PV} = \frac{1}{N!(\beta P)^{N+1}}\int dx\, x^N e^{-x} = \frac{1}{N!(\beta P)^{N+1}}\Gamma(N+1) = \left(\frac{k_BT}{P}\right)^N. \tag{15.36}$$

Therefore, (I ignore the difference between N and $N+1$)

$$Y(T,P) = \left[\left(\frac{2\pi m}{h^2}\right)^{3/2}\frac{(k_BT)^{5/2}}{P}\right]^N. \tag{15.37}$$

(4) Thus,

$$G = -k_BT\log Y = Nk_BT\log P + \cdots, \tag{15.38}$$

[284]Notice that A is a convex function of V, because E is. A is a concave function of T. Thus, A is a rather complicated multivariate function.

We know $dG = VdP - SdT + \cdots$, so

$$V = \left.\frac{\partial G}{\partial P}\right|_T = \frac{Nk_BT}{P}. \tag{15.39}$$

Incidentally, the relation between Y and Z is, as seen from (15.31),

$$PV = k_BT\log\frac{Z(T,V)}{Y(T,P)} = k_BT\log\frac{V^N/N!}{(k_BT/P)^N} = Nk_BT\log\frac{PVe}{Nk_BT}. \tag{15.40}$$

Here we have used $N! \simeq (N/e)^N$. This implies that $x = PV/Nk_BT$ satisfies

$$x = 1 + \log x. \tag{15.41}$$

$x = 1$ is the unique real solution (as you can easily see graphically).

D8.2 [Elementary problem about spin system]

"Due to the ligand field the degeneracy of the d-orbitals of the chromium ion Cr^{3+} is lifted, and the spin Hamiltonian has the following form

$$H = D(S_z^2 - S(S+1)/2), \tag{15.42}$$

where $D > 0$ is a constant with $S = 3/2$ (the cation is in the term ${}^4\mathrm{F}_{3/2}$)."

This is the way a spin state question is asked, e.g., in a Qual (the problem is an actual qual problem). However, to answer the statistical-mechanical questions, you need not understand the quantum mechanical setup, but you have only to understand the following facts about the system:
Each ion has states with energies $\varepsilon = 3D/8$ and $\varepsilon = -13D/8$ and both are doubly degenerate (that is, there are two states each with either of ε).

(0) Why can you apply statistical mechanics to this 'single' ion?
(1) Compute the occupation probability of each state at temperature T (you may use the standard notation $\beta = 1/k_BT$).
(2) Calculate the entropy.
(3) At high temperatures approximately the specific heat of the system is approximately $C = k_B(T_0/T)^2$ with $T_0 = 0.18$ K. Determine D/k_B in K.

Solution
(0) Statistical mechanics can compute the probability of a set of microstates
(i) that may be specified by a small number of conditions, and
(ii) that contains $\mathcal{N}$ microstates such that $\log\mathcal{N}$ is extensive ($O[N]$, where N is the total number of particles).

In particular, if all the N microscopic variables are statistically independent as in the systems consisting of non-interacting particles, although a single particle state itself is not macroscopic, a set of microstates in which the particle assumes a particular single particle state obviously satisfies (i) and (ii). The outcome looks as if we can apply statistical mechanics directly to a single molecular state: Let h_i be the single particle Hamiltonian of the ith particle and the specified single particle be $i = 0$. Then, the (canonical) probability for a set of microstates in which $h_0 = \varepsilon$ is given by

$$P(h_0 = \varepsilon) = \frac{1}{Z} \sum_{\{h_i\}_{i\neq 0},\, h_0=\varepsilon} e^{-\beta \sum_i h_i} \propto e^{-\beta\varepsilon}. \tag{15.43}$$

(1) There are 4 states, but there are only two energy levels with $\varepsilon = 3D/8$ and $-13D/8$. Therefore, a one-particle (or single-spin) state with $\varepsilon = 3D/8$ is with

$$p = \frac{e^{-3\beta D/8}}{2(e^{-3\beta D/8} + e^{13\beta D/8})} = \frac{1}{2(1 + e^{2\beta D})}. \tag{15.44}$$

Do not forget the 1/2 factor. The one-particle state with $\varepsilon = -13D/8$ is with

$$p' = \frac{e^{13\beta D/8}}{2(e^{-3\beta D/8} + e^{13\beta D/8})} = \frac{e^{2\beta D}}{2(1 + e^{2\beta D})}. \tag{15.45}$$

(2) The easiest method is to use the Shannon formula:[285]

$$S = -2k_B \left[\frac{1}{2(1+x)} \log \frac{1}{2(1+x)} + \frac{x}{2(1+x)} \log \frac{x}{2(1+x)}\right] = k_B \left\{\log[2(1+x)] - \frac{x}{1+x} \log x\right\}, \tag{15.46}$$

where $x = e^{2\beta D}$.

(3) Setting x as above, we have

$$C = T\frac{dS}{dT} = -(2D\beta)\frac{dS}{d2D\beta} = -2D\beta\frac{dx}{d2D\beta}\frac{dS}{dx} = -2D\beta x\frac{dS}{dx} = k_B(2D\beta)^2\frac{x}{(1+x)^2}. \tag{15.47}$$

That is, for large T (small β), $x \simeq 1$, so

$$C = k_B(D/k_B)^2/T^2. \tag{15.48}$$

Therefore, $D/k_B = T_0$ or D/k_B is 0.18 K.

D8.3 [Collection of permanent dipoles]

Let us consider a collection of non-interacting electric dipoles $\{\boldsymbol{p}_i\}$ sitting on the lattice points $\{i\}$ as illustrated in Fig. 15.6. We ignore its rotational kinetic energy, so the system Hamiltonian (the total intrinsic energy) is 0.

[285] There are several ways to compute entropy. If you know probability explicitly, the Shannon formula may be useful. In this case, you must not forget that the sum is over the *elementary events*. The microcanonical way is probably the least useful in practice. When you compute S from the canonical ensemble, use $S = (E - A)/T$ with E being calculated by the Gibbs-Helmholtz relation $[\partial(A/T)/\partial(1/T)]_V = -\partial \log Z/\partial\beta = E$. Do NOT, in practice, use $S = -(\partial A/\partial T)_V$ directly.

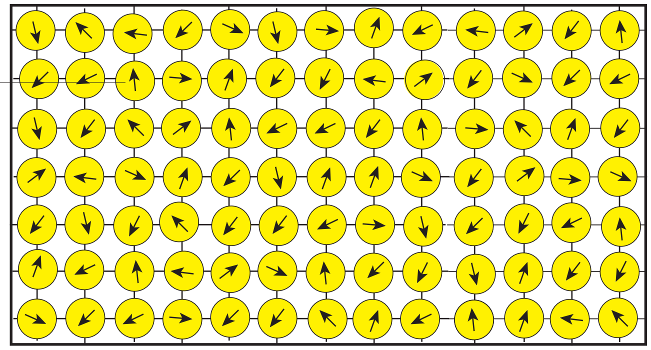

Figure 15.6: Dipole moments sitting on a lattice (the dipoles are actually three-dimensional)

A permanent electric dipole $\boldsymbol{p}$ has a potential energy $u = -\boldsymbol{p} \cdot \boldsymbol{E}$, if an external electric field $\boldsymbol{E}$ is imposed. Thus, the total potential energy of the system in the electric field reads

$$U = -\boldsymbol{E} \cdot \boldsymbol{P}, \tag{15.49}$$

where $\boldsymbol{P}$ is the electric polarization defined as

$$\boldsymbol{P} = \sum_i \boldsymbol{p}_i. \tag{15.50}$$

We wish to obtain $\boldsymbol{P}$ ($\simeq$ its expectation value thanks to the LLN) as a function of T and $\boldsymbol{E}$.

(0) The 'standard' statistical mechanical textbooks proceed as follows. The system Hamiltonian is

$$`H' = -\boldsymbol{E} \cdot \boldsymbol{P}. \tag{15.51}$$

Therefore, the internal energy is its (e.g., canonical) average:

$$E = \langle `H' \rangle. \tag{15.52}$$

The (canonical) partition function is thus given by

$$`Z' = \left[\int d^3\boldsymbol{p}\, e^{\beta \boldsymbol{E} \cdot \boldsymbol{p}} \right]^N. \tag{15.53}$$

From this, we obtain the (Helmholtz) free energy A as usual: $`A' = -k_BT \log `Z'$, whose Gibbs relation is understood to be

$$d`A' = -SdT - \boldsymbol{P} \cdot d\boldsymbol{E}. \tag{15.54}$$

What is wrong (at least awkward) with the above logic?[286]

To answer this question correctly, let us proceed according to the correct statistical

[286] However, most textbooks avoid explicit embarrassment by not mentioning the names of the free

thermodynamics.
(1) What is the thermodynamic coordinates for the system?
(2) What is its internal energy?
(3) What is the definition of the microcanonical ensemble for the system?
(4) Fixing $\boldsymbol{P}$ is inconvenient. Also we do not wish to put the system in an adiabatic condition, so we wish to keep the system temperature constant (isothermal). Then, for our system what is the convenient thermodynamic potential Φ? Also write down the Gibbs relation for Φ.
(5) What sort of statistical ensemble you should employ to obtain Φ directly? That is, what is the corresponding partition function $\tilde{Z}$?[287]
(6) Compute $\Phi = -k_B T \log \tilde{Z}$.
(7) Compute $\boldsymbol{P}$ as a function of $\boldsymbol{E}$ and T.

Solution
(0) The key physics observations are:
(i) The internal energy is the energy stored in the system itself,
(ii) The potential energy like U in this problem (or $-\boldsymbol{B} \cdot \boldsymbol{M}$ for magnetic systems) is not stored solely in the system itself, but it is stored in the 'relationship' between the system and the external field or the device making the external field (just as the volume energy PV; it is there only because something (external to the system) maintains P).

Thus, 'H' is not the system Hamiltonian.[288] In this case the system Hamiltonian is zero, since we ignore the kinetic energy and since the dipoles are not interacting with each other. Therefore, inevitably $E = 0$; since 'H' is not the system Hamiltonian, 'E' cannot be the system internal energy (but is one of the generalized Enthalpies as we will see later).

This misidentification of energy (or the system Hamiltonian) totally screws up the statistical thermodynamic description of the system. Needless to say 'Z' is not the usual canonical partition function, since 'H' is not the system Hamiltonian. If you can declare 'A' to be the system Helmholtz free energy $A = E - TS$, then the Gibbs relation

$$d\text{`}A\text{'} = TdS + \boldsymbol{E} \cdot d\boldsymbol{P} \tag{15.55}$$

must hold, but in 'A' $\boldsymbol{P}$ does not appear anywhere (it was averaged or summed away when you compute 'Z'). Therefore, in the standard books they 'declare' that

energy explicitly and not writing the Gibbs relations explicitly; basically evading thermodynamics. Garrod, Wolfe, Reichl, Greiner et al., Le Bellac et al., etc., follow this line (probably without never thinking). Therefore, in practice, you should look at the definition of the 'Hamiltonian' and the partition functions, and then determine which Gibbs relation you should use when you read usual books or attend usual courses. Perhaps, to be successful as scientists these days, don't be too serious.

[287] Recall the 'max-sum' correspondence.

[288] You could say it is the Hamiltonian of the system and a part of the electric field modified by the presence of the dipoles.

this 'Helmholtz free energy' obeys (15.54) to 'correct' wrong identifications of quantities.[289]

(1) Generally, it is the (internal) energy E and $\boldsymbol{P}$ (recall that they must be energy and work coordinates that are extensive). In the present case $E = 0$ because the system Hamiltonian is zero. Thus, actually, there is only one coordinate $\boldsymbol{P}$ because of the artificial simplification of the problem that has no interactions among different lattice sites.

(2) This is already answered. $E = 0$, invariant. Thus, the Gibbs relation is actually

$$0 = TdS + \boldsymbol{E} \cdot d\boldsymbol{P}, \tag{15.56}$$

but you may identify this with dE as usual (while noting that it is always 0).

(3) Since the thermodynamic coordinates are E $(= 0)$ and $\boldsymbol{P}$, the microcanonical ensemble consists of microstates with a fixed $\boldsymbol{P}$.[290] Accordingly, the microcanonical partition function $W(E, \boldsymbol{P})$ (actually, $W(0, \boldsymbol{P})$) is the total number of microstates with $\boldsymbol{P}$ (with a leeway).

(4) Since we do not wish to fix $\boldsymbol{P}$, we must allow its change. If there is an external electric field $\boldsymbol{E}$, we must allow the system (+ the field) to change its interaction energy freely. Also we wish to allow the system to exchange heat freely with its environment. Thus, instead of the total energy $E + U$ (though not of the system), we should study $\Phi = (E - Q) + U$ (actually a Legendre transform of E as we see in (5)), where $U = -\boldsymbol{E} \cdot \boldsymbol{P}$, the total potential energy. The Gibbs relation for Φ reads

$$d\Phi = d(A - \boldsymbol{E} \cdot \boldsymbol{P}) = -SdT - \boldsymbol{P} \cdot d\boldsymbol{E}, \tag{15.57}$$

where A is not the fake Helmholtz free energy (= 'A') but the true Helmholtz free energy of the system.

(5) The Legendre transformation used in (4) is actually

$$-\Phi = \max_{\boldsymbol{P}} [\boldsymbol{E} \cdot \boldsymbol{P} + ST - E] \tag{15.58}$$

energetically, or (recall $d(-S) = (-1/T)dE + (\boldsymbol{E}/T) \cdot d\boldsymbol{P}$ and $-S$ is convex).

$$-\frac{\Phi}{T} = \max_{\boldsymbol{P}} \left[\frac{\boldsymbol{E}}{T} \cdot \boldsymbol{P} - \frac{E}{T} - (-S) \right]. \tag{15.59}$$

However, since $E = 0$ definitely in our system, you may drop it from the above formulas.

[289] A professor told me that good students should know the difference. Yes, but I believe it is better to point out the conceptual mistake in the usual books and to correct it.

[290] More precisely, we must allow some macroscopic leeway such that $\boldsymbol{P}$ is in a (macroscopically) small volume element of $\boldsymbol{P}$.

From either of the above relations we can write

$$-\beta\Phi = \max_{\boldsymbol{P}} \left[\frac{S}{k_B} + \beta \boldsymbol{E} \cdot \boldsymbol{P} \right]. \tag{15.60}$$

or

$$e^{-\beta\Phi} = \max_{\boldsymbol{P}} W(0, \boldsymbol{P}) e^{\beta \boldsymbol{E} \cdot \boldsymbol{P}}. \tag{15.61}$$

Thus, with the relative error of $O[\log N/N]$, we can use the 'max-sum' correspondence:

$$e^{-\beta\Phi} = \sum_{\boldsymbol{P}} W(0, \boldsymbol{P}) e^{\beta \boldsymbol{E} \cdot \boldsymbol{P}} \equiv \tilde{Z}(T, \boldsymbol{E}). \tag{15.62}$$

Since E does not change, you might wonder how we can introduce T into the description. Although we have β, it appears only in combination with $\boldsymbol{E}$ (and as Φ/T). Thus, the entropic form of the Gibbs relation $dS = -(\boldsymbol{E}/T) \cdot d\boldsymbol{P}$ that cannot define T alone causes no difficulty. Even though we write $\tilde{Z}(T, \boldsymbol{E})$, it is actually a function of $\boldsymbol{E}/T$.

(6) Since the summation or the integration over $\boldsymbol{P}$ may be decomposed into the sums or integrals for individual molecular dipoles, we can write

$$\tilde{Z} = \left[\sum_{\boldsymbol{p}_1} e^{\beta \boldsymbol{E} \cdot \boldsymbol{p}_1} \right]^N. \tag{15.63}$$

Here, the first dipole is used as the representative.

Thus, we have only to compute[291]

$$z(\boldsymbol{E}) = \int d\boldsymbol{e}\, e^{\beta p \boldsymbol{e} \cdot \boldsymbol{E}} = \int d\boldsymbol{e}\, e^{\beta p E \cos\theta}, \tag{15.64}$$

where $\boldsymbol{e}$ is the directional unit vector of the dipole moment with respect to the electric field direction ($\boldsymbol{p} = p\boldsymbol{e}$ with $p = |\boldsymbol{p}|$), $E = |\boldsymbol{E}|$, and the angle between $\boldsymbol{E}$ and $\boldsymbol{p}$ (or $\boldsymbol{e}$) is θ.

The integration is on the unit sphere and we can compute the 'single-body' or 'single-site' canonical partition function as

$$z(\boldsymbol{E}) = 2\pi \int_0^\pi d\theta\, \sin\theta\, e^{\beta p E \cos\theta} = 2\pi \int_{-1}^1 dx\, e^{\beta p E x} = \frac{4\pi}{\beta p E} \sinh \beta p E. \tag{15.65}$$

Therefore, we have arrived at

$$\Phi = -N k_B T \log \left(\frac{4\pi}{\beta p E} \sinh \beta p E \right). \tag{15.66}$$

[291]The summation is actually over the directions of the dipole, so the following integral is over the directions, but you need not worry about this and may integrate over $\boldsymbol{p}$; $|\boldsymbol{p}|$ is constant, so the resultant Φ is shifted only by a constant.

(7) The Gibbs relation $d\Phi = -SdT - \boldsymbol{P}\cdot d\boldsymbol{E}$ (see (4)) tells us

$$\boldsymbol{P} = -\left.\frac{\partial \Phi}{\partial \boldsymbol{E}}\right|_T. \tag{15.67}$$

From the structure of z we can immediately see

$$\langle \boldsymbol{p}\rangle = k_BT\frac{\partial}{\partial \boldsymbol{E}}\log z(\boldsymbol{E}) = p\frac{\partial}{\partial \beta p\boldsymbol{E}}\log\left(\frac{\sinh\beta pE}{\beta pE}\right) = pL(\beta pE)\frac{\partial E}{\partial \boldsymbol{E}}, \tag{15.68}$$

where $L(x)$ is the Langevin function

$$L(x) = \frac{d}{dx}(\log\sinh x - \log x) = \coth x - \frac{1}{x}. \tag{15.69}$$

The last derivative with respect to $\boldsymbol{E}$ (that is a kind of gradient) may be most easily computed from the differentiation of $E^2 = \boldsymbol{E}\cdot\boldsymbol{E}$:

$$EdE = \boldsymbol{E}\cdot d\boldsymbol{E}. \tag{15.70}$$

From this we get (or see (22.70))

$$\frac{\partial E}{\partial \boldsymbol{E}} = \frac{\boldsymbol{E}}{E}. \tag{15.71}$$

Thus,

$$\boldsymbol{P} = N\langle \boldsymbol{p}\rangle = pNL(\beta pE)\frac{\boldsymbol{E}}{E}. \tag{15.72}$$

If you wish to do all the calculation componentwisely, we can proceed as follows.

$$P_i = \left.\frac{\partial \Phi}{\partial E_i}\right|_T = Nk_BT\frac{\partial}{\partial E_i}\log\frac{\sinh\beta pE}{\beta pE} = pN\frac{\partial}{\partial \beta pE_i}\log\frac{\sinh\beta pE}{\beta pE} \tag{15.73}$$

$$= pNL(\beta pE)\frac{\partial E}{\partial E_i} = pNL(\beta pE)\frac{E_i}{E}. \tag{15.74}$$

This is just (15.72). Here, we used

$$\frac{\partial E}{\partial E_i} = \frac{\partial |\boldsymbol{E}|}{\partial E_i} = \frac{\partial\sqrt{\sum_i E_i^2}}{\partial E_i} = \frac{2E_i}{2\sqrt{\sum_i E_i^2}} = \frac{E_i}{|\boldsymbol{E}|}. \tag{15.75}$$

D8.4. [Information rudiments]

Suppose there are two fair dice. We assume that one dice is red and the other is green (that is, distinguishable). Let us record the numbers that are up in the red-green order as (m,n) $(m,n \in \{1,2,\cdots,6\})$.
(1) To know a particular pair of numbers (a,b) unambiguously what amount of information (in bits) do you need?
$(*)$ Actually, how many 'yes-no' questions do you need to pinpoint the outcome?
(2) You are told that the sum $a+b$ is not less than 5. What is the amount of information you gain from this message?
(3) Next, you are told, one of the dice shows the face less than 3. What is the amount of information you gain? (You know the info obtained from (2) already.)
(4) Now, you are told that actually, the one of the dice in (3) is the red one. What is the amount of information of this message?
(5) Finally, you are told that face pair is actually $(2,5)$. What is the amount of information in this final statement?

As you guess, in whatever order the information is given, the total information you gain does not depend on the actual 'path,' because the extent of your ignorance is a 'state function.'

Solution.
(1) There are 36 distinguishable states and they are all equally probable. Therefore, the total uncertainty is $\log_2 36 = 5.17$ bits, or the surprisal you have, when you are told, say, $(1,1)$ actually happens, is 5.17 bits. That is, you need 5.17 bits of information to pinpoint a particular elementary event. $(*)$ Let us devise the 'cleverest' way to ask the needed questions:
(i) Divide the 36 cases into two even set of cases 18 + 18 and ask which contains the outcome. 1 bit question.
(ii) Divide the right 18 cases into two even set of cases 9 + 9 and ask which contains the outcome. 1 bit question.
(iii) Divide 9 into 4+4+1, and ask which '4' contains the outcome. 1 bit question.

(iiia) If the answer is 'neither of them,' we know the answer, but with probability 1/9.

(iiib) If the answer is one of '4' (with probability 8/9), we must continue to ask
(iv) two questions further to pinpoint the pair in '4'. 2 bit questions.

Thus the expected number of the 'questions' is

$$\frac{1}{9} \times 3 + \frac{8}{9} \times 5 = \frac{43}{9} < 5.17. \tag{15.76}$$

How come? Since the total information we need must be 'path-independent,' some question(s) must not be a genuine 1 bit question.

Indeed, we exploited the discreteness of the problem and 'cheated' by devising questions that are not really the 1 bit yes-no question. The question asked at 4+4+1 juncture is not an honest 1 bit question. Actually, if you wish to be as 'fairly' as possible, $36 \to 18+18 \to 4+5 \to (2,2)$ or $(2,3)$ $\cdots$ certainly requires more than 5 questions on the average.

In this case '$18 \to 6+6+6$ and $6 \to 2+2+2$' is the cleverest and you need only 4 questions. In this case, the three choice question gives you $\log_2 3 = 1.58$ bits, so the total information you get is 1+ 1.585 + 1.585 +1 = 5.17 bits.

Real life lessons are that you should try to maximize the information you can get from a single yes-no question (make cases as even as possible) and that (in real life) an answer to a single 'yes-no' question could give you more than 1 bit.

(2) There is no simpler way than to list actually all the elementary states. The following 6 states: (1,1), (1,2), (1,3), (2,1), (2,2), (3, 1) are excluded. Remaining are 30 states, all equally probable, so $\log_2 30 = 4.91$ bits is the uncertainty. That is, $5.17 - 4.91 = 0.26$ bits is the amount of information in the message.

(3) Red = 1: Green = 4, 5 or 6
Red = 2: Green = 3, 4, 5 or 6.
Therefore, there are $7 \times 2 = 14$ states remaining. This uncertainty is $\log_2 14 = 3.81$. We had 4.91 bits of uncertainty, so this message must have conveyed 1.1 bits.
(4) Obviously, 1 bit.

(5) There is no uncertainty remaining, so 2.81 bits (this is, needless to say, the surprisal of an event of probability 1/7).

D8.5 [Information rudiments 2]
Suppose a student D cheats in a yes-no quiz by copying the answer of an all A student A who is correct with probability 92%. Assuming that the success rate of D is 65%, what is the information gain of D on the average by copying the solutions of student A's?

Solution.
The key point is the relation between 'information' and entropy'. The entropy of a state is the required information to describe the state unambiguously. Thus, decreasing entropy (importing 'negentropy') is adding information.

The entropy (in the Shannon sense) of student A's answer (or his brain state) is

$$h = -(0.92 \log_2 0.92 + 0.08 \log_2 0.08) = 0.402 \text{ bits}. \tag{15.77}$$

This means the amount of information $1 - h = 0.6$ bits is needed further for student A to be perfect.

On the other the entropy of student D's answer is

$$h' = -(0.65 \log_2 0.65 + 0.35 \log_2 0.35) = 0.934 \text{ bits}. \tag{15.78}$$

We need almost 1 bit (close to the entropy of randomness) of o=information to describe the mess of D's brain.

Thus, his brain state is 'improved' (i.e., its entropy becomes closer to zero) through cheating by $0.934 - 0.402 = 0.532$ bits.

Exercise 8

E8.1 [Constant magnetic field ensemble]

"There is a lattice containing N lattice sites on which non-interacting spins of $S = 1$ (in the term ^3P) sit. The spin Hamiltonian at each site reads

$$H = DS_z^2. \tag{15.79}$$

The system is imposed a magnetic field B in the z-direction and the magnetic moment of of the system is μS_z. Compute the magnetization of the system as a function of B and T."

This is the way a question in Qual goes, but what this tells you is that the problem is just as:
At each site is an entity[292] that can take $s = 0$ or ± 1, whose energy is given by

$$h = Ds^2. \tag{15.80}$$

The potential energy of the entity in a magnetic field B (actually, the z-component of $\boldsymbol{B}$) is given by $U = -\mu s B$. Compute $M = \mu N\langle s\rangle$ as a function of T and B.
(1) What is the thermodynamic coordinates of this "magnetic" system?
(2) We wish to describe the system under constant B and T instead of constant M and E. What is the most convenient thermodynamic potential Ψ?
(3) Find the most convenient partition function $\tilde{Z}$ such that $\Psi = -k_B T \log \tilde{Z}$.
(4) Compute Ψ.
(5) Write down its Gibbs relation for Ψ. What is

$$\left.\frac{\partial \Psi/T}{\partial 1/T}\right|_B \ ? \tag{15.81}$$

(6) Compute the magnetization M as a function of the magnetic field and temperature.
(7) Can you compute the internal energy of the system?

Solution.
(1) E and M are the respectable thermodynamic coordinates. In this case, the internal energy is not zero nor constant, even if there is no external field.

(2) We must pay attention to the (system + a part of environment) energy $E - BM$ and allow free exchange of heat, so we consider the thermodynamic potential defined as $\Psi = E - BM - Q = A - BM$, where A is the (true, not 'fake') Helmholtz free energy. That is, the proper Legendre transformation relevant to the current situation is

$$-\Psi = \max_{S,M}\,[ST + BM - E] \tag{15.82}$$

[292]actually the z-component of a spin.

energetically or[293] (since E is monotonic in S for each M)

$$-\frac{\Psi}{T} = \max_{E,M}\left[S + \left(\frac{B}{T}\right)M - E\right]. \tag{15.84}$$

Therefore,

$$e^{-\beta\Psi} = \max_{E,M} e^{S/k_B - \beta E + \beta BM} = \max_{E,M}\left[W(E,M)e^{-\beta E+\beta MB}\right]. \tag{15.85}$$

(3) Now, we can appeal to the general 'max-sum' correspondence, ignoring the relative errors of $O[\log N/N]$:

$$e^{-\beta\Psi} = \sum_{E,M} W(E,M)e^{-\beta E+\beta MB}. \tag{15.86}$$

Therefore, the most convenient partition function is

$$\tilde{Z}(T,B) = \sum_{E,M} W(E,M)e^{-\beta E+\beta MB} = \sum_{s_i\in\{0,\pm 1\}\text{ for all sites}} e^{-\beta E+\beta MB}. \tag{15.87}$$

Up to this point, everything is explained from scratch; in your report, you can simply write down the needed formulas (by guessing).

(4) We may separate the sum into the sums on each lattice sites, so

$$\tilde{Z}(T,B) = \left[\sum_{s\in\{0,\pm 1\}} e^{-\beta Ds^2+\beta\mu sB}\right]^N. \tag{15.88}$$

That is,

$$\tilde{Z}(T,B) = (1 + e^{-\beta D+\beta\mu B} + e^{-\beta D-\beta\mu B})^N. \tag{15.89}$$

Therefore,

$$\Psi = -Nk_BT\log(1 + e^{-\beta D+\beta\mu B} + e^{-\beta D-\beta\mu B}). \tag{15.90}$$

(5) The Gibbs relation is (recall (15.82))

$$d\Psi = -SdT - MdB. \tag{15.91}$$

Therefore,

$$\left.\frac{\partial\Psi/T}{\partial 1/T}\right|_B = \Psi - T\left.\frac{\partial\Psi}{\partial T}\right|_B = \Psi + ST = E - BM. \tag{15.92}$$

[293] Or, entropically, Legendre transformation of $-S$ directly gives

$$-\frac{\Psi}{T} = \max_{E,M}\left[\frac{B}{T}M + \left(-\frac{1}{T}\right)E - (-S)\right]. \tag{15.83}$$

This is a sort of enthalpy (cf. $H = E - (-P)V$). It is not the internal energy; if you misidentify Ψ with the Helmholtz free energy, then you might think the quantity obtained in (15.92) is the internal energy, but, as you see, it is obviously different; $(\partial(E - BM)/\partial M)_S$ is not B!

If you use the Gibbs relation for $-\Psi/T$:

$$d\left(-\frac{\Psi}{T}\right) = -Ed\frac{1}{T} + Md\frac{B}{T}, \tag{15.93}$$

you might compute (15.81) as the internal energy. This is a bit 'delicate,' because, fixing B/T in (15.93) gives

$$\left.\frac{\partial \Psi/T}{\partial 1/T}\right|_{B/T} = E. \tag{15.94}$$

Since we must fix B, we cannot use (15.93) immediately; first we rewrite it as

$$d\left(-\frac{\Psi}{T}\right) = -Ed\frac{1}{T} + MBd\frac{1}{T} + \frac{M}{T}dB. \tag{15.95}$$

Then, we obtain (15.92).

Therefore,

$$E - B \cdot M = N\frac{(D - \mu B)e^{-\beta D + \beta\mu B} + (D + \mu B)e^{-\beta D - \beta\mu B}}{1 + e^{-\beta D + \beta\mu B} + e^{-\beta D - \beta\mu B}}. \tag{15.96}$$

(6) From (15.91) we get

$$M = -\left.\frac{\partial \Psi}{\partial B}\right|_T, \tag{15.97}$$

or from (15.93) we get

$$M = -\left.\frac{\partial \Psi/T}{\partial B/T}\right|_T = -\left.\frac{\partial \Psi}{\partial B}\right|_T = \left.\frac{\partial \log \tilde{Z}}{\partial \beta B}\right|_\beta = N\mu\frac{e^{-\beta D + \beta\mu B} - e^{-\beta D - \beta\mu B}}{1 + e^{-\beta D + \beta\mu B} + e^{-\beta D - \beta\mu B}}. \tag{15.98}$$

(7) Now, we know $E - BM$ and BM, we can obtain the internal energy

$$E = ND\frac{e^{-\beta D + \beta\mu B} + e^{-\beta D - \beta\mu B}}{1 + e^{-\beta D + \beta\mu B} + e^{-\beta D - \beta\mu B}}. \tag{15.99}$$

E8.2 [Information rudiments]
There are red and green tetrahedral fair dice. Thus, the outcome one simultaneous slowing gives (m, n), $(m, n \in \{1, 2, 3, 4\})$. (1) Initially you do not know anything about the outcome. How many bits do you need to pinpoint the outcome? What is

the ‘entropy’ h of your brain state?
(2) Can you devise a scheme to pinpoint the outcome on the average less than 4 ‘yes-no’ questions?
(3) You get a message that the sum $n + m > 4$. After knowing this, what is your brain ‘entropy’? What is the information you have obtained from the message?
(4) Then, you are told that the red gives larger face value than the green. After knowing this, what is your brain ‘entropy’? What is the information you have obtained from the message?
(5) Now you are told the outcome: (4,3). What is the information you get from this final message?

Solution.
(1) There are 16 cases all expected to occur evenly. You need $\log_2 16 = 4$ bits of information to pinpoint the outcome. Your knowledge level is perfect if you know 6 bits, your ignorance level is 4 bits. That is your brain ‘entropy’ is 4 bits.

(2) I believe less than 3 questions is possible, because $\log_3 16 = 2.5$.

(3) $m + n > 4$ means that we must exclude (1,1), (1,2), (2,1), (1,3), (3,1), (2,2). Thus, there are 10 states remaining. You still need $\log_2 10 = 3.32$ bits of information to pinpoint the outcome. Thus, your ignorance level is 3.32 bits. That is your brain ‘entropy’ is 3.32 bits. This is improved from 4 bits by $4 - 3.32 = 0.68$ bits. This must be the amount of information in the message.

(4) You are told that the ‘red value’ is actually larger than the ‘green value.’ Therefore, the possible outcomes are (3,2), (4,1), (4,2), or (4,3), 4 states. Thus, your brain entropy is now 2 bits. Thus, you obtained $3.32 - 2 = 1.32$ bits. This is the amount of information in the message.
(5) Obviously, 2 bits.

16 Specific heat of solid

Summary
∗ Quantization forbids incremental increase of energy, so quantization generally reduces specific heat.
∗ If you take into account the proper dispersion relation of a crystal, quantized harmonic oscillators can explain solid specific heat.

Key words
quantum harmonic oscillator, Debye model, T^3-law, equipartition of energy

What you should be able to do
∗ Explain why quantization usually reduces specific heats.
∗ Be able to compute the canonical partition function of the quantized harmonic oscillator.

16.1 Review: never think physics does not demand memorizing

Let's collect the formulas you must remember (their names are not mentioned), no definitions of symbols are provided, but a pretty standard convention (adopted in these lectures) is followed. You must be able to explain what they are and how to use them:

$$\Delta E = Q + W, \tag{16.1}$$

$$dS \geq \frac{1}{T_e} d'Q. \tag{16.2}$$

$$dE = TdS - PdV + \mu dN + \boldsymbol{B} \cdot d\boldsymbol{M} + \cdots. \tag{16.3}$$

$$A = E - TS, \;\; G = A + PV, \;\; H = E + PV. \tag{16.4}$$

$$\begin{aligned} dH &= TdS + VdP + \mu dN + \boldsymbol{B} \cdot d\boldsymbol{M} + \cdots. & (16.5)\\ dA &= -SdT - PdV + \mu dN + \boldsymbol{B} \cdot d\boldsymbol{M} + \cdots. & (16.6)\\ dG &= -SdT + VdP + \mu dN + \boldsymbol{B} \cdot d\boldsymbol{M} + \cdots. & (16.7) \end{aligned}$$

$$\Delta A \leq W. \tag{16.8}$$

$$S = k_B \log w(E, X). \tag{16.9}$$

$$A = -k_B T \log Z(T, X). \tag{16.10}$$

$$Z = \sum_E w(E, X) e^{-\beta E} = Tr\, e^{-\beta H} = \frac{1}{h^{3N} N!} \int d\Gamma\, e^{-\beta H}. \tag{16.11}$$

$$S = -k_B \int d\Gamma\, p \log p, \;\; H(p) = -\sum_i p_i \log p_i. \tag{16.12}$$

16.2 Ideal gas with internal degrees of freedom

If an ideal gas particle has internal degrees of freedom, the Hamiltonian of the gas consists of two parts:

$$H = H_0 + H_i, \tag{16.13}$$

where H_0 is the Hamiltonian of the translational motion

$$H_0 = \sum_{i=1}^{N} \frac{1}{2m} \boldsymbol{p}_i^2, \tag{16.14}$$

and H_i is the Hamiltonian governing the internal degrees of freedom, which is a sum of Hamiltonians h_i governing individual molecular internal motions:

$$H_i = \sum_{i=1}^{N} h_i. \tag{16.15}$$

The translational degrees and internal degrees of freedom are not interacting, so they are completely independent (mechanically and statistically). Hence, the canonical partition function reads

$$Z = Z_{ideal} Z_i, \tag{16.16}$$

where Z_{ideal} is the partition function for a monatomic ideal gas we computed before, and Z_i is the "internal" partition function

$$Z_i = z^N, \tag{16.17}$$

with

$$z = \sum e^{-\beta h}. \tag{16.18}$$

Here, the suffix to denote a particular molecule has been dropped, since all the internal partition functions are identical for identical molecules.

16.3 Collection of harmonic oscillators: classical approach

An important internal motion of gas molecules is vibration. Let us consider a diatomic molecule whose vibrational degree of freedom may be described as a 1D harmonic oscillator of (effective mass) m and angular frequency ω:

$$h = \frac{1}{2m}(p^2 + m^2\omega^2 q^2). \tag{16.19}$$

Although we already know that this oscillator should not be treated classically, let us study it classically to know how bad the result is:

$$z = \frac{1}{h}\int dpdq\, e^{-\beta(p^2+m^2\omega^2q^2)/2m} = \frac{1}{h}\left(\frac{2\pi m}{\beta}\frac{2\pi}{m\omega^2\beta}\right)^{1/2} = \frac{k_BT}{\hbar\omega}. \tag{16.20}$$

Therefore,

$$Z_i = \left(\frac{k_BT}{\hbar\omega}\right)^N = (\beta\hbar\omega)^{-N}. \tag{16.21}$$

At this juncture, we must realize that the partition function Z_i is also the canonical partition function of a collection of 1D oscillators sitting individually at lattice points.

The internal energy of a collection of N 1D oscillators is

$$E = N\frac{\partial}{\partial\beta}\log(\beta\hbar\omega) = N/\beta = Nk_BT. \tag{16.22}$$

16.4 Entropy of classical harmonic oscillator

Using E, we immediately get

$$S = (E - A)/T = Nk_B + Nk_B\log(k_BT/\hbar\omega) = Nk_B\log T + \text{ const.} \tag{16.23}$$

The result implies that in the $T \to 0$ limit $S \to -\infty$. Therefore, to describe a harmonic oscillator at T knowing only the state information at much lower temperature T_0 a large amount of additional information $\sim \log(T/T_0)$ is required, especially if T_0 is close to zero. This must violate a certain fundamental principle: *the finiteness principle* that a finite object with finite energy should require only a finite amount of information for its complete description (if totally isolated).[294]

This is a good occasion to discuss another principle of thermodynamics: the third law.

[294]《**Consequence of the finiteness principle**》If we combine Boltzmann's principle and this finiteness principle, then Boltzmann's principle must not be applicable to an extremely small phase volumes. That is there must be 'information quantum' that has the dimension of (action)^{3N}. Thus, notice that the existence of a fundamental quantity with the dimension of action (something like h) is required by the finiteness principle and thermodynamics.

16.5 The third law of thermodynamics

Nernst empirically found that all the entropy changes asymptotically vanish in the $T \to 0$ limit. In particular, all the derivatives of entropy S vanish as $T \to 0$ (*Nernst's law*). All the specific heat vanishes as $T \to 0$. Nernst concluded that entropy becomes constant (independent of any thermodynamic variables) in the $T \to 0$ limit. Later, Planck chose this constant to be zero (the concept of *absolute entropy*).

We adopt the following as *the third law of thermodynamics*:

Reversible change of entropy ΔS vanishes in the $T \to 0$ limit.

This implies that to describe the state of a macroscopic system at $T = 0$, required information is subextensive, or the number of YES-NO questions needed to know the macrostate is zero per particle.

The entropy we computed classically above must be wrong.

16.6 3D crystal; classical treatment

Consider a crystal made of N atoms, having $3N$ mechanical degrees of freedom. Small displacements of atoms around their mechanical equilibrium positions should be a kind of harmonic oscillation. Thus, we may regard the crystal as a set of $3N$ independent harmonic oscillators (modes) of various frequencies (due to coupling among atoms). The canonical partition function of the total system is the product of the canonical partition function for each harmonic mode.

Treating the system completely classically and using the definition of the classical partition function (16.20), the partition function reads

$$Z = \prod_{i=1}^{3N} \frac{k_B T}{\hbar \omega_i}. \tag{16.24}$$

The contribution of these oscillators to the internal energy is readily obtained from the equipartition of energy **14.16** as

$$E = 3N k_B T. \tag{16.25}$$

If the volume is kept constant, the frequencies are also kept constant. Therefore, the constant volume specific heat C_V is given by

$$C_V = 3N k_B. \tag{16.26}$$

This is called *Dulong-Petit's law*, which is independent of temperature, a contradiction to the third law of thermodynamics: $C_V \to 0$ in the $T \to 0$ limit.

Its entropy is just as (16.23)

$$S = 3N k_B \log T + \text{ const.} \tag{16.27}$$

Thus, entropy goes to $-\infty$ as $T \to 0$. This of course contradicts the third law.

16.7 Necessity of quantization

We must guess that $C_V \searrow 0$ should be a quantum effect. Quantization of energy implies that you cannot pay the energy cost 'in installments.' Since T indicates your energy payment capability, if T is smaller, then quantized systems are generally harder to excite. Recall Schottky type specific heat **13.5**: it goes to zero in the $T \to 0$ limit because of the energy gap: to excite the system, you must pay this amount at one time.[295]

16.8 1D quantum oscillator

Consider a collection of $3N$ 1-dimensional harmonic oscillators which are not interacting with each other at all.

Let us first examine a single oscillator of frequency ν (angular frequency $\omega = 2\pi\nu$). Elementary quantum mechanics tells us that the energy of the system is quantized as

$$\varepsilon = \left(\frac{1}{2} + n\right)\hbar\omega,\ n = 0, 1, 2, \cdots. \tag{16.28}$$

Each eigenstate is nondegenerate. Thus, if we specify the quantum number n, the microscopic state of a single oscillator is completely specified. The canonical partition function for a single oscillator reads

$$z = \sum_{n=0}^{\infty} \exp\left[-\beta\left(\frac{1}{2} + n\right)\hbar\omega\right]. \tag{16.29}$$

Using $(1-x)^{-1} = 1 + x + x^2 + x^3 + \cdots$ ($|x| < 1$), we get

$$z = \mathrm{e}^{-\beta\hbar\omega/2}(1 - \mathrm{e}^{-\beta\hbar\omega})^{-1} = \left(2\sinh\frac{\beta\hbar\omega}{2}\right)^{-1}. \tag{16.30}$$

16.9 Einstein model of crystal

If we may understand a 3D crystal as a collection of identical $3N$ independent 1D oscillators, the canonical partition function for the system should be

$$Z = z^{3N}. \tag{16.31}$$

[295] At higher temperatures, the specific heat again goes to zero in this case, because there is nothing remaining to be excited; even if you are rich, now you have nothing to buy.

From (16.31) we obtain

$$A(N) = 3Nk_BT\log\left(2\sinh\frac{\beta\hbar\omega}{2}\right), \tag{16.32}$$

and[296*]

$$E = \frac{3}{2}N\hbar\omega\coth\left(\frac{\beta\hbar\omega}{2}\right) = 3N\left(\frac{1}{2}\hbar\omega + \frac{\hbar\omega}{\mathrm{e}^{\beta\hbar\omega}-1}\right). \tag{16.33}$$

Hence, the specific heat is

$$C_V = 3Nk_B\left(\frac{\hbar\omega}{k_BT}\right)^2\frac{\mathrm{e}^{\beta\hbar\omega}}{(\mathrm{e}^{\beta\hbar\omega}-1)^2}. \tag{16.34}$$

At sufficiently high temperatures ($\hbar\omega/k_BT \ll 1$) quantum effects should not be important. As expected we recover the classical result (16.26):

$$C_V \to 3Nk_B. \tag{16.35}$$

For sufficiently low temperatures ($\hbar\omega/k_BT \gg 1$) (16.34) reduces to

$$C_V \simeq 3Nk_B\left(\frac{\hbar\omega}{k_BT}\right)^2\mathrm{e}^{-\beta\hbar\omega}. \tag{16.36}$$

Thus, C_V vanishes at $T = 0$, and the third law behavior is exhibited, but notice that this is a Schottky type specific heat **13.5** due to the energy gap of size $\hbar\omega$.

16.10 Real 3D crystal: Debye model

C_V just obtained goes to zero exponentially fast at variance with the empirical law:

$$C_V \sim T^3. \tag{16.37}$$

As we know from the Schottky type specific heat **13.5** it is the rule that whenever there is a finite energy gap ε between the ground and the first excited states, the specific heat behaves like $\exp(-\beta\varepsilon)$ at low temperatures. The empirical result (16.37) implies that there is no finite energy gap in real crystals.

In a real crystal there is a distribution in vibrational frequencies (= dispersion) as can be seen from Fig. 16.1.

[296*]

$$\coth\frac{x}{2} = \frac{e^{x/2}+e^{-x/2}}{e^{x/2}-e^{-x/2}} = \frac{e^{x/2}-e^{-x/2}+2e^{-x/2}}{e^{x/2}-e^{-x/2}} = 1+\frac{2}{e^x-1}$$

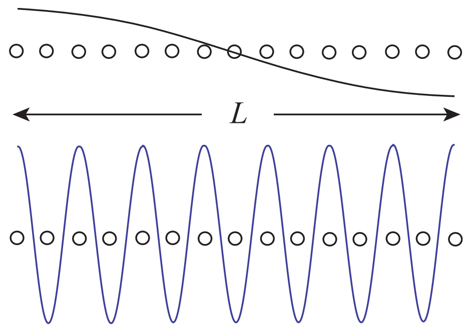

Figure 16.1: Above: The lowest frequency mode; Below: The highest frequency mode (for a 1D lattice of length L).

Not all the vibrations contribute significantly to the low temperature heat capacity of solids. Elastic vibrations in a crystal can be classified into two branches, optical and acoustic (Fig. 16.2). Only the acoustic modes are relevant. We must study the number of acoustic modes with a given angular frequency about ω.

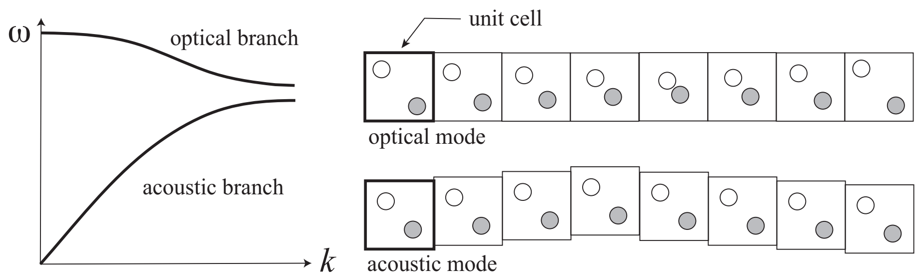

Figure 16.2: The optical modes do not displace the crystal unit cells, but the acoustic modes (here a transversal mode is depicted) displace unit cells. Thus, we have only to count the number of unit cells to count the number of degrees of freedom relevant to the low temperature heat capacity (i.e., the total number of the acoustic modes).

16.11 How to count the number of modes

As can be seen from Fig. 16.1 in a 1D direction the possible wavelengths are $\lambda = 2L, 2L/2, \cdots, 2L/N$ or in wave numbers $k = \pi/L, 2\pi/L, \cdots, N\pi/L$. We have already seen such a sequence before: the de Broglie wave length of a free particle confined in a box which we used to study the classical ideal gas **14.8**. This implies we can compute the number of modes in the volume V just as the number of eigenvalues as follows (we will encounter this approach repeatedly later, so you need not understand it now). Let the number of modes with angular frequency between ω and $\omega + d\omega$ be $\mathcal{D}(\omega)$. Then, we have

$$\int_0^\omega \mathcal{D}(\omega) d\omega = \frac{1}{h^3} \int d\boldsymbol{r} \int_{|\boldsymbol{p}| \le p(\omega)} d\boldsymbol{p}, \tag{16.38}$$

where $p(\omega) = \hbar k = \hbar\omega/c$ (dispersion relation), and c is the sound speed. Therefore, the number of modes between ω and $\omega + d\omega$ is

$$\mathcal{D}(\omega) = \frac{V}{h^3} 4\pi p(\omega)^2 \frac{dp(\omega)}{d\omega} = 4\pi V \frac{\hbar^3}{h^3 c^3}\omega^2 = \frac{1}{2\pi^2} V \frac{\omega^2}{c^3}. \tag{16.39}$$

In reality, there are one longitudinal and two transversal modes for each ω, so the actual number is this times 3.

In contrast to the classical gas case there are two important differences. $\mathcal{D}(\omega) \propto \omega^2$ holds only for low frequency modes where the material may be regarded as an elastic continuum body. Furthermore, the wavelength cannot be indefinitely small as seen from Fig. 16.1. Debye introduced the following approximation:

$$\mathcal{D}(\omega) = A\omega^2 \Theta(\omega_D - \omega), \tag{16.40}$$

where ω_D is the Debye cutoff frequency (which is a materials 'constant' in good approximation) and A is fixed to have the total number of modes (= the total number of lattice cells $N \times 3$) correctly

$$\int_0^{\omega_D} \mathcal{D}(\omega) d\omega = 3N. \tag{16.41}$$

Therefore, $A = 9N/\omega_D^3$.

16.12 Debye model specific heat

Since we know the energy of the mode with ω (16.33), the total energy (the internal energy due to lattice vibration) is

$$E = \int d\omega\, \mathcal{D}(\omega) \left(\frac{1}{2}\hbar\omega + \frac{\hbar\omega}{e^{\beta\hbar\omega} - 1} \right), \tag{16.42}$$

and from (16.34)

$$C_V = k_B \int d\omega\, \mathcal{D}(\omega) \left(\frac{\hbar\omega}{k_B T}\right)^2 \frac{\mathrm{e}^{\beta\hbar\omega}}{(\mathrm{e}^{\beta\hbar\omega} - 1)^2}. \tag{16.43}$$

Although the integration range has an upper bound ω_D, when the temperature is small, replacing this with ∞ does not change the integral appreciably. Therefore, C_V behaves just as T^3 in the low temperature limit; the dimension of the integral is $[\omega]^3$, and we know $[\hbar\omega/k_B T] = 1$, so we may conclude $[\omega]^3 \propto T^3$ simply with the aid of dimensional analysis (or power counting).

17 How to manipulate partial derivatives

Summary
∗ Understand thermodynamics and microscopic picture of the thermal properties of a rubber band.
∗ Review partial derivatives.
∗ The Jacobian technique may be fully utilized if you remember three elementary rules/formulas:

$$\frac{\partial(X,Y)}{\partial(A,B)} = -\frac{\partial(X,Y)}{\partial(B,A)} = \frac{\partial(Y,X)}{\partial(B,A)} = -\frac{\partial(Y,X)}{\partial(A,B)},$$

$$\frac{\partial(X,Y)}{\partial(Z,W)} = \frac{\partial(X,Y)}{\partial(A,B)}\frac{\partial(A,B)}{\partial(Z,W)},$$

and Maxwell's relation for conjugate pairs (X,x) and (Y,y):

$$\frac{\partial(X,x)}{\partial(y,Y)} = 1.$$

Key words
entropic elasticity, Maxwell's relation, adiabatic cooling, adiabatic demagnetization.

What you should be able to do
∗ Practice the Jacobian technique.
∗ Intuitively explain rubber elasticity; be able to get various signs of partial derivatives, and to explain them intuitively.
∗ Explain adiabatic demagnetization.

17.1 Rubber band experiments

Let us perform a small experiment of quasistatic adiabatic processes using a rubber band. Prepare a thick rubber band (that is used to bundle, e.g., asparagus). Use your lip as a temperature sensor. Initially, putting the rubber band to your lip, you sense the room temperature (cool). Now, you hold the both ends of a small portion of the band with your hands and stretch it tightly and quickly (Fig. 17.1).

Then, feel the temperature of the stretched portion with your lip. It must be warm. You have just demonstrated

$$\left.\frac{\partial T}{\partial L}\right|_S > 0, \tag{17.1}$$

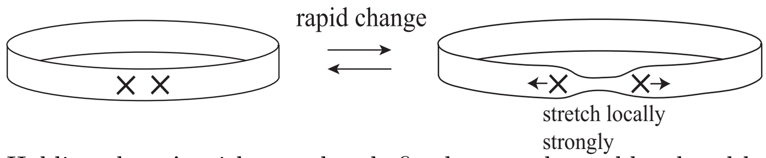

Figure 17.1: Holding the $\times$'s with your hands firmly, stretch a rubber band locally rapidly and strongly to realize (almost) adiabatic and quasistatic processes.

where L is the length of the stretched portion of the rubber band. The Gibbs relation for a rubber band reads

$$dE = TdS + FdL, \tag{17.2}$$

where F is the force (the component of the force parallel to the stretching direction of the force) stretching the band. Since the process is adiabatic and quasistatic, S is constant. Even if you rapidly pull the band, the maximum stretching rate you can realize is very small from the molecular point of view, so the process is (almost) quasistatic. Since the heat conduction is not a very rapid process, during quick stretch the system is virtually thermally isolated (= adiabatic). Thus, S is virtually constant.

17.2 Polymer chain is just as kids playing hand in hand

To begin with, let us try to understand 'microscopically' what we have observed macroscopically. A rubber band is made of a bunch of polymer chains. Take a single chain that is wiggling due to thermal motion (Fig. 17.2a).

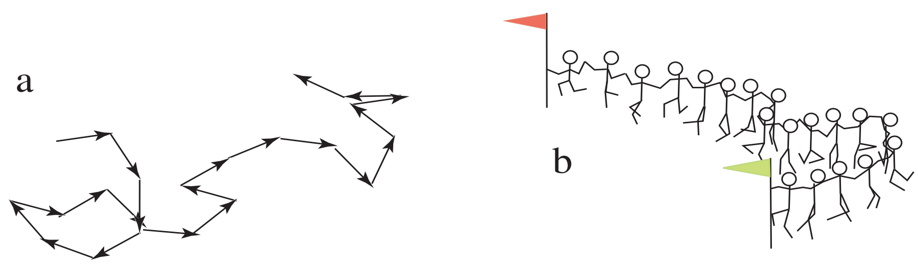

Figure 17.2: **a**: A schematic picture of a single polymer chain. Each arrow is called a monomer. **b**: Polymer-kid analogy. The temperature represents how vigorously kids are moving around. This also includes 'vibration' of individual bodies. The figure is after N. Saito, *Polymer Physics* (Shokabo, 1967) (The original picture was due to T. Sakai's lecture according to Saito). The entropy of a chain is monotonically related to the width of the range kids can play around easily, which becomes smaller if the distance between the flags is increased.

Stretching the chain corresponds to increasing the space between the flags of Fig. 17.2b in the playing kid analogy. If the chain does not break, the spatial room for moving is decreased, but since the kids must keep their entropy, the restricted dancing motion must find substitute degrees of freedom: shaking bodies (i.e., room in the momentum subspace). That is, the temperature of the system should go up. This suggests that if the chain is stretched under constant T, entropy should go down:

$$\left.\frac{\partial S}{\partial L}\right|_T < 0. \tag{17.3}$$

Can you conclude this from what you observed (17.1)? Yes, you can, but you must know how to manipulate partial derivatives efficiently (see toward the end of this section).

17.3 Freely jointed polymer chain

Before explaining useful thermodynamic techniques, let us try to understand the polymer chain system statistical-mechanically. For simplicity, let us consider a polymer chain along the x-axis (Fig. 17.3).

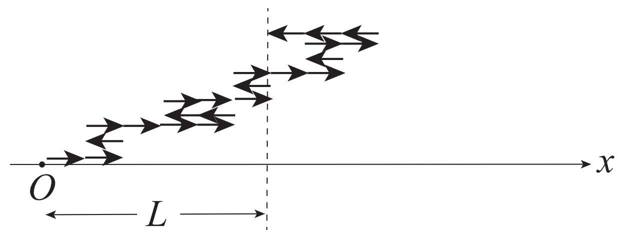

Figure 17.3: It is expanded in the vertical direction to avoid cluttering. Monomers can take the + or − direction. The right and left direction monomer numbers $N_\pm$ ($N_+ + N_- = N$) can be used to compute the number of conformations.

We assume that the chain is free-jointed, that is, there is no energy cost to change its conformation at all (just as an ideal gas can change its configuration without any energy cost). The Hamiltonian of this free-jointed polymer consists of the chain kinetic energy K only, which is, in any case, independent of the conformation of the chain. The Gibbs relation is

$$dE = TdS + FdL, \tag{17.4}$$

where, as above, L is the length (i.e., the end-to-end distance) of the chain, and F is the stretching force. Do not forget that E depends only on T, since it is (just the averaged) K.[297]

We can easily compute the entropy of the ideal rubber band using Boltzmann's principle. Following the figure caption of Fig. 17.3, let us introduce $N_\pm$ so that $N_+ + N_- = N$, and $N_+ - N_- = X \equiv L/\ell$. We have

$$N_\pm = \frac{1}{2}(N \pm X). \tag{17.5}$$

Therefore, (recognize that this is exactly the same problem as the Schottky defect

[297] Since E does not depend on L, you might wonder where the work we do is stored when we stretch the rubber. Since E does not depend on L, it is surely stored not in the chain conformations, but is stored as the kinetic energy (so the temperature goes up). The situation is exactly the same as the ideal gas. In this case, the volume work done to the system is stored as its kinetic energy, since E does not depend on V.

problem **13.2** as to obtaining the entropy)

$$w(X) = \binom{N}{N_+}. \tag{17.6}$$

From this, immediately we obtain (see **13.3**)

$$S = -Nk_B\left[\frac{N_+}{N}\log\frac{N_+}{N} + \frac{N_-}{N}\log\frac{N_-}{N}\right]. \tag{17.7}$$

or

$$S = -Nk_B\left[\frac{N+X}{2N}\log\frac{N+X}{2N} + \frac{N-X}{2N}\log\frac{N-X}{2N}\right]. \tag{17.8}$$

With the aid of the Gibbs relation, we obtain (note that $\ell X = L$)

$$F = -\frac{T}{\ell}\left.\frac{\partial S}{\partial X}\right| = \frac{k_BT}{2\ell}\log\frac{N+X}{N-X}. \tag{17.9}$$

This implies

$$L = N\ell\tanh(\beta\ell F). \tag{17.10}$$

Since $\tanh x \simeq x$ for small x, this implies a Hookean spring

$$F = (k_BT/N\ell^2)L. \tag{17.11}$$

That is, $k_BT/\langle R^2\rangle$ is the spring constant, where $\langle R^2\rangle = N\ell^2$ is the mean square end-to-end distance of a polymer chain.

17.4 Ideal rubber band

Can we explain what we have experienced at the beginning of this section using this entropy? Never. (17.8) implies that if L is fixed, then S is fixed. This is physically obvious, because the set of allowed conformations is completely determined by L. It is clear that we need thermal motion. Then, the entropy should read

$$S = Nk_B\left[\frac{N+X}{2N}\log\frac{N+X}{2N} + \frac{N-X}{2N}\log\frac{N-X}{2N}\right] + S_e(E), \tag{17.12}$$

where S_e is the entropy dependent only on the internal energy E which is solely due to thermal motion.[298] This implies that the temperature-internal energy relation is independent of L (just as the internal energy of the ideal gas is independent of V). Such a rubber is called an *ideal rubber*.

[298] Recall that the ideal gas entropy **10.16** has this form.

We can make a more detailed model of a rubber band to compute more realistic entropy, but without such microscopic details thermodynamics can tell you many qualitative features. To this end, we must be able to manipulate thermodynamic quantities and derivatives more efficiently. Let us begin with a review of partial differentiation.

17.5 Partial derivative review

Let us write down the definition of partial derivatives. Consider a two-variable function $f = f(x, y)$. Then, partial derivatives are defined as

$$\frac{\partial f}{\partial x} \equiv f_x(x, y) = \lim_{\delta x \to 0} \frac{f(x + \delta x, y) - f(x, y)}{\delta x}, \tag{17.13}$$

$$\frac{\partial f}{\partial y} \equiv f_y(x, y) = \lim_{\delta y \to 0} \frac{f(x, y + \delta y) - f(x, y)}{\delta y}. \tag{17.14}$$

Partial differentiation is extremely tricky in general. For example, even if $\partial f/\partial x$ and $\partial f/\partial y$ exist at a point, f can be discontinuous at the same point. E is once continuously differentiable with respect to S and work coordinates, so we need a stronger concept of differentiability in the many-variable case.

17.6 Derivative of multivariate function

Let f be a function of several variables $\boldsymbol{x} = (x_1, \cdots, x_n)$. We could understand f as a function of the vector $\boldsymbol{x}$. We wish to study its 'linear response' to the change $\boldsymbol{x} \to \boldsymbol{x} + \delta\boldsymbol{x}$:

$$\delta f(\boldsymbol{x}) = f(\boldsymbol{x} + \delta\boldsymbol{x}) - f(\boldsymbol{x}) = Df(\boldsymbol{x})d\boldsymbol{x} + o[\delta\boldsymbol{x}], \tag{17.15}$$

where o denotes higher order terms that vanish faster than $\|\delta\boldsymbol{x}\|$, when the limit $\delta\boldsymbol{x} \to 0$ is taken. Here, Df is a linear operator[299] that can be written as

$$Df(\boldsymbol{x})d\boldsymbol{x} = \sum_i \frac{\partial f}{\partial x_i} dx_i. \tag{17.16}$$

If such a linear map Df is well-defined, we say that f is (totally) differentiable (or strongly differentiable). If there are only two variables, we may write

$$Df(x, y)(dx, dy) = \frac{\partial f}{\partial x} dx + \frac{\partial f}{\partial y} dy. \tag{17.17}$$

[299] [This is a repetition for convenience.] L is a linear operator acting on a function set $\mathcal{F}$, if it is a map from $\mathcal{F}$ to some other vector space such that

$$L(\alpha f + \beta g) = \alpha L f + \beta L g,$$

where $f, g \in \mathcal{F}$ and α, β are numbers.

17.7 Maxwell's relations

Let us closely look at $f(x+\delta x, y+\delta y) - f(x,y)$. There are two ways to go from (x,y) to $(x+\delta x, y+\delta y)$, δx first or δy first:

$$\begin{aligned} f(x+\delta x, y+\delta y) - f(x,y) &= f(x+\delta x, y+\delta y) - f(x+\delta x, y) + f(x+\delta x, y) - f(x,y) \\ &= f_y(x+\delta x, y)\delta y + f_x(x,y)\delta x, \quad (17.18) \\ f(x+\delta x, y+\delta y) - f(x,y) &= f(x+\delta x, y+\delta y) - f(x, y+\delta y) + f(x, y+\delta y) - f(x,y) \\ &= f_x(x, y+\delta y)\delta x + f_y(x,y)\delta y. \quad (17.19) \end{aligned}$$

The difference between these two formulas is

$$[f_y(x+\delta x, y) - f_y(x,y)]\delta y - [f_x(x, y+\delta y) - f_x(x,y)]\delta x = [f_{xy}(x,y) - f_{yx}(x,y)]\delta x\delta y. \quad (17.20)$$

This must vanish if the surface defined by f is at least twice differentiable.[300] That is,

$$f_{xy} = f_{yx}. \quad (17.21)$$

For example, for a rubber band $dE = TdS + FdL$, so

$$\left.\frac{\partial T}{\partial L}\right|_S = \left.\frac{\partial F}{\partial S}\right|_L. \quad (17.22)$$

Such relations are called *Maxwell's relations* in thermodynamics.

17.8 Jacobian technique: preamble

To manipulate many partial derivatives, it is very convenient to use the so-called *Jacobian technique*. This technique may not even be taught in graduate courses, but it is easy to memorize, and easy to use. It can greatly reduce the insight and skill required in thermodynamics, especially with the Jacobian version of Maxwell's relation (17.39).[301]

17.9 Jacobian and its basic properties

The Jacobian for two functions X and Y of two independent variables x, y is defined

[300] We must say something more careful mathematically, but let us be contented with this for now.

[301] Mathematically rigorously speaking, some people would claim that there can be many dangerous things, but in thermodynamics, the manipulation is perfectly mechanical (formal), so virtually there is no danger of making any logical errors.

by the following determinant:

$$\frac{\partial(X,Y)}{\partial(x,y)} \equiv \begin{vmatrix} \left.\frac{\partial X}{\partial x}\right|_y & \left.\frac{\partial X}{\partial y}\right|_x \\ \left.\frac{\partial Y}{\partial x}\right|_y & \left.\frac{\partial Y}{\partial y}\right|_x \end{vmatrix} = \left.\frac{\partial X}{\partial x}\right|_y \left.\frac{\partial Y}{\partial y}\right|_x - \left.\frac{\partial Y}{\partial x}\right|_y \left.\frac{\partial X}{\partial y}\right|_x . \tag{17.23}$$

In particular, we observe

$$\frac{\partial(X,y)}{\partial(x,y)} = \left.\frac{\partial X}{\partial x}\right|_y , \tag{17.24}$$

which is the key observation of this technique. Obviously,[302]

$$\frac{\partial(X,Y)}{\partial(X,Y)} = 1. \tag{17.25}$$

There are only two or three formulas you should learn by heart (they are very easy to memorize). One is straightforwardly obtained from the definition of determinants: exchanging rows or columns switches the sign:

$$\frac{\partial(X,Y)}{\partial(x,y)} = -\frac{\partial(X,Y)}{\partial(y,x)} = \frac{\partial(Y,X)}{\partial(y,x)} = -\frac{\partial(Y,X)}{\partial(x,y)}. \tag{17.26}$$

Also notice that for a constant c

$$\frac{\partial(cX,Y)}{\partial(x,y)} = c\frac{\partial(X,Y)}{\partial(x,y)}. \tag{17.27}$$

17.10 Chain rule in terms of Jacobians

If we assume that X and Y are functions of a and b, and that a and b are, in turn, functions of x and y, we have the following multiplicative relation:

$$\frac{\partial(X,Y)}{\partial(a,b)}\frac{\partial(a,b)}{\partial(x,y)} = \frac{\partial(X,Y)}{\partial(x,y)}. \tag{17.28}$$

This is a disguised chain rule:

$$\left.\frac{\partial X}{\partial x}\right|_y = \left.\frac{\partial X}{\partial a}\right|_b \left.\frac{\partial a}{\partial x}\right|_y + \left.\frac{\partial X}{\partial b}\right|_a \left.\frac{\partial b}{\partial x}\right|_y , \tag{17.29}$$

etc. Confirm (17.28) by yourself (use $det(AB) = (detA)(detB)$; See **D9.1**).

The technical significance of (17.28) must be obvious; calculus becomes algebra!

[302] In this case, we regard X and Y are independent variables. In the Jacobian expression, all the letters appearing upstairs are regarded dependent variables of the variables itemized downstairs.

You may think $\partial(A,B)$ just as an ordinary number: formally we can do as follows.[303] First split the 'fraction' and then throw in the identical factors you wish to introduce:

$$\frac{\partial(X,Y)}{\partial(x,y)} = \frac{\partial(X,Y)}{}\frac{}{\partial(x,y)} = \frac{\partial(X,Y)}{\partial(A,B)}\frac{\partial(A,B)}{\partial(x,y)}. \tag{17.30}$$

From (17.28) we get at once

$$\frac{\partial(X,Y)}{\partial(A,B)} = 1 \bigg/ \frac{\partial(A,B)}{\partial(X,Y)}\,. \tag{17.31}$$

In particular, we have[304]

$$\left.\frac{\partial X}{\partial x}\right|_Y = 1 \bigg/ \left.\frac{\partial x}{\partial X}\right|_Y\,. \tag{17.32}$$

17.11 Some illustrations of Jacobian technique

Using these relations, we can easily demonstrate

$$\left.\frac{\partial X}{\partial y}\right|_x = -\left.\frac{\partial x}{\partial y}\right|_X \bigg/ \left.\frac{\partial x}{\partial X}\right|_y \tag{17.33}$$

as follows:

$$\frac{\partial(X,x)}{\partial(y,x)} \overset{(17.28)}{=} \frac{\partial(X,x)}{\partial(y,X)}\frac{\partial(y,X)}{\partial(y,x)} \overset{(17.26)}{=} -\frac{\partial(x,X)}{\partial(y,X)}\frac{\partial(X,y)}{\partial(x,y)}. \tag{17.34}$$

Then, use (17.31). A concrete example of this formula is

$$\left.\frac{\partial P}{\partial T}\right|_V = -\left.\frac{\partial V}{\partial T}\right|_P \bigg/ \left.\frac{\partial V}{\partial P}\right|_T, \tag{17.35}$$

which relates thermal expansivity and isothermal compressibility.

For a rubber band

$$\left.\frac{\partial L}{\partial S}\right|_F = \frac{\partial(L,F)}{\partial(S,F)} = \frac{\partial(L,F)}{\partial(T,F)}\frac{\partial(T,F)}{\partial(S,F)} = \left.\frac{\partial L}{\partial T}\right|_F \left.\frac{\partial T}{\partial S}\right|_F, \tag{17.36}$$

which reads

$$\left.\frac{\partial L}{\partial S}\right|_F = \left.\frac{\partial L}{\partial T}\right|_F \bigg/ \left.\frac{\partial S}{\partial T}\right|_F = T\left.\frac{\partial L}{\partial T}\right|_F \bigg/ C_F. \tag{17.37}$$

Here, C_F is the heat capacity under constant force. It is explained in **17.12**.

[303] In pragmatic thermodynamics, you can be maximally formal and seldom make any mistake.

[304] Mathematically properly speaking, on the LHS we regard X and Y as functions of x and y, and $Y = Y(x,y)$ is fixed. In contrast, on the RHS x and y are understood as a function of X and Y, and Y is being kept constant. Thus, the derived relation is rather nontrivial, although formally obvious.

17.12 Specific heat and entropy

The relation between heat and entropy (Clausius' equality) tells us $d'Q = TdS$, so if we differentiate this with respect to T under constant F, it must be the heat capacity under constant F. Generally speaking, the heat capacity under constant X (which can be extensive or intensive) always have the following expression:

$$C_X = T \left.\frac{\partial S}{\partial T}\right|_X . \tag{17.38}$$

We will learn the consequence of the stability of the equilibrium states in Section 18: the stability of the equilibrium state implies $C_X \geq 0$ (usually strictly positive). Imagine the contrary. If you inject heat into a system, its temperature goes down, so it sucks more heat from the surrounding world, and further reduces its temperature. That is, such a system becomes a bottomless heat sink.

17.13 (Unified) Maxwell's relation

All the Maxwell's relations can be unified in the following form

$$\frac{\partial(X,x)}{\partial(Y,y)} = -1, \tag{17.39}$$

where (x, X) and (y, Y) are conjugate pairs. This is the third equality you should memorize. When you use this, do not forget that $(-P, V)$ (not (P, V)) is the conjugate pair.

Let us demonstrate this. From $\cdots + xdX + ydY + \cdots$ Maxwell's relation reads

$$\left.\frac{\partial x}{\partial Y}\right|_X = \left.\frac{\partial y}{\partial X}\right|_Y . \tag{17.40}$$

That is,

$$\frac{\partial(x,X)}{\partial(Y,X)} = \frac{\partial(y,Y)}{\partial(X,Y)}. \tag{17.41}$$

This implies (mere $a/b = c/d \Rightarrow a/c = b/d$!)

$$\frac{\partial(x,X)}{\partial(y,Y)} = \frac{\partial(Y,X)}{\partial(X,Y)} = -1. \tag{17.42}$$

Perhaps, the following may be better:[305]

$$\frac{\partial(X,x)}{\partial(y,Y)} = 1. \tag{17.43}$$

For example, (17.22) can be obtained as follows:

$$\left.\frac{\partial T}{\partial L}\right|_S = \frac{\partial(T,S)}{\partial(L,S)} = \frac{\partial(L,F)}{\partial(L,S)}\frac{\partial(T,S)}{\partial(L,F)} = \left.\frac{\partial F}{\partial S}\right|_L. \tag{17.44}$$

17.14 Rubber band thermodynamics

Equipped with the machinery, let us study the rubber band in more detail. The rubber band is elastic because of the thermal motion of the polymer chains. That is, resistance to reducing entropy is the cause of elastic bouncing. Thus, such elasticity is called the *entropic elasticity*.[306] An important feature is that the elastic force increases with T under constant length (which is easily understood from the kid picture Fig. 17.2):

$$\left.\frac{\partial F}{\partial T}\right|_L > 0. \tag{17.45}$$

Is this related to what we have observed (17.1)? Yes. Follow the following logic (as a practice):

$$0 < \left.\frac{\partial T}{\partial L}\right|_S = \frac{\partial(T,S)}{\partial(L,S)} = \frac{\partial(T,S)}{\partial(L,F)}\frac{\partial(L,F)}{\partial(L,S)} = \frac{\partial(L,F)}{\partial(L,S)} \tag{17.46}$$

$$= \frac{\partial(L,F)}{\partial(T,L)}\frac{\partial(T,L)}{\partial(L,S)} = \frac{\partial(F,L)}{\partial(T,L)}\Big/\frac{\partial(S,L)}{\partial(T,L)} = \left.\frac{\partial F}{\partial T}\right|_L \frac{T}{C_L}. \tag{17.47}$$

Or

$$0 < \left.\frac{\partial T}{\partial L}\right|_S = \frac{\partial(T,S)}{\partial(L,S)} = \frac{\partial(T,S)}{\partial(T,L)}\frac{\partial(T,L)}{\partial(L,S)} = -\frac{\partial(T,S)}{\partial(T,L)}\frac{T}{C_L} \tag{17.48}$$

$$= -\frac{\partial(F,L)}{\partial(T,L)}\frac{\partial(T,S)}{\partial(F,L)}\frac{T}{C_L} = \left.\frac{\partial F}{\partial T}\right|_L \frac{T}{C_L}. \tag{17.49}$$

[305]If you know the theory of differential forms, this must be trivial: since $d^2E = d(\cdots + xdX + ydY + \cdots) = 0$, if you change only X and Y, $dx\wedge dX = -dy \wedge dY$. The ratio of the infinitesimal areas on both sides is the Jacobian. Thus, the relation is simply a conequence of thermodynamic quantities being state variables (not due to the conservation law as erroneously claimed in a published awkward demonstration in Am. J. Phys.).

[306]In contrast, the usual elasticity is called *energetic elasticity*, which is caused by opposing increase of energy.

That is, you do not need any foresight.

From our microscopic imagination visualized in Fig. 17.2, we guessed

$$\left.\frac{\partial S}{\partial L}\right|_T < 0. \tag{17.50}$$

Let us derive this from (17.1).

$$\left.\frac{\partial S}{\partial L}\right|_T = \frac{\partial(S,T)}{\partial(L,T)} = \frac{\partial(S,T)}{\partial(L,S)}\frac{\partial(L,S)}{\partial(L,T)} = -\left.\frac{\partial T}{\partial L}\right|_S \frac{C_L}{T} < 0. \tag{17.51}$$

17.15 Adiabatic cooling with rubber band

If a tightly stretched rubber band is suddenly relaxed (= adiabatically relaxed) after equilibrating with the room temperature, what do you observe? You can feelwith your lip that the band becomes very cool.

This is not surprising, because

$$\left.\frac{\partial T}{\partial L}\right|_S > 0; \tag{17.52}$$

Now, L is reduced under constant S, so must decrease T. This is the principle of *adiabatic cooling* (see Fig. 17.4).

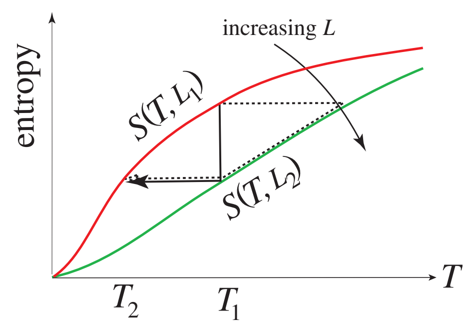

Figure 17.4: Initially, the system is at T_1. Isothermally, L is increased as $L_1 \to L_2$. This decreases entropy. Now, L is returned to the original smaller value adiabatically and reversibly. The entropy is maintained, and the temperature decreases (adiabatic cooling) to T_2. The dotted path is the one you experienced by initial rapid stretching of a rubber band. Instead, you could isothermally stretch the band and then relax adiabatically (along the full line with an arrowhead).

17.16 Cooling via adiabatic demagnetization

Unfortunately, we cannot use a rubber band to cool a system to a very low temperature, since it becomes brittle (chain motion freezes out easily and equilibration becomes difficult). In actual low temperature experiments, a collection of almost non-interacting magnetic dipoles (i.e., a paramagnetic material) is used. The system is closely related to polymer chains as illustrated in Fig. 17.5.

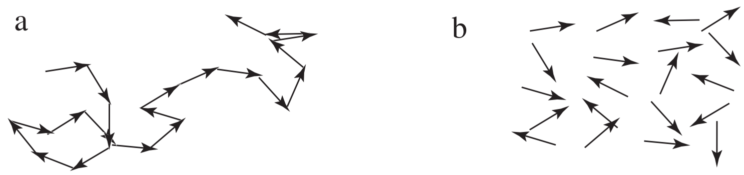

Figure 17.5: **a** of Fig. 17.2 corresponds to **b** a paramagnet, a collection of only weakly interacting magnetic dipoles.

The Gibbs relation of the magnetic system is

$$dE = TdS + BdM, \tag{17.53}$$

where B is the magnetic field, and M the magnetization. The correspondences $B \leftrightarrow F$ and $M \leftrightarrow L$ are almost perfect: M is the sum of small dipole vectors, and L is also the sum of (the projected components) of 'steps' (monomer orientation vectors). Thus, we expect

$$\left.\frac{\partial T}{\partial M}\right|_S > 0 \tag{17.54}$$

and adiabatic cooling can be realized; first apply a strong magnetic field and align all the dipoles. We can do this slowly and isothermally. Then, turn off the magnetic field to make $M \to 0$ (demagnetization) adfiabatically. Simply replacing L with M in Fig. 17.4, we can understand this adiabatic demagnetization strategy to cool a system.

17.17 Ideal magnetic system

We can imagine a collection of noninteracting magnetic dipoles (called spins) taking only up or down (or $s = \pm 1$) values.[307] The total magnetization of the system reads

$$M = \mu \sum_{i=1}^{N} s_i, \tag{17.55}$$

where μ is the ratio of the magnetic moment and the spin (the gyromagnetic ratio). It is a good exercise to compute S as a function of M, but, as you can guess easily,

$$M = \mu N \tanh \beta\mu B, \tag{17.56}$$

where B is the magnetic field. The relation between M and B for small B corresponds to Hooke's law (17.11):

$$M = (N\mu^2/k_BT)B, \tag{17.57}$$

[307] If magnetic atoms are dilute in an insulating solid, they do not interact with each other.

which is called *Curie's law*: the magnetic susceptibility $\chi = N\mu^2/k_BT$.

Just as in the freely-jointed polymer model we discussed (without the S_e term), there is no kinetic energy of spins (or of the entities carrying spins), so the entropy of this model is constant under constant M. Thus, just as in the ideal rubber model, without the term similar to S_e the model cannot explain the use of adiabatic demagnetization to cool other systems as a refrigerating mechanism.

However, if we are interested in the spins themselves, then their coupling to other degrees of freedom (the so-called spin-lattice coupling) should not be large. Under this condition, the system can be described by the present model, so under the adiabatic demagnetization condition M is constant, because S is constant. Thus, since (17.57) or (17.56) implies B/T is constant, reducing B implies decreasing T.[308]

If we use the magnet as a coolant to cool other systems, we are interested in

$$\left.\frac{\partial T}{\partial B}\right|_S = \frac{\partial(T,S)}{\partial(B,S)} = \frac{\partial(T,S)}{\partial(B,M)}\frac{\partial(B,M)}{\partial(B,S)} = -\frac{\partial(B,M)}{\partial(B,S)} \tag{17.58}$$

$$= -\frac{\partial(B,T)}{\partial(B,S)}\frac{\partial(B,M)}{\partial(B,T)} = -\frac{T}{C_B}\left.\frac{\partial M}{\partial T}\right|_B. \tag{17.59}$$

Therefore, if Curie's law of the form $M = a(B/T)$ holds, then

$$\delta T = \frac{aB}{C_BT}\delta B \tag{17.60}$$

gives the cooling rate.

[308]For a rubber band, reducing F while keeping L constant in order to change T is experimentally unthinkable.

Q17.1[Basic problems]
(1) $F = x \sin y$, and $y = x + z$. Express

$$\left.\frac{\partial F}{\partial x}\right|_y \quad \text{and} \quad \left.\frac{\partial F}{\partial x}\right|_z \tag{17.61}$$

in terms of x and y. [$\sin y$; $\sin y + x \cos y$]
(2) For a gas PV and E are functions of T only. Show that actually PV/T is a constant. [Compute $(\partial E/\partial V)_T = T(\partial S/\partial V)_T - P = T(\partial P/\partial T)_V - P = 0$.]
(3) For a general gas, find the temperature change dT due to adiabatic free expansion $V \to V + dV$. [Compute $(\partial T/\partial V)_E$. $(\partial T/\partial V)_E = [P - T(\partial P/\partial T)_V]/C_V$]
(4) If M is a function of B/T, E is a function of T only. [Show $(\partial E/\partial B)_T = 0$ using $(\partial B/\partial T)_M = B/T$; quite parallel to (2).]

18 Stability, fluctuation, and response

Summary
* We can derive the universal stability (and evolution) criterion $\delta^2 S < 0$ (> 0) that is independent of the environmental constraints (say, isothermal, constant volume or not, etc.)
* $\partial(X,Y)/\partial(x,y) > 0$.
* In equilibrium changes occur in the direction to discourage further changes (to avoid run-away processes) (Le Chatelier-Braun principle). Our world is generally stable!
* A generalized Gibbs free energy: $\tilde{G}(T,x) = -k_B T \log \sum e^{-\beta(H - x\hat{X})}$.
* Susceptibilities are directly related to the second moments of fluctuations (fluctuation-response relation).

Key words
universal stability criterion, universal evolution criterion, positive definite quadratic form, Le Chatelier principle, Le Chatelier-Braun principle, generalized Gibbs free energy, generalized canonical partition function, fluctuation-response relation

What you should be able to do
* Be able to derive the universal stability criterion.
* To mention some of the crucial conclusions due to the stability criterion (say, $C_X > 0$, $C_x > C_X$, etc.).
* Be able to build a convenient partition function to obtain a convenient thermodynamic potential directly.
* Be able to recognize important conclusions we can obtain from the fluctuation-response relation.
* Be able to explain why fluctuation studies are important.

18.1 Stability question and need for stability criteria

What is the sign of

$$\left.\frac{\partial S}{\partial F}\right|_L \tag{18.1}$$

for a rubber band? Intuition tells us that it must be positive (To increase F while keeping L, we must invigorate the motion of chains, so we must raise the temperature, resulting in the increase of entropy). Let us check this, starting with our empirical result

$$\left.\frac{\partial T}{\partial L}\right|_S > 0. \tag{18.2}$$

What you should do first is to rewrite the partial derivative in terms of Jacobians:

$$\left.\frac{\partial S}{\partial F}\right|_L = \frac{\partial(S, L)}{\partial(F, L)}. \tag{18.3}$$

(18.2) is

$$\left.\frac{\partial T}{\partial L}\right|_S = \frac{\partial(T, S)}{\partial(L, S)}, \tag{18.4}$$

so we should keep (L, S), which appears in both the formulas above, and insert (T, S):

$$\left.\frac{\partial S}{\partial F}\right|_L = \frac{\partial(S, L)}{\partial(F, L)} = \frac{\partial(S, L)}{\partial(T, S)}\frac{\partial(T, S)}{\partial(F, L)} = -\frac{\partial(S, L)}{\partial(T, S)} = \frac{\partial(L, S)}{\partial(T, S)} > 0. \tag{18.5}$$

We have used a Maxwell's relation: $\partial(T, S)/\partial(F, L) = -1$.

One more for a gas: How about the sign of

$$\left.\frac{\partial S}{\partial P}\right|_V ? \tag{18.6}$$

To increase P under constant V, (usually) we have to raise the temperature, resulting in the increase of entropy, so the sign must be positive. The cleverest approach may be

$$\left.\frac{\partial S}{\partial P}\right|_V = \frac{\partial(S, V)}{\partial(P, V)} = \frac{\partial(S, V)}{\partial(T, -P)}\frac{\partial(T, -P)}{\partial(P, V)} = \frac{\partial(S, V)}{\partial(T, -P)}\bigg/\left.\frac{\partial V}{\partial T}\right|_P. \tag{18.7}$$

Therefore, (18.6) and $(\partial V/\partial T)_P$ have the same sign, but to understand this statement we need the following inequality resulting from the system stability:

$$\frac{\partial(S, V)}{\partial(T, -P)} > 0. \tag{18.8}$$

For a gas $(\partial V/\partial T)_P > 0$ without doubt, but this sign is not due to some reason of principle nature (in contradistinction to the inequality (18.8)). For liquid water below 4°C under the atmospheric pressure, this derivative is indeed negative.

18.2 Two kinds of inequalities, sacred and not

As we will see in this section we encounter two different types of inequalities in thermodynamics; one class is due to some reason of thermodynamic principle, and the other is only due to materialistic accident. Generally speaking, what is not forbidden by thermodynamics does happen in our world.

According to our ordinary experiences (and also due to the microscopic picture of materials) $(\partial V/\partial T)_P > 0$ looks quite natural, but thermodynamics does not say anything about this sign. That is, even if it is negative, thermodynamics would not complain, and indeed what is not forbidden by thermodynamics does happen in this case.

18.3 Universal stability criteria

Clausius told us that if a spontaneous change occurs in an isolated system,

$$\Delta S \geq 0. \tag{18.9}$$

We use the standard trick to study a non-isolated system S as a small part of a huge isolated system (Fig. 18.1) whose intensive variables are kept constant, but their conjugate extensive variables may be exchanged freely between S and its surrounding reservoir.

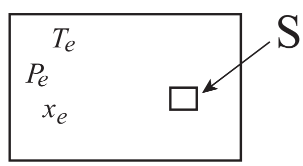

Figure 18.1: S is a part of a huge isolated system whose intensive parameters T_e, P_e, x_e, etc., are kept constant. This is virtually possible because the whole system is huge. Their conjugate extensive quantities S (or heat), V, X, etc., can be freely exchanged between the system S and the rest.

If something spontaneous can happen, the total entropy must increase. In the system something irreversible might have happened, so we cannot compute ΔS directly with the aid of imported quantities $\Delta E, \Delta V$, etc. However, for the reservoir, since we assume it is always in equilibrium, we can write its entropy change as

$$\Delta S_{res} = -\frac{1}{T_e}\Delta E - \frac{P_e}{T_e}\Delta V + \frac{x_e}{T_e}\Delta X. \tag{18.10}$$

Here, ΔE, etc., are the quantities seen from the system S ('+ signs' for importing to S), so $-\Delta E$, $-\Delta V$, etc., are the imported quantities to the reservoir. That is why the signs in (18.10) are different from the usual Gibbs relation. Thus, the total entropy change is $\Delta S + \Delta S_{res}$, and the Clausius' inequality for the isolated system reads

$$\Delta S - \frac{1}{T_e}\Delta E - \frac{P_e}{T_e}\Delta V + \frac{x_e}{T_e}\Delta X + \frac{\mu_e}{T_e}\Delta N \geq 0. \tag{18.11}$$

Here, although we have not yet discussed the change of number N of particles and its conjugate variable μ (chemical potential), since it is formally quite similar to other terms, for the later convenience, the last term is added, which will be discussed in

Section 20.

If the equilibrium state is stable, then

$$\Delta S - \frac{1}{T_e}\Delta E - \frac{P_e}{T_e}\Delta V + \frac{x_e}{T_e}\Delta X + \frac{\mu_e}{T_e}\Delta N < 0. \tag{18.12}$$

Now, let us look at ΔS more closely. If the changes are very small, we can Taylor-expand ΔS into a power series of $\delta E = \Delta E$, $\delta V = \Delta V$, etc. (here Δ for the independent variables is replaced by δ to make it clear that all changes are small). We can separate the entropy change into the first order small quantity δS, the second order small quantity $\delta^2 S$, etc., as

$$\Delta S = \delta S + \delta^2 S + \cdots. \tag{18.13}$$

The first order term reads

$$\delta S = \frac{1}{T_e}\delta E + \frac{P_e}{T_e}\delta V - \frac{x_e}{T_e}\delta X - \frac{\mu_e}{T_e}\delta N, \tag{18.14}$$

because the derivatives are computed around the equilibrium state. Combining this expression, (18.12) and (18.13), we conclude that the stability condition of the equilibrium state is

$$\delta^2 S < 0 \tag{18.15}$$

irrespective of the constraints imposed on the system S (that is, independent of whether some extensive quantities are allowed to be exchanged or not). Thus, this is the *universal stability condition* for the equilibrium state.

Notice that (18.15) was concluded for isolated systems before as the max entropy principle, but here it is about the general non-isolated system, so this *does not* imply max entropy; irrespective of S being max or not, $\delta^2 S < 0$ is the stability condition.

18.4 Universal stability criterion in terms of internal energy

(18.12) may be rearranged as

$$\Delta E > T_e \Delta S - P_e \Delta V + x_e \Delta X + \mu_e \Delta N. \tag{18.16}$$

Now, restricting the variations to small ones, we can Taylor-expand ΔE just as we did for ΔS. You should immediately realize that a very similar logic as above can give us another, but equivalent universal stability criterion

$$\delta^2 E > 0. \tag{18.17}$$

18.5 Le Chatelier's principle

Let us study the consequences of the stability criterion (18.17): a general expression is

$$\sum_{i,j} \frac{\partial^2 E}{\partial X_i \partial X_j} \delta X_i \delta X_j > 0. \tag{18.18}$$

This is a positive definite quadratic form, and we can express it as

$$(\delta S, \delta V, \delta N) \begin{pmatrix} \left.\frac{\partial T}{\partial S}\right|_{V,N} & \left.\frac{\partial T}{\partial V}\right|_{S,N} & \left.\frac{\partial T}{\partial N}\right|_{S,V} \\ -\left.\frac{\partial P}{\partial S}\right|_{V,N} & -\left.\frac{\partial P}{\partial V}\right|_{S,N} & -\left.\frac{\partial P}{\partial N}\right|_{S,V} \\ \left.\frac{\partial \mu}{\partial S}\right|_{V,N} & \left.\frac{\partial \mu}{\partial V}\right|_{S,N} & \left.\frac{\partial \mu}{\partial N}\right|_{S,V} \end{pmatrix} \begin{pmatrix} \delta S \\ \delta V \\ \delta N \end{pmatrix} > 0. \tag{18.19}$$

Let us assume N is constant for simplicity. The sign of (18.19) must always be positive irrespective of the choice of δS and δV (unless both are zero). Therefore, all the diagonal terms must be positive:

$$0 < \left.\frac{\partial T}{\partial S}\right|_V = \frac{T}{C_V}, \tag{18.20}$$

and in terms of the adiabatic compressibility $\kappa_S = -(\partial V/\partial P)_S/V$

$$0 < -\left.\frac{\partial P}{\partial V}\right|_S = \frac{1}{V\kappa_S}. \tag{18.21}$$

You must be able to imagine what happens if these signs are flipped.

The diagonal inequalities are called *Le Chatelier's principle*.[309] We can verbally state the consequence as follows:

In equilibrium changes occur in the direction to discourage further changes (to avoid run-away processes).

For example, if ΔS is injected (e.g., heat is injected) into the system, its temperature goes up, which usually discourages further injection of heat. In the case of compressibility, decrease of the volume of the system increases the pressure, resisting further squishing. Thus, no runaway phenomenon is realized in the world we live in.

18.6 Le Chatelier-Braun's principle

Which is larger, the susceptibility under constant extensive quantity and that under constant intensive quantity? An example is: which is larger C_P or C_V? A general

[309] Henry Louis Le Chatelier (1850-1936): Compt. rend., **99**, 786 (1884).
[1884 Boltzmann derived the Stefan-Boltzmann law; Poynting vector was introduced; Friedrich Nietzsche: *Also sprach Zarathustra* (publication concluded); Georges-Pierre Seurat, *Bathers at Asniéres*; Mahler Symphony No. 1 D major (Bernstein, VPO); Brahms *Symphony No 4* (Haitink, European CO); John Singer Sargent, *Portrait of Madame X*].

answer is called the Le Chatelier-Braun's principle. Since $dX = \left.\frac{\partial X}{\partial x}\right|_y dx + \left.\frac{\partial X}{\partial y}\right|_x dy + \cdots$

$$\left.\frac{\partial X}{\partial x}\right|_Y = \left.\frac{\partial X}{\partial x}\right|_y + \left.\frac{\partial X}{\partial y}\right|_x \left.\frac{\partial y}{\partial x}\right|_Y \tag{18.22}$$

$$= \left.\frac{\partial X}{\partial x}\right|_y + \left.\frac{\partial X}{\partial y}\right|_x \frac{\partial(y,Y)}{\partial(x,Y)} \tag{18.23}$$

$$= \left.\frac{\partial X}{\partial x}\right|_y + \left.\frac{\partial X}{\partial y}\right|_x \frac{\partial(y,Y)}{\partial(X,x)} \frac{\partial(X,x)}{\partial(y,x)} \frac{\partial(y,x)}{\partial(x,Y)} \tag{18.24}$$

$$= \left.\frac{\partial X}{\partial x}\right|_y - \left.\frac{\partial X}{\partial y}\right|_x^2 \left.\frac{\partial y}{\partial Y}\right|_x . \tag{18.25}$$

Here, a Maxwell's relation has been used. This implies that

$$\left.\frac{\partial X}{\partial x}\right|_y > \left.\frac{\partial X}{\partial x}\right|_Y . \tag{18.26}$$

Therefore, the indirect change in extensive quantities (of Y in the above formula) occurs in the direction to reduce the effect of the perturbation (*Le Chatelier-Braun's principle*).[310] As already noted, a typical example is $C_P \geq C_V$: larger specific heat implies that it is harder to warm up, that is, the system becomes harder to heat up if the volume change (i.e., the indirect change) is allowed.

18.7 2×2 stability criterion

A necessary and sufficient condition for (18.19) is the positivity of all the principal minors[311] of the matrix in (18.19). Therefore, in particular,

$$\frac{\partial(T,-P)}{\partial(S,V)} > 0. \tag{18.27}$$

Generally,

$$\frac{\partial(X,Y)}{\partial(x,y)} > 0, \tag{18.28}$$

[310] Karl Ferdinand Braun (1850-1918): Z. physik. Chen., **1**, 269 (1887), Ann. Physik, **33**, 337 (1888) [the inventor of the cathode-ray tube, the discoverer of principle of semiconductor diode, shared the Nobel prize with Marconi for wireless technology]. The history of this principle can be found in J. de Heer, "The principle of le Chatelier and Braun," J. Chem. Educ., **34**, 375 (1957). The form stated here is due to Ehrenfest.
[1888: Clausius died; van Gogh cuts off his left ear, *The Night Cafe*; Paul Gauguin *Vision After the Sermon*; Tchaikovsky, *5th Symphony*; Mahler *No 2 Resurrection* (Jansons, Concertgebouw).]

[311] You sample the same row and column numbers (say, 1, 3, 7 and 8th columns and 1, 3, 7 and 8th rows from the original matrix and make a determinant $\det(a_{ij})$, where $i,j \in \{1,3,7,8\}$). Such determinants are called *principal minors*.

where (x, X) and (y, Y) are conjugate pairs. This is perhaps the last formula you should remember when you use the Jacobian technique.

18.8 Importance of fluctuations

We already know that the mesoscopic world is dominated by fluctuations, which allow us to have a glimpse of the atomic world underlying the world we experience daily. We also know that the equilibrium state of a macroscopic systems is always tested by fluctuations; δ in the stability criterion is actually spontaneously realized by thermal fluctuations.

Thus, there is no doubt about the importance of fluctuations qualitatively. How about quantitatively? We will see that the system response to perturbation is quantitatively related to fluctuations.

18.9 Fluctuation-response relation: Generalized Gibbs free energy

Take a finite (classical) system and observe a work coordinate X there. We assume that the system is maintained at temperature T. Let us look at the response of X to the modification of its conjugate variable x (with respect to energy). We wish to study the susceptibility

$$\chi = \left.\frac{\partial X}{\partial x}\right|_{T,\cdots}. \tag{18.29}$$

Here, $\cdots$ depends on the system we study. Since we wish to use $T, x, \cdots$ as independent variables, we wish to have a system that can freely exchange their conjugate extensive quantities with its environment. Then, it is convenient to use the thermodynamic potential $\tilde{G}$ defined by the following Legendre transformation:

$$E \to \tilde{G} = E - TS - xX = A - xX. \tag{18.30}$$

$\tilde{G}$ is a *generalized Gibbs free energy.* Why is this convenient? Recall the original Gibbs free energy $G = A + PV$ (do not forget that the conjugate variable of V is $-P$), for which T and P are independent variables, and we have $dG = -SdT + VdP$.

If we wish to use statistical mechanics, entropy is more fundamental and convenient, so we need the corresponding Legendre transformation for entropy:

$$S \to -\tilde{G}/T = S - E/T + xX/T = -A/T + xX/T. \tag{18.31}$$

18.10 Generalized canonical ensemble

How can we directly compute $\tilde{G}$ statistical mechanically?

Compare the following relations:

$$S/k_B = \log w(E,X) \quad \leftrightarrow \quad w(E,X) \tag{18.32}$$

$$S/k_B - E/k_BT = -\frac{A}{k_BT} = \log Z(T,X) \quad \leftrightarrow \quad Z(T,X) = \sum_E w(E,X)e^{-E/k_BT}. \tag{18.33}$$

You must have already guessed:

$$\frac{1}{k_B}(S - E/T + xX/T) = -\frac{\tilde{G}}{k_BT} = \log \tilde{Z}(T,x) \leftrightarrow \tilde{Z}(T,x) = \sum_E w(E,X)e^{(-E+xX)/k_BT}. \tag{18.34}$$

Notice that

$$\tilde{Z}(T,x) = \sum_X Z(T,X)e^{xX/k_BT} = \sum e^{-\beta(H-xX)}, \tag{18.35}$$

and

$$\tilde{G}(T,x) = -k_BT \log \tilde{Z}(T,x). \tag{18.36}$$

$\tilde{Z}$ is called a *generalized canonical partition function*. These relations just look like the ones we are very familiar with.

18.11 Fluctuation-response relation

The susceptibility $\chi = (\partial X/\partial x)_{T,V}$ of the response X to the change of x reads

$$\chi = \beta \frac{\partial^2 \log \tilde{Z}}{\partial(\beta x)^2}. \tag{18.37}$$

Let us compute this with the aid of the expression of the generalized canonical partition function. First, we obtain

$$X = \frac{\partial \log \tilde{Z}}{\partial \beta x} = \frac{1}{\tilde{Z}} \sum \hat{X} e^{-\beta H + \beta x \hat{X}}. \tag{18.38}$$

Let's differentiate this once more:

$$\chi = \beta \frac{\partial X}{\partial \beta x} = -\frac{1}{\tilde{Z}^2}\left(\sum \hat{X} e^{-\beta H + \beta x \hat{X}}\right)^2 + \frac{1}{\tilde{Z}} \sum \hat{X}^2 e^{-\beta H + \beta x \hat{X}}. \tag{18.39}$$

That is,

$$= \beta\left(\langle \hat{X}^2 \rangle - \langle \hat{X} \rangle^2\right) = \beta \langle \delta \hat{X}^2 \rangle \geq 0, \tag{18.40}$$

where $\delta \hat{X} = \hat{X} - \langle \hat{X} \rangle$.

$$\chi\left(= \beta \frac{\partial X}{\partial \beta x}\right) = \beta \langle \delta \hat{X}^2 \rangle \tag{18.41}$$

is called the *fluctuation-response relation*.

18.12 Fluctuation-response relation, many variable case

If have many variables. what can we have? Probably, you guessed the following form:

$$\chi_{ij} \left(= \beta \frac{\partial X_i}{\partial \beta x_j} \right) = \beta \langle \delta \hat{X}_i \delta \hat{X}_j \rangle. \tag{18.42}$$

This is correct.

18.13 Three key outcomes of fluctuation-response relation

We can make three important observations from the fluctuation-response relation (18.41):

(i) The 'ease' of response results from 'large' fluctuations. Notice that χ describes the response to an external perturbation, but the variance of $\hat{X}$ is due to spontaneous thermal fluctuations. Gentle nudging of the system (reversible change) must respect the spontaneity of the system.

(ii) Since X is extensive and x is intensive, χ must be extensive (proportional to the number of particles there, N). Therefore, $\delta X = O[\sqrt{N}]$.[312]

(iii) χ cannot be negative. This is the manifestation of the stability of the equilibrium state as we have already discussed.

18.14 Importance of fluctuation

Thus, we have realized that studying fluctuation is quite important; it could be a non-invasive method to study the system response. The study of fluctuation is a mesoscopic scale study of the system, so it is the study of large deviation. Thus, if we know the large deviation function I, we are done. Einstein gave I for equilibrium fluctuations. This we will discuss in the next lecture.

[312] away from critical points. There, χ can diverge, so nothing can be said from this argument.

Q18.1 [Signs of derivatives].
(1) What is the sign of

$$\left.\frac{\partial S}{\partial V}\right|_P \tag{18.43}$$

for liquid water below 4 °C (under the atmospheric pressure). You may use the empirical fact $(\partial V/\partial T)_P < 0$.
(2) Using the experimental result you confirmed for a rubber band (i.e., $(\partial T/\partial L)_S > 0$), find the sign of

$$\left.\frac{\partial L}{\partial S}\right|_F. \tag{18.44}$$

Then, give an intuitive explanation of your result. You may use the fact $(\partial X/\partial x)_Y > 0$ for any conjugate pair (x, X) and for any variable Y (need not be extensive).
(3) There is an elastic body for which $(\partial S/\partial L)_T > 0$. Find the sign of

$$\left.\frac{\partial L}{\partial T}\right|_F, \tag{18.45}$$

where F is the tensile force, and L is the length. You may use the fact $(\partial X/\partial x)_Y > 0$ for any conjugate pair (x, X) and for any variable Y (need not be extensive, even though it is in the upper case.).

Solution.
I strongly recommend you to use the Jacobian technique, since you do not need any insight. The following (1) explains step by step how this technique works.
(1) First, write the partial derivative in terms of a Jacobian and then split the denominator and the numerator:

$$\left.\frac{\partial S}{\partial V}\right|_P = \frac{\partial(S,P)}{\partial(V,P)} = \frac{\partial(S,P)}{---}\frac{---}{\partial(V,P)}. \tag{18.46}$$

Now, you must look at what is given or what you wish: it is $(\partial V/\partial T)_P < 0$:

$$\frac{\partial(V,P)}{\partial(T,P)} = 1 \bigg/ \frac{\partial(T,P)}{\partial(V,P)}. \tag{18.47}$$

Since (18.46) already contains (V, P), we should introduce (T, P):

$$\frac{\partial(S,P)}{---}\frac{---}{\partial(V,P)} = \frac{\partial(S,P)}{\partial(T,P)}\frac{\partial(T,P)}{\partial(V,P)} = \frac{C_P}{T} \bigg/ \left.\frac{\partial V}{\partial T}\right|_P < 0, \tag{18.48}$$

since the specific heat is positive, or the diagonal terms of the Hessian of E is positive.
(2)

$$\left.\frac{\partial L}{\partial S}\right|_F = \frac{\partial(L,F)}{\partial(S,F)} = \frac{\partial(L,F)}{\partial(T,S)}\frac{\partial(T,S)}{\partial(S,F)} \tag{18.49}$$

$$= \frac{\partial(T,S)}{\partial(L,S)}\frac{\partial(L,S)}{\partial(S,F)} = -\left.\frac{\partial T}{\partial L}\right|_S \left.\frac{\partial L}{\partial F}\right|_S < 0. \tag{18.50}$$

Here, a Maxwell's relation

$$\frac{\partial(L,F)}{\partial(T,S)} = 1 \tag{18.51}$$

has been used.
(3)

$$\left.\frac{\partial L}{\partial T}\right|_F = \frac{\partial(L,F)}{\partial(T,F)} = \frac{\partial(L,F)}{\partial(T,S)}\frac{\partial(T,S)}{\partial(T,F)} = \frac{\partial(T,S)}{\partial(T,F)} \tag{18.52}$$

$$= \frac{\partial(T,S)}{\partial(T,L)}\frac{\partial(T,L)}{\partial(T,F)} > 0. \tag{18.53}$$

Q18.2 [Le Chatelier-Braun ezmaples].
(1) Consider a rubber band whose Gibbs relation is $dE = TdS + FdL$ (as usual). Which is larger, the constant length specific heat C_L or the constant force specific heat C_F? You may be able to guess this, but I ask you to prove this using the stability criterion.
(2) For a fluid which is larger, the isothermal compressibility κ_T or the adiabatic compressibility κ_S? You may be able to guess this, but I ask you to prove this using the stability criterion.

Solution.
(1) Le Chatelier-Braun tells $C_L \le C_F$. Let us demonstrate this, using

$$dS = \left.\frac{\partial S}{\partial T}\right|_F dT + \left.\frac{\partial S}{\partial F}\right|_T dF. \tag{18.54}$$

This implies (we wish to have the red factor squared)

$$\left.\frac{\partial S}{\partial T}\right|_L = \left.\frac{\partial S}{\partial T}\right|_F + \left.\frac{\partial S}{\partial F}\right|_T \left.\frac{\partial F}{\partial T}\right|_L \tag{18.55}$$

$$= \left.\frac{\partial S}{\partial T}\right|_F + \left.\frac{\partial S}{\partial F}\right|_T \frac{\partial(F,L)}{\partial(T,L)} \tag{18.56}$$

$$= \left.\frac{\partial S}{\partial T}\right|_F + \left.\frac{\partial S}{\partial F}\right|_T \frac{\partial(F,L)}{\partial(S,T)}\frac{\partial(S,T)}{\partial(F,T)}\frac{\partial(F,T)}{\partial(T,L)} \tag{18.57}$$

$$= \left.\frac{\partial S}{\partial T}\right|_F + \left.\frac{\partial S}{\partial F}\right|_T^2 \frac{\partial(F,T)}{\partial(T,L)}, \tag{18.58}$$

where we used a Maxwell's relation

$$\frac{\partial(F,L)}{\partial(S,T)} = 1. \tag{18.59}$$

Now,

$$\left.\frac{\partial S}{\partial T}\right|_L = \left.\frac{\partial S}{\partial T}\right|_F - \left.\frac{\partial S}{\partial F}\right|_T^2 \left.\frac{\partial F}{\partial L}\right|_T. \tag{18.60}$$

Thanks to the stability the second term is negative, so

$$\left.\frac{\partial S}{\partial T}\right|_L \le \left.\frac{\partial S}{\partial T}\right|_F. \tag{18.61}$$

Therefore,

$$C_L \le C_F. \tag{18.62}$$

You must think whether this is natural or not. Take a polymer chain or a rubber band. Under constant length, increasing the temperature increases the force, which opposes chain conformational entropy increase. In contrast, under constant force, more conformational varieties are available than the former case, so more heat is needed to increase the system temperature. Thus, C_L should be smaller than C_F. A parallel argument should be possible for systems with energetic elasticity. Try.

Let us follow the above strategy to show $C_V \le C_P$ for practice sake.

$$\begin{aligned}
\left.\frac{\partial S}{\partial T}\right|_V &= \left.\frac{\partial S}{\partial T}\right|_P + \left.\frac{\partial S}{\partial P}\right|_T \left.\frac{\partial P}{\partial T}\right|_V & (18.63)\\
&= \left.\frac{\partial S}{\partial T}\right|_P + \left.\frac{\partial S}{\partial P}\right|_T \frac{\partial(P,V)}{\partial(T,V)} & (18.64)\\
&= \left.\frac{\partial S}{\partial T}\right|_P + \left.\frac{\partial S}{\partial P}\right|_T \frac{\partial(P,V)}{\partial(S,T)}\frac{\partial(S,T)}{\partial(P,T)}\frac{\partial(P,T)}{\partial(T,V)} & (18.65)\\
&= \left.\frac{\partial S}{\partial T}\right|_P - \left.\frac{\partial S}{\partial P}\right|_T^2 \frac{\partial(P,T)}{\partial(T,V)} & (18.66)\\
&= \left.\frac{\partial S}{\partial T}\right|_P + \left.\frac{\partial S}{\partial P}\right|_T^2 \left.\frac{\partial P}{\partial V}\right|_T, & (18.67)
\end{aligned}$$

where we used a Maxwell's relation (note $-P$ is the conjugate of V)

$$\frac{\partial(P,V)}{\partial(S,T)} = -1. \tag{18.68}$$

Thus,

$$C_V \le C_P, \tag{18.69}$$

because $\partial P/\partial V < 0$.
(2) Let us start with

$$dV = \left.\frac{\partial V}{\partial P}\right|_T dP + \left.\frac{\partial V}{\partial T}\right|_P dT, \tag{18.70}$$

Thus,

$$\begin{aligned}
\left.\frac{\partial V}{\partial P}\right|_S &= \left.\frac{\partial V}{\partial P}\right|_T + \left.\frac{\partial V}{\partial T}\right|_P \left.\frac{\partial T}{\partial P}\right|_S && (18.71)\\
&= \left.\frac{\partial V}{\partial P}\right|_T + \left.\frac{\partial V}{\partial T}\right|_P \frac{\partial(T,S)}{\partial(V,P)}\frac{\partial(V,P)}{\partial(T,P)}\frac{\partial(T,P)}{\partial(P,S)} && (18.72)\\
&= \left.\frac{\partial V}{\partial P}\right|_T - \left.\frac{\partial V}{\partial T}\right|_P^2 \frac{\partial(T,P)}{\partial(P,S)}, && (18.73)
\end{aligned}$$

where a Maxwell relation

$$\frac{\partial(T,S)}{\partial(V,P)} = -1 \tag{18.74}$$

is used.

$$\left.\frac{\partial V}{\partial P}\right|_S = \left.\frac{\partial V}{\partial P}\right|_T + \left.\frac{\partial V}{\partial T}\right|_P^2 \left.\frac{\partial T}{\partial S}\right|_P. \tag{18.75}$$

Hence,

$$\left.\frac{\partial V}{\partial P}\right|_S \geq \left.\frac{\partial V}{\partial P}\right|_T. \tag{18.76}$$

Notice these derivatives are negative, and compressibilities are defined with negative signs, so

$$\kappa_S \leq \kappa_T. \tag{18.77}$$

Is this natural? We know that under adiabatic conditions if we compress an ideal gas PV^γ = constant ($\gamma > 1$) or $V \propto 1/P^{1/\gamma}$. Under isothermal conditions PV is constant, or $V \propto 1/P$. Therefore, V is smaller under isothermal compression. That is, it is easier to squish under const T than const S. More intuitively, adiabatic compression usually increases the gas temperature, so isothermal compression should be easier.

Q18.3 [Fluctuation of internal energy]
We wish to study the fluctuation of the total energy E of a closed system (a system without any material exchange) under constant volume V and temperature T (i.e., thermostatted). To what heat capacity of the system (say, under constant pressure or constant volume) does $\langle \delta E^2 \rangle$ directly related? Notice that microscopically E is just the system Hamiltonian $\mathcal{H}$, so we are interested in $\langle \mathcal{H}^2 \rangle - \langle \mathcal{H} \rangle^2$. The most straightforward way to answer this question is to compute this variance.

Solution.
$Z = \sum e^{-\beta\mathcal{H}}$, so

$$\langle \mathcal{H} \rangle = \left.\frac{\partial \log Z}{\partial(-\beta)}\right|_V = \frac{1}{Z}\sum \mathcal{H} e^{-\beta\mathcal{H}}.$$

Therefore,

$$\left.\frac{\partial\langle\mathcal{H}\rangle}{\partial(-\beta)}\right|_V = -\frac{1}{Z^2}(\sum \mathcal{H}e^{-\beta\mathcal{H}})^2 + \frac{1}{Z}\sum \mathcal{H}^2 e^{-\beta\mathcal{H}} = \langle\mathcal{H}^2\rangle - \langle\mathcal{H}\rangle^2.$$

We know

$$\left.\frac{\partial\langle\mathcal{H}\rangle}{\partial(-\beta)}\right|_V = k_B T^2 \left.\frac{\partial E}{\partial T}\right|_V = k_B T^2 C_V.$$

19 Thermodynamic approach to fluctuations

Summary
∗ Einstein gave a universal probability distribution for mesoscopic scale fluctuations around equilibrium states.
∗ Thermodynamic stability and equilibrium work needed to create fluctuations are closely related to this universal distribution.

Key words
fluctuation-response relation, large deviation rate function, fundamental formula for thermodynamic fluctuations (Einstein's theory), multivariate Gaussian distribution

What you should be able to do
∗ Explain why Einstein's theory is always correct.
∗ Computation of second moments of fluctuations, or how to use Einstein's theory
∗ How to use multivariate Gaussian distribution; you must be able to compute its normalization constant.

19.1 Mesoscopic fluctuations: introduction to Einstein's theory

The story up to this point is about a whole finite system. You may regard it as a mesoscopic subsystem of a larger system that is of our daily scale. If this is what we want, however, there is a reason that we may avoid the detailed statistical-mechanical setup just we have discussed. Recall the universal stability criterion for an equilibrium state $\delta^2 S < 0$ **18.3**. This is independent of the environmental constraints, and it is a condition preventing fluctuations from going wild. Then, there should be a theory that can determine the distribution of fluctuations almost independent of the environmental constraints imposed on the system. As we will see soon, Einstein just constructed such a theoretical framework.

19.2 Large deviation and mesoscopic fluctuation

The study of fluctuation is a mesoscopic scale study of the system, so it is the study of large deviation. Since we study a small volume V in the system, the following type of large deviation must be natural:

$$P\left(\frac{1}{V}X(V) \sim y\right) \approx e^{-VI(y)}, \tag{19.1}$$

where I is the large deviation function (or rate function).[313] If we know I, basically we know everything we wish to know about fluctuations.

In practice, even if we say the volume we observe is tiny, since we are macroscopic organisms, the volume is sufficiently large from the microscopic point of view. Therefore, fluctuations should not be very large, and we have only to consider the second moments to quantify fluctuations. That is, we need the quadratic approximation to I, which was provided by Einstein.

19.3 Einstein's fundamental formula for small fluctuations

Einstein in 1910[314] studied the deviation of thermodynamic observables in a small domain of a system from their equilibrium values in order to understand critical fluctuations, which we will discuss towards the end of this course.[315]

To obtain the probability of fluctuations, he inverted the Boltzmann principle as

$$w(\{X\}) = e^{S(\{X\})/k_B}, \tag{19.2}$$

where $\{X\}$ collectively denotes extensive variables. Then, he postulated that the statistical weight for the value of X deviated from its equilibrium value may also be obtained by (19.2). Since we know the statistical weights, we can compute the probability of observing $\{X\}$ as

$$P(\{X\}) = \frac{w(\{X\})}{\sum_{\{X\}} w(\{X\})}. \tag{19.3}$$

The denominator may be replaced with the largest term in the summands (recall **14.4**), so we may rewrite the formula as

$$P(\{X\}) \simeq \frac{w(\{X\})}{w(\{X_{eq}\})} = e^{[S(\{X\})-S(\{X_{eq}\})]/k_B} = e^{-|\Delta S|/k_B}, \tag{19.4}$$

where $\simeq$ implies the equality up to a certain unimportant numerical coefficient, and $\{X_{eq}\}$ is the value of $\{X\}$ that gives the largest w (maximizes the entropy), that is,

[313] If X is extensive, $X(V)$ is the total amount in V (i.e., $X(V)/V$ is its density). If X is intensive, then $X(V)/V$ should be interpreted as the average value in the volume V.

[314] [1910: Russel and Whitehead started to publish *Principia Mathematica* (∼1913); Stravinsky, *Firebird* premiered; Rilke, *Die Aufzeichnungen des Malte Laurids Brigg*; the Mexican revolution began, Tolstoy, Cannizzaro, Nightingale died.]

[315] A. Einstein, "Theorie der Opaleszenz von homogenen Flüssigkeitsgemischen in der Nahe des kritischen Zustandes," Ann. Phys., **33**, 1275-1298 (1910). [Theory of critical opalescence of homogeneous fluid mixture near the critical state]. J. D. Jackson, *Classical Electrodynamics*, 2nd Edition (Wiley, 1975) Sect. 9.7 is a good summary of related topics.

the equilibrium value. $\Delta S = S(\{X\}) - S(\{X_{eq}\})$ is written as $-|\Delta S|$ to emphasize the sign of ΔS (i.e., negative). To the second order this reads

$$P(\{\delta X\}) \propto e^{-|\delta^2 S|/k_B}. \tag{19.5}$$

Einstein proposed this as the *fundamental formula for small fluctuations* in a small portion of *any* equilibrium system

The above derivation of (19.5) assumed that a mesoscopic portion of the system is isolated. However, as noted before, the second order deviation of any thermodynamic potential around its equilibrium point is given by $-T\delta^2 S$, so (19.5) is valid under *any* condition; Einstein is always correct.[316]

19.4 Practical form of fluctuation probability

To study the fluctuation we need the second order variation $\delta^2 S$ of the system entropy. This can be computed from the Gibbs relation (here δ means the so-called 'virtual variation,' but notice that such variations are actually spontaneously realized by thermal fluctuations)

$$\delta S = \frac{1}{T}(\delta E + P\delta V - \mu\delta N - x\delta X) \tag{19.6}$$

as follows (this is the second order term of the Taylor expansion, so do not forget

[316]If you do not trust Einstein, use the 'generalized canonical partition function' (appropriate for the constraints imposed on the small portion) as

$$\tilde{Z}(X) = e^{S/k_B - xX/k_B T},$$

and compute the probability for the fluctuation δX: $P(\delta X)$. You get the identical conclusion.

the overall factor 1/2):[317]

$$\delta^2 S = \frac{1}{2}\left[\delta\left(\frac{1}{T}\right)(\delta E + P\delta V - \mu\delta N - x\delta X) + \frac{1}{T}(\delta P\delta V - \delta\mu\delta N - \delta x\delta X)\right], \tag{19.7}$$

$$= -\frac{\delta T}{2T^2}T\delta S + \frac{1}{2T}(\delta P\delta V - \delta\mu\delta N - \delta x\delta X). \tag{19.8}$$

Thus, we have arrived at the following useful expression worth remembering (actually, almost nothing to remember anew; cf. $-\delta E = -T\delta S + P\delta V - \mu\delta N - x\delta X$):[318]

$$\delta^2 S = \frac{-\delta T\delta S + \delta P\delta V - \delta\mu\delta N - \delta x\delta X}{2T}. \tag{19.9}$$

Don't forget 2 downstairs.

Consequently, the probability density of fluctuation can have the following form, which is the starting point of practical calculation of fluctuations (second moments):

$$P(\text{fluctuation}) \propto \exp\left\{-\frac{1}{2k_BT}(\delta T\delta S - \delta P\delta V + \delta\mu\delta N + \delta x\delta X)\right\}. \tag{19.10}$$

19.5 Fluctuation and reversible work needed to create it

A similar calculation gives

$$\delta^2 E = \frac{1}{2}(\delta T\delta S - \delta P\delta V + \delta\mu\delta N + \delta x\delta X). \tag{19.11}$$

[317] If the reader has some trouble in understanding (19.8), look at a simple example: $f = f(x, y)$, where x and y are regarded as independent variables. If we can write

$$\delta f = X\delta x + Y\delta y,$$

then

$$\delta X = \frac{\partial X}{\partial x}\delta x + \frac{\partial X}{\partial y}\delta y, \quad \delta Y = \frac{\partial Y}{\partial x}\delta x + \frac{\partial Y}{\partial y}\delta y.$$

Therefore, the second order Taylor expansion term reads

$$\delta^2 f = \frac{1}{2}\left(\frac{\partial X}{\partial x}\delta x^2 + \frac{\partial X}{\partial y}\delta y\delta x + \frac{\partial Y}{\partial x}\delta x\delta y + \frac{\partial Y}{\partial y}\delta y^2\right) = \frac{1}{2}(\delta X\delta x + \delta Y\delta y).$$

In short, the second variations of independent variables are zero (i.e., $\delta^2 x = \delta^2 y = 0$, everybody must know this):

$$\delta[X\delta x + Y\delta y] = \delta X\delta x + X\delta^2 x + \delta Y\delta y + Y\delta^2 y = \delta X\delta x + \delta Y\delta y.$$

We used this relation.

[318] As has already been stated when we discussed the general stability criterion, δS need not be zero. The derivation of this formula by Einstein was indeed a feat.

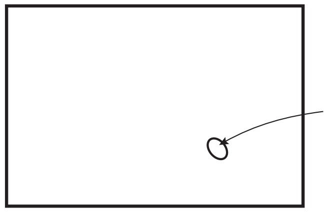

Figure 19.1: The formula (19.10) applies to a small portion of a big system. For example, you can spectroscopically measure the temperature fluctuation in a small volume with appropriate probe molecules. If the observation volume is fixed, obviously we cannot choose V as an independent variable, but virtually any independent variables may be chosen to study fluctuations in the small portion of a macroscopic system.

$\delta^2 E$ can be understood as the (free) energy we must supply as the reversible work, if we wish to create the fluctuation. Therefore, we may rewrite (19.10) as

$$P(\text{fluctuation}) \propto e^{-\beta W_f}, \tag{19.12}$$

where W_f is the reversible work required to create the fluctuation. This is a practically very useful formula.

19.6 How to use the practical formula

To use the practical formula (19.10) we must choose the independent variables.

What variables should we choose as independent variables to compute the second variation? Suppose we study a system that requires n thermodynamic coordinates (i.e., its thermodynamic space is n-dimensional). Such a system requires n conjugate pairs (S, T), $(V, -P)$, (x_i, X_i), etc. Choosing a statistical ensembles corresponds to choosing one variable from each pair. We know, however, any ensemble may be used to study the second moments of thermodynamic fluctuations. Thus, we may choose n independent variables arbitrarily selecting one (i.e., X or x) from each conjugate pair $\{x, X\}$. Any choice will do, but sometimes a clever choice may (drastically) simplify the calculation.

After choosing the independent variables, the formula in the round parentheses of (19.10) becomes a quadratic form in independent variations (of our choice, say, $\{\delta T, \delta V, \delta x\}$).

For an example, let us calculate the temperature fluctuation. We must first choose independent variables (variations). δT must be a convenient choice. We need one more independent variable (if $n = 2$).

Let us choose δV as the other variation. We could choose δP, but we wish to exploit the following general fact:

$$\langle \delta X_i \delta x_j \rangle = k_B T \delta_{ij}, \tag{19.13}$$

where X_i is an extensive variable, and x_j an intensive variable; we understand that

(X_i, x_i) is a conjugate pair.[319*]

Thus, for δT δV is a convenient partner:

$$\frac{1}{k_B}\delta^2 S = -\frac{1}{2k_BT}\delta S\delta T + \cdots = -\frac{1}{2k_BT}\left.\frac{\partial S}{\partial T}\right|_V \delta T^2 + \cdots = -\frac{C_V}{2k_BT^2}\delta T^2 + \cdots. \tag{19.15}$$

Therefore, we can easily conclude

$$\langle \delta T^2 \rangle = k_B T^2 / C_V. \tag{19.16}$$

This is the fluctuation of the average temperature in a small volume whose constant volume heat capacity is C_V. If the observation volume is reduced, then C_V is reduced as well (recall that C_V is an extensive quantity), so the fluctuation increases. Very natural.

One more example: the pressure fluctuation. We should choose P and S as independent variables, since we know $\langle \delta P \delta S \rangle = 0$:

$$\frac{1}{2k_BT}\delta P \delta V = \frac{1}{2k_BT}\left.\frac{\partial V}{\partial P}\right|_S \delta P^2 + \cdots = -\frac{V}{2k_BT}\kappa_S \delta P^2 + \cdots, \tag{19.17}$$

where κ_S is the adiabatic compressibility

$$\kappa_S = -\frac{1}{V}\left.\frac{\partial V}{\partial P}\right|_S. \tag{19.18}$$

Therefore,[320]

$$\langle \delta P^2 \rangle = k_B T / V \kappa_S. \tag{19.19}$$

Such small tricks to save our energy are useful, but as is clear, generally speaking, we must know how to handle *multivariate Gaussian distribution*.

19.7 Multivariate Gaussian distribution

A multivariate distribution is called the *Gaussian* distribution, if any marginal distribution is Gaussian. Or more practically, we could say that if the negative log of

[319*] This can be demonstrated with the aid of the fluctuation-response relation (18.42). Let us choose first $X_1, \cdots, X_n$ as our independent variables. Using the chain rule, we obtain

$$\langle \delta X_i \delta x_j \rangle = \left\langle \delta X_i \sum_k \frac{\partial x_j}{\partial X_k}\delta X_k \right\rangle = k_B T \sum_k \frac{\partial x_j}{\partial X_k}\frac{\partial X_k}{\partial x_i} = k_B T \frac{\partial x_j}{\partial x_i} = k_B T \delta_{ij}. \tag{19.14}$$

In the above calculation, in the last partial derivative, independent variables are switched to $x_1, \cdots, x_n$.

[320] The fluctuations of the quantities that may be interpreted as the expectation values of microscopic-mechanically expressible quantities (e.g., internal energy, volume, pressure) tend to zero in the $T \to 0$ limit as we see here. However, the fluctuations of entropy and the quantities obtained by differentiating it do not satisfy the above property.

the density distribution function is a positive definite quadratic form (apart from a constant term due to normalization) of the deviations from the expectation values, the distribution is Gaussian:

$$f(\boldsymbol{x}) = \frac{1}{\sqrt{det(2\pi V)}} \exp\left(-\frac{1}{2}(\boldsymbol{x}-\boldsymbol{m})^T V^{-1}(\boldsymbol{x}-\boldsymbol{m})\right), \tag{19.20}$$

where $\langle \boldsymbol{x} \rangle = \boldsymbol{m}$, the mean, and V is the *covariance matrix* defined as (do not forget that our vectors are column vectors)

$$V = \langle (\boldsymbol{x}-\boldsymbol{m})(\boldsymbol{x}-\boldsymbol{m})^T \rangle. \tag{19.21}$$

The reader must not have any difficulty in demonstrating that (19.20) is correctly normalized. [Hint: choose eigendirections of V as the orthogonal coordinates.]

In particular, for the two variable case:

$$f(x, y) \propto \exp\left\{-\frac{1}{2}\left(ax^2 + 2bxy + cy^2\right)\right\}, \tag{19.22}$$

then

$$V = \Lambda^{-1} = \begin{pmatrix} a & b \\ b & c \end{pmatrix}^{-1} = \frac{1}{det\,\Lambda}\begin{pmatrix} c & -b \\ -b & a \end{pmatrix}. \tag{19.23}$$

That is,

$$\langle x^2 \rangle = c/det\,\Lambda, \quad \langle xy \rangle = -b/det\,\Lambda, \quad \langle y^2 \rangle = a/det\,\Lambda. \tag{19.24}$$

Q19.1 [Fluctuation and nonlinear spring]
There is a deformable macromolecule (due to conformational changes) whose end-to-end distance is L. The ambient temperature is $T = 300$ K.
(1) If the amplitude of the deformation is small, the system may be understood as a harmonic spring. What is the effective spring constant k of this macromolecule, when the length variance is known to be $\langle \delta L^2 \rangle$? [Hint: k is the inverse susceptibility of L against F under constant temperature.]
(2) Suppose the needed force F to maintain the end-to-end length to be L is

$$F = k(L - L_0) + \frac{1}{3}\alpha(L - L_0)^3, \tag{19.25}$$

where L_0 and α are positive constants. What is the fluctuation of L around $L = L_1$? Notice that in this way without measuring F you could reconstruct the F-L relation.

Soln.
(1) A fluctuation-response relation applied to our case around $F = 0$ is

$$k_B T \left. \frac{\partial L}{\partial F} \right|_T = \langle \delta L^2 \rangle. \tag{19.26}$$

Therefore,

$$\frac{k_B T}{k} = \langle \delta L^2 \rangle. \tag{19.27}$$

You must have seen something like this for a polymer chain.
By the way, we discussed that the susceptibility or $(\partial X/\partial x)$ is extensive. In our example, L is extensive, so $1/k$ must be extensive. It means that if the length of the spring is doubled, its Hooke's constant is halved, as we know well.

(2) Using the fluctuation-response relation, we have when $L = L_1$ (by applying an appropriate force)

$$\langle \delta L^2 \rangle = k_B T \left. \frac{\partial L}{\partial F} \right|_T = \frac{k_B T}{k + \alpha(L_1 - L_0)^2}. \tag{19.28}$$

Notice that $\langle \delta L^2 \rangle$ here and that in (1) are different quantities, because the states around which we observe fluctuations are distinct. In (1) it is the unstretched state, but here, it is somehow stretched and its mean length is L_1. It is much easier to measure the position than the force, so experimentally, the derivative of F wrt L may be obtained by measuring only the positions under unspecified appropriate forces.

Q19.2 [Easy questions about fluctuations]
(1) Consider a small portion of a big system in equilibrium. Let us assume that the small portion contains a constant number of particles. Find the fluctuation of entropy $\langle \delta S^2 \rangle$ in terms of an appropriate heat capacity of the small portion.

(2) Take a (constant volume) small portion of a solution of some substance in a solvent. Let c be the concentration of the solute. Show that $\langle \delta c\, \delta T \rangle = 0$, that is, concentration fluctuation and temperature fluctuation are uncorrelated in equilibrium.

Soln

(1) We use (needless to say, we use Einstein's thermodynamic fluctuation theory)

$$-\frac{1}{2k_BT}\delta T \delta S + \cdots .$$

Choose S and P as independent variables.[321] Then we can rewrite this as

$$-\frac{1}{2k_BT}\left.\frac{\partial T}{\partial S}\right|_P \delta S^2 + \cdots = -\frac{1}{2k_BC_P}\delta S^2 + \cdots .$$

Therefore, $\langle \delta S^2 \rangle = k_B C_P$, where C_P is the constant pressure specific heat of the small portion.

(2) This is obvious from $\langle \delta N \delta T \rangle = 0$.

[321] You need not, but since $\langle \delta S \delta P \rangle = 0$, computation is (drastically) simplified.

Discussion 9

We will discuss Jacobian technique, thermodynamic stability and fluctuations

D9.1 [Use of Jacobian].
In thermodynamics, we often need a partial derivative of a state function A by another state function B, while keeping the third state function C:

$$\left.\frac{\partial A}{\partial B}\right|_C . \tag{19.29}$$

For example, for a fluid with the Gibbs relation $dE = TdS - PdV$, we may consider the following question:

$$\left.\frac{\partial S}{\partial V}\right|_P > 0 \text{ or } < 0\,? \tag{19.30}$$

That is, does the entropy of a fluid increase or decrease, when the volume is increased under constant pressure (i.e., isobarically)? Its sign may not immediately be clear.

To this end we should be able to handle such partial derivatives freely. The only systematic way that allows us to do so with ease is the Jacobian technique explained in Section 17.

The key ingredients are:

$$\left.\frac{\partial A}{\partial B}\right|_C = \frac{\partial(A,C)}{\partial(B,C)} \tag{19.31}$$

and that the factors $\partial(X,Y)$ may be treated as an algebraic object:

$$\frac{\partial(X,Y)}{\partial(A,B)}\frac{\partial(A,B)}{\partial(x,y)} = \frac{\partial(X,Y)}{\partial(x,y)}. \tag{19.32}$$

This is only a disguised usual chain rule for two variable functions.

Let us demonstrate this relation.

(1) Confirm

$$\begin{pmatrix} \left.\frac{\partial X}{\partial x}\right|_y \\ \left.\frac{\partial Y}{\partial x}\right|_y \end{pmatrix} = \begin{pmatrix} \left.\frac{\partial X}{\partial A}\right|_B & \left.\frac{\partial X}{\partial B}\right|_A \\ \left.\frac{\partial Y}{\partial A}\right|_B & \left.\frac{\partial Y}{\partial B}\right|_A \end{pmatrix} \begin{pmatrix} \left.\frac{\partial A}{\partial x}\right|_y \\ \left.\frac{\partial B}{\partial x}\right|_y \end{pmatrix}. \tag{19.33}$$

(2) We can write analogous formulas for derivatives with respect to y (keeping x). Combining both, check the following formula:

$$\begin{pmatrix} \left.\frac{\partial X}{\partial x}\right|_y & \left.\frac{\partial X}{\partial y}\right|_x \\ \left.\frac{\partial Y}{\partial x}\right|_y & \left.\frac{\partial Y}{\partial y}\right|_x \end{pmatrix} = \begin{pmatrix} \left.\frac{\partial X}{\partial A}\right|_B & \left.\frac{\partial X}{\partial B}\right|_A \\ \left.\frac{\partial Y}{\partial A}\right|_B & \left.\frac{\partial Y}{\partial B}\right|_A \end{pmatrix} \begin{pmatrix} \left.\frac{\partial A}{\partial x}\right|_y & \left.\frac{\partial A}{\partial y}\right|_x \\ \left.\frac{\partial B}{\partial x}\right|_y & \left.\frac{\partial B}{\partial y}\right|_x \end{pmatrix}. \tag{19.34}$$

(3) Conclude your demonstration of (19.32), using the definition of the Jacobian.

Solution.
(1) We know, thanks to the chain rule,

$$\left.\frac{\partial X}{\partial x}\right|_y = \left.\frac{\partial X}{\partial A}\right|_B \left.\frac{\partial A}{\partial x}\right|_y + \left.\frac{\partial X}{\partial B}\right|_A \left.\frac{\partial B}{\partial x}\right|_y, \tag{19.35}$$

$$\left.\frac{\partial Y}{\partial x}\right|_y = \left.\frac{\partial Y}{\partial A}\right|_B \left.\frac{\partial A}{\partial x}\right|_y + \left.\frac{\partial Y}{\partial B}\right|_A \left.\frac{\partial B}{\partial x}\right|_y. \tag{19.36}$$

Rewriting these using the vector notation, we get (19.33).

(2) We have used the y-derivative counterpart of the above chain rules:

$$\left.\frac{\partial X}{\partial y}\right|_x = \left.\frac{\partial X}{\partial A}\right|_B \left.\frac{\partial A}{\partial y}\right|_x + \left.\frac{\partial X}{\partial B}\right|_A \left.\frac{\partial B}{\partial y}\right|_x, \tag{19.37}$$

$$\left.\frac{\partial Y}{\partial y}\right|_x = \left.\frac{\partial Y}{\partial A}\right|_B \left.\frac{\partial A}{\partial y}\right|_x + \left.\frac{\partial Y}{\partial B}\right|_A \left.\frac{\partial B}{\partial y}\right|_x.$$

Checking (19.34) is very easy.

(3) Note that the Jacobian is the determinant of the matrices we see above (recall $\det A = \det A^T$):

$$\frac{\partial(X,Y)}{\partial(A,B)} = \det\begin{pmatrix} \left.\frac{\partial X}{\partial A}\right|_B & \left.\frac{\partial Y}{\partial A}\right|_B \\ \left.\frac{\partial X}{\partial B}\right|_A & \left.\frac{\partial Y}{\partial B}\right|_A \end{pmatrix} = \det\begin{pmatrix} \left.\frac{\partial X}{\partial A}\right|_B & \left.\frac{\partial X}{\partial B}\right|_A \\ \left.\frac{\partial Y}{\partial A}\right|_B & \left.\frac{\partial Y}{\partial B}\right|_A. \end{pmatrix}. \tag{19.38}$$

We can finish the demonstration with the aid of $\det(AB) = \det(A)\det(B)$ for square matrices A and B.

The Jacobian technique becomes really powerful with the following observation: All the Maxwell's relations can be unified as

$$\frac{\partial X, x)}{\partial(y,Y)} = 1, \tag{19.39}$$

where (X,x) and (Y,y) are extensive-intensive conjugate pairs (with respect to E). (S,T), $(V,-P)$, (M,B), etc., are the examples, because $dE = TdS - PdV + BdM + \cdots$. This can be used as (consider a rubber band; (S,T) and (L,F) are conjugate pairs)

$$\left.\frac{\partial S}{\partial L}\right|_T = \frac{\partial(S,T)}{\partial(L,T)} = \frac{\partial(S,T)}{\partial(F,L)}\frac{\partial(F,L)}{\partial(L,T)} = \frac{\partial(F,L)}{\partial(L,T)} = -\frac{\partial(F,L)}{\partial(T,L)} = -\left.\frac{\partial F}{\partial T}\right|_L. \tag{19.40}$$

Explain intuitively why this relation is plausible for a rubber band.

(4) What do you say about the sign of (19.30)?

Remember that in thermodynamics there are two kinds of inequality, sacred (thermodynamic) and fetish (materials-specific):

All the sacred inequalities come from the stability inequalities (which is due to the second law): all the principal minors of the second derivative matrix (the Hessian matrix) of E with respect to S and the work coordinates are positive. In particular,

$$\left.\frac{\partial x}{\partial X}\right|_{Y,\cdots} = 1 \Big/ \left.\frac{\partial X}{\partial x}\right|_{Y,\cdots} > 0, \tag{19.41}$$

where upper case letters denote extensive variables, and (X, x) is a conjugate pair.

Solution.
Without any thinking, first you should use a Jacobian:

$$\left.\frac{\partial S}{\partial V}\right|_P = \frac{\partial(S, P)}{\partial(V, P)}. \tag{19.42}$$

We wish to related this to something whose sign we know definitely (i.e., sacred). In this case, C_P is a natural choice:

$$\left.\frac{\partial S}{\partial V}\right|_P = \frac{\partial(S, P)}{\partial(T, P)}\frac{\partial(T, P)}{\partial(V, P)} = \frac{C_P}{T} \Big/ \left.\frac{\partial V}{\partial T}\right|_P. \tag{19.43}$$

$C_P > 0$ is sacred. However, even for a fluid we know the sign of $(\partial V/\partial T)_P$ can change. Thus, there is no sacred inequality for it. (19.43) tells us that the signs of the partial derivatives in it must be the same; this relation is sacred.

(5)* How about

$$\left.\frac{\partial S}{\partial V}\right|_T ? \tag{19.44}$$

Explain your conclusion as 'microscopically as possible' (perhaps in terms of information you need).

Solution.
Always rewrite the partial derivative in terms of a Jacobian:

$$\left.\frac{\partial S}{\partial V}\right|_T = \frac{\partial(S, T)}{\partial(V, T)}. \tag{19.45}$$

I have no idea, so let us try Maxwell (recall $(V, -P)$ is a conjugate pair):

$$\left.\frac{\partial S}{\partial V}\right|_T = \frac{\partial(S, T)}{\partial(V, T)} = \frac{\partial(S, T)}{\partial(V, P)}\frac{\partial(V, P)}{\partial(V, T)} = \frac{\partial(V, P)}{\partial(V, T)} = \left.\frac{\partial P}{\partial T}\right|_V. \tag{19.46}$$

This we can understand, but we can further modify this as

$$\left.\frac{\partial S}{\partial V}\right|_T = \left.\frac{\partial P}{\partial T}\right|_V = \frac{\partial(V, P)}{\partial(V, T)} = \frac{\partial(T, P)}{\partial(V, T)}\frac{\partial(V, P)}{\partial(T, P)} = -\left.\frac{\partial P}{\partial V}\right|_T \left.\frac{\partial V}{\partial T}\right|_P. \tag{19.47}$$

The sign of the first derivative is sacred. It is negative. Therefore, the sign of (19.44) is the same as the sign of the thermal 'expansion' coefficient. It could be negative; not sacred.

In the case of cold water, our result tells us that compression increases entropy! To make the ordered hydrogen bonding network possible in ice, we need more space than in the liquid phase (you know the density of ice is less than the water around 0°C). Squishing breaks hydrogen bond networks, increasing the structural entropy.

(6) Find the following derivative

$$\left.\frac{\partial T}{\partial V}\right|_E \tag{19.48}$$

for a fluid (the Gibbs relation $dE = TdS - PdV$) in terms of T, P, C_V, β and α, where

$$C_V = T\left.\frac{\partial S}{\partial T}\right|_V, \ \beta = -\frac{1}{V}\left.\frac{\partial V}{\partial P}\right|_T, \ \alpha = \frac{1}{V}\left.\frac{\partial V}{\partial T}\right|_P. \tag{19.49}$$

Confirm that the result indeed vanishes for an ideal gas.

Solution.
There may be a cleverer method, but here I choose the least insightful approach:

$$\left.\frac{\partial T}{\partial V}\right|_E = \frac{\partial(T,E)}{\partial(V,E)} = \frac{\partial(V,S)}{\partial(V,E)}\frac{\partial(T,E)}{\partial(V,S)} = \frac{\partial(T,E)}{\partial(V,S)}\Big/\frac{\partial(V,E)}{\partial(V,S)} \tag{19.50}$$

$$= \frac{\partial(T,E)}{\partial(V,S)}\Big/\left.\frac{\partial E}{\partial S}\right|_V = \frac{1}{T}\frac{\partial(T,E)}{\partial(V,S)} \tag{19.51}$$

$$= \frac{1}{T}\frac{\partial(V,T)}{\partial(V,S)}\frac{\partial(T,E)}{\partial(V,T)} = -\frac{1}{C_V}\frac{\partial(E,T)}{\partial(V,T)} = -\frac{1}{C_V}\left.\frac{\partial E}{\partial V}\right|_T, \tag{19.52}$$

which may be obtained more cleverly with the aid of $C_V = (\partial E/\partial T)_V$ as

$$\left.\frac{\partial T}{\partial V}\right|_E = \frac{\partial(T,E)}{\partial(V,E)} = \frac{\partial(V,T)}{\partial(V,E)}\frac{\partial(T,E)}{\partial(V,T)} = -\frac{1}{C_V}\left.\frac{\partial E}{\partial V}\right|_T \tag{19.53}$$

$$= -\frac{1}{C_V}\left[T\left.\frac{\partial S}{\partial V}\right|_T - P\right] = -\frac{1}{C_V}\left[T\frac{\partial(S,T)}{\partial(V,T)} - P\right] \tag{19.54}$$

$$= \frac{1}{C_V}\left[P - T\frac{\partial(S,T)}{\partial(V,P)}\frac{\partial(V,P)}{\partial(V,T)}\right] = \frac{1}{C_V}\left[P - T\frac{\partial(V,P)}{\partial(V,T)}\right] \tag{19.55}$$

$$= \frac{1}{C_V}\left[P - T\frac{\partial(V,P)}{\partial(P,T)}\frac{\partial(P,T)}{\partial(V,T)}\right] = \frac{1}{C_V}(P - T\alpha/\beta). \tag{19.56}$$

You could directly cook $\partial(T,E)/\partial(V,S)$, explicitly calculating the determinant.

If you understand the above derivation without difficulty, you are thermodynamically in good shape.

For an ideal gas

$$\alpha/\beta = \frac{\partial(V,P)}{\partial(V,T)} = \frac{P}{T}, \tag{19.57}$$

so the derivative vanishes as we know well.

D9.2 [Fluctuation review]

We have learned two important theories (or theoretical results) as to fluctuations, the fluctuation-response relation and (Einstein's) thermodynamic theory of fluctuation. Practically, almost no interesting quantities may be computed purely theoretically. Therefore, experimentally accessible windows provided by fluctuations are of great importance.

(1) Using Einstein's theory, compute the fluctuation $\langle \delta X^2 \rangle$ for a general extensive quantity X for a small portion in a given system. Assume that the Gibbs relation for the system is $dE = TdS - PdV + xdX$. You can use the susceptibility $\chi_{T,P} = (\partial X/\partial x)_{T,P}$. Confirm the agreement of the Einstein theory result with the corresponding formula obtainable by the fluctuation-response relation. That is, using the thermodynamic fluctuation theory, derive

$$\langle \delta X^2 \rangle = k_B T \left. \frac{\partial X}{\partial x} \right|_{T,P}. \tag{19.58}$$

In choosing basic fluctuation variables pay attention to the general result

$$\langle \delta X_i \delta x_j \rangle = k_B T \delta_{ij}. \tag{19.59}$$

Solution.

The fundamental equation for the probability of fluctuation is

$$P \propto \exp\left\{ -\frac{1}{2k_B T}[\delta S \delta T - \delta P \delta V + \delta x \delta X] \right\}. \tag{19.60}$$

Choosing δX as one of the basic fluctuation variables is the least perverse approach. The remaining two may be chosen freely from individual conjugate pairs, $\{V, -P\}$ and $\{S, T\}$, but (19.59) strongly advises us to choose δP and δT.[322] Then, the cross correlations (i.e., covariances) vanish, so we have only to study

$$\frac{1}{2k_B T}[\delta S \delta T - \delta P \delta V + \delta x \delta X] = \frac{1}{2k_B T} \left. \frac{\partial x}{\partial X} \right|_{T,P} \delta X^2 + \cdots, \tag{19.61}$$

[322] However, to get the correct answer, any choice is OK. HOWEVER, you can save time (a lot in this case) by avoiding extensive variables δS and δV. Using these variables can be a very good exercise for your thermodynamic muscle.

where the unwritten terms do not contain δX. That is, the (density) distribution function is the following Gaussian:

$$\propto \exp\left[-\frac{1}{2k_BT}\left.\frac{\partial x}{\partial X}\right|_{T,P}\delta X^2+\cdots\right]. \tag{19.62}$$

Therefore,

$$\langle \delta X^2\rangle = k_BT \left/ \left.\frac{\partial x}{\partial X}\right|_{T,P}\right. = k_BT\left.\frac{\partial X}{\partial x}\right|_{T,P} = k_BT\chi_{T,P} > 0. \tag{19.63}$$

This is indeed the result of the fluctuation-response relation. The positivity of the susceptibility is a thermodynamically sacred inequality. The positivity of $\langle \delta X^2\rangle$ is far more fundamental than physics.

(2) Consider a system whose Gibbs relation is given by, for simplicity, $dE = TdS + xdX$. Let us demonstrate (an example of) Le Chatelier-Braun's principle,

$$\left.\frac{\partial X}{\partial x}\right|_T \geq \left.\frac{\partial X}{\partial x}\right|_S, \tag{19.64}$$

using Einstein's thermodynamic fluctuation theory. As usual, X is extensive and x its intensive partner: X and x make a conjugate pair.
(i) Find $\langle \delta x^2\rangle$ and $\langle \delta X^2\rangle$; the second one has been (virtually) computed in (1). [Mimic the calculations of $\langle \delta T^2\rangle$ or $\langle \delta S^2\rangle$.]
(ii) Demonstrate the inequality $\langle \delta x\delta X\rangle^2 \leq \langle \delta x^2\rangle\langle \delta X^2\rangle$ (Cauchy's inequality). [Hint: consider $\langle (t\delta x+\delta X)^2\rangle \geq 0$ for any t.]
(iii) Show that Cauchy's inequality implies (a) Le Chatelier-Braun's principle (19.64). Do not forget (19.59).

Solution.
(i) The fundamental equation we need is the same as above:

$$P \propto \exp\left\{-\frac{1}{2k_BT}[\delta S\delta T+\delta x\delta X]\right\}. \tag{19.65}$$

Therefore, choosing δx and δS as independent variables, we have only to study

$$\frac{1}{2k_BT}[\delta S\delta T+\delta x\delta X] = \frac{1}{2k_BT}\left.\frac{\partial X}{\partial x}\right|_S\delta x^2+\cdots. \tag{19.66}$$

That is ,

$$\langle \delta x^2\rangle = k_BT\left/\left.\frac{\partial X}{\partial x}\right|_S\right.. \tag{19.67}$$

We know (see (19.63))

$$\langle \delta X^2 \rangle = k_B T \left. \frac{\partial X}{\partial x} \right|_T . \tag{19.68}$$

(ii) Consider $\langle (t\delta x + \delta X)^2 \rangle$ as a quadratic form for t. Since this is positive definite, its discriminant must be negative. That is,

$$\langle \delta x^2 \rangle t^2 + 2\langle \delta x \delta X \rangle t + \langle \delta X^2 \rangle \geq 0 \tag{19.69}$$

implies its discriminant must be negative:

$$\langle \delta x \delta X \rangle^2 - \langle \delta x^2 \rangle \langle \delta X^2 \rangle \leq 0. \tag{19.70}$$

(iii) Using the results in (i), we can convert Cauchy's inequality into

$$(k_B T)^2 \leq k_B T \left. \frac{\partial X}{\partial x} \right|_T k_B T \Bigg/ \left. \frac{\partial X}{\partial x} \right|_S . \tag{19.71}$$

That is (notice that the derivatives are positive),

$$\left. \frac{\partial X}{\partial x} \right|_S \leq \left. \frac{\partial X}{\partial x} \right|_T . \tag{19.72}$$

D9.3 [Stretching a chain] (this is ∼a past qual question[323])
A one-dimensional chain consists of $N \gg 1$ monomers (Fig. 19.2). Each monomer can assume two states (without degeneracy) A and B; in A its length is a, and in B its length is $2a$, where a is a positive constant. To change the shape of a monomer from A to B you need energy ε (> 0). We ignore the contribution of kinetic energy.

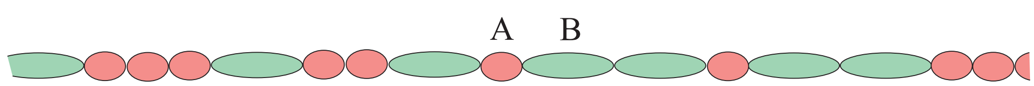

Figure 19.2: Polymer model with monomer conformational changes

(1) When the total length of the chain is L, find the entropy S microcanonically. Use $M \equiv L/a$ to compute the number of microstates.

Solution.
Let ℓ_i be the length of the i-th monomer: $\ell_i = a$ or $2a$. $L = \sum \ell_i = Ma$. Let the number of B state monomers be N_B. Then, since $L = a(N - N_B) + 2aN_B = a(N + N_B)$,

$$M = N + N_B. \tag{19.73}$$

[323] However, sophisticated thermodynamic questions are unlikely to be asked, because our faculty is materials oriented.

Therefore, the number of microstates compatible with the length $L = aM$ macrostate is

$$W(M) = \binom{N}{M-N} \tag{19.74}$$

for $N \le M \le 2N$. For other M the system is not defined. Therefore, we immediately obtain

$$S = -Nk_B \left[\frac{M-N}{N} \log \frac{M-N}{N} + \frac{2N-M}{N} \log \frac{2N-M}{N} \right]. \tag{19.75}$$

Notice that the total energy is $E = \varepsilon N_B = (M-N)\varepsilon$. Therefore, constant E and constant L are identical constraints, so the system has only one thermodynamic coordinate; you can choose L or E ($dE = (\varepsilon/a)dL$).

(2) What is the required (stretching) force F (cf. for a rubber band, it is the force that resists stretching, if $F > 0$) to maintain its length at L at temperature T?
Solution.
The Gibbs relation is

$$dE = (\varepsilon/a)dL = TdS + FdL. \tag{19.76}$$

Here F is a tensile force. Therefore,

$$F = \varepsilon/a - T\frac{dS}{dL}. \tag{19.77}$$

Note that S is only dependent on $L = aM$. Thus,

$$F = \varepsilon/a - \frac{k_B T}{a} \log \frac{2N-M}{M-N} \tag{19.78}$$

or

$$aF = \varepsilon - k_B T \log \frac{2N-M}{M-N}. \tag{19.79}$$

The formula implies that if the monomers are almost all in state A (i.e., $M \sim N$), $F \ll 0$. That is, the system pushes out with a tremendous force. If all in B (i.e., $M \sim 2N$), then again a tremendous force is needed, but this time a stretching force ($F \gg 0$).

(3) What happens to the change of the chain temperature, if it is reversibly and adiabatically stretched? [You must think whether this is a meaningful question or not for the model.]

Solution.

The question asks the following derivative, which we experimentally studied with a rubber band:

$$\left.\frac{\partial T}{\partial L}\right|_S = \frac{\partial(T,S)}{\partial(L,S)} = \frac{\partial(T,L)}{\partial(L,S)}\frac{\partial(T,S)}{\partial(T,L)}. \tag{19.80}$$

However, in contrast to the real rubber band, for our present model (or the ideal rubber band without thermal motion) S and E are functions of L only. Therefore, the above derivative is meaningless: you cannot change L while fixing S. Thus, "no experiment can be done to study it, so it is meaningless in physics" may be the only reasonable answer.

However, in the real chain (even the ideal chain) case $S = S(L, E)$ with E and L being independent variables, we can change E independently with S, and the specific heat under constant length C_L (this asks how S changes under constant L; this is meaningless in our over-idealized model) is meaningful and we would get something like

$$\left.\frac{\partial T}{\partial L}\right|_S = \frac{T}{C_L}\left.\frac{\partial S}{\partial L}\right|_T = \frac{(aF-\varepsilon)T}{C_L}. \tag{19.81}$$

(4) Study the same system using the canonical formalism. Then, confirm that the entropy above (19.75) and that obtained from the free energy indeed agree.

Solution.
The system energy is $\varepsilon N_B = \varepsilon(M-N)$, so the canonical partition function reads

$$Z(T) = \sum_{M=N}^{2N} W(M)e^{-\beta\varepsilon(M-N)} = \sum_{M=N}^{2N}\binom{N}{M-N}e^{-\beta\varepsilon(M-N)}. \tag{19.82}$$

If we introduce $X = M - N$,

$$Z(T) = \sum_{X=0}^{N}\binom{N}{X}e^{-\beta\varepsilon X} = (1+e^{-\beta\varepsilon})^N. \tag{19.83}$$

The internal energy is obtained as (notice that there is only one variable, because E and L are connected tightly)

$$E = -\frac{d\log Z}{d\beta} = N\frac{\varepsilon}{1+e^{\beta\varepsilon}}. \tag{19.84}$$

so

$$ST = E - A = N\frac{\varepsilon}{1+e^{\beta\varepsilon}} + Nk_BT\log(1+e^{-\beta\varepsilon}). \tag{19.85}$$

This is the entropy obtained by the canonical ensemble approach.

(19.84) implies

$$\frac{M-N}{N} = \frac{e^{-\beta\varepsilon}}{1+e^{-\beta\varepsilon}},\quad \frac{2N-M}{N} = \frac{1}{1+e^{-\beta\varepsilon}}. \tag{19.86}$$

Thus, (19.75), the microcanonical result, reads

$$\begin{aligned} S &= -Nk_B\left[\frac{e^{-\beta\varepsilon}}{1+e^{-\beta\varepsilon}}\log\frac{e^{-\beta\varepsilon}}{1+e^{-\beta\varepsilon}} + \frac{1}{1+e^{-\beta\varepsilon}}\log\frac{1}{1+e^{-\beta\varepsilon}}\right] && (19.87)\\ &= Nk_B\log(1+e^{-\beta\varepsilon}) - Nk_B\frac{e^{-\beta\varepsilon}}{1+e^{-\beta\varepsilon}}\log e^{-\beta\varepsilon}, && (19.88)\end{aligned}$$

which agrees with (19.85).

(5) Study the same system using the constant T-F ensemble, noting that under an external force F the system has a potential energy $-FL$. Then, confirm that F obtained by this scheme and (19.78) agree.

Solution.

The thermodynamic potential we use is now $\Phi = E - ST - FL$ and the Gibbs relation is

$$d\Phi = d(E - LF - TS) = -SdT - LdF. \tag{19.89}$$

Needless to say, E is just $\varepsilon(M-N)$, so it is NOT an independent quantity; as you see from (19.78) F is just a function of E (and vice versa). This means $\beta\Phi$ is actually a function of βF alone.[324] The convenient partition function Y reads ($X = M - N$)

$$\begin{aligned} Y &= \sum_{M=N}^{2N} W(M) e^{-\beta\varepsilon(M-N)+\beta a M F} = \sum_{X=0}^{N} \binom{N}{X} e^{-\beta(\varepsilon - aF)X + \beta a N F} && (19.90) \\ &= e^{\beta a F N}(1 + e^{-\beta(\varepsilon - aF)})^N. && (19.91) \end{aligned}$$

Thus,

$$\Phi = -k_B T \log Y = -aFN - Nk_B T \log(1 + e^{-\beta(\varepsilon - aF)}). \tag{19.92}$$

From this we get the chain length L as

$$L = -\left.\frac{\partial \Phi}{\partial F}\right|_T = aN + aN\frac{e^{-\beta(\varepsilon - aF)}}{1 + e^{-\beta(\varepsilon - aF)}}. \tag{19.93}$$

or

$$M = N + N\frac{e^{-\beta(\varepsilon - aF)}}{1 + e^{-\beta(\varepsilon - aF)}}. \tag{19.94}$$

Therefore,

$$M/N = 1 + \frac{x}{1+x} \;\Rightarrow\; x \equiv e^{-\beta(\varepsilon - aF)} = \frac{M-N}{2N-M}, \tag{19.95}$$

or

$$\beta(\varepsilon - aF) = \log\frac{2N-M}{M-N}. \tag{19.96}$$

This is just (19.78):

$$F = \varepsilon/a - \frac{k_B T}{a}\log\frac{2N-M}{M-N} \tag{19.97}$$

obtained microcanonically.

[324]Dimensional analysis also tells us so.

Exercise 9

E9.1 [Basic use of Jacobian technique].
Consider an elastic rod of length L. Its Gibbs relation reads

$$dE = TdS + FdL, \tag{19.98}$$

where F is the (tensile) force.[325] There are two kinds of elasticity, entropic and energetic, according to the sign of $(\partial S/\partial L)_T$; entropic (resp. energetic) if negative (resp. positive).

What can you say about the signs of the following partial derivatives for these different elasticities? If you can find the answer(s) in the lecture notes, you can quote it. If obvious, say so with a brief reason. [You'd better try 'intuitive' explanations of the results you would obtain.]
(1)

$$\left.\frac{\partial F}{\partial L}\right|_S . \tag{19.99}$$

(2)

$$\left.\frac{\partial L}{\partial T}\right|_S . \tag{19.100}$$

(3)

$$\left.\frac{\partial S}{\partial L}\right|_F . \tag{19.101}$$

(4) Under stretching condition $F > 0$,

$$\left.\frac{\partial S}{\partial L}\right|_E . \tag{19.102}$$

Solution.
The thermodynamic stability criterion $\delta^2 E > 0$ implies the positive definiteness of the Hessian of E with respect to extensive variables, so

$$\left.\frac{\partial x}{\partial X}\right|_Y > 0 \tag{19.103}$$

and

$$\frac{\partial(x,y)}{\partial(X,Y)} > 0 \tag{19.104}$$

follow.

(1) This is a diagonal term, so it must be positive due to the stability of the equilibrium state. No demonstration is needed.

(2) We know its reciprocal, so it is positive for the entropic case, and opposite for

[325] Thermodynamics of elastic bodies is not this simple, but let us study the bare-bone version.

the energetic case. Or we can honestly proceed as:

$$\left.\frac{\partial L}{\partial T}\right|_S = \frac{\partial(L,S)}{\partial(L,T)}\frac{\partial(L,T)}{\partial(T,S)} = -\frac{C_L}{T}\frac{\partial(L,T)}{\partial(S,T)} = -\left.\frac{C_L}{T}\Big/\frac{\partial S}{\partial L}\right|_T. \tag{19.105}$$

For example, for a polymer chain if you wish to keep S while raising T, you must suppress the wiggling by increasing F, so L must increase. For a metal rod if you wish to keep S while raising T, you must suppress the structural disorder by decreasing the interatomic distances, so L should decrease.

(3)

$$\begin{aligned}\left.\frac{\partial S}{\partial L}\right|_F &= \frac{\partial(S,F)}{\partial(L,F)} = \frac{\partial(S,F)}{\partial(T,S)}\frac{\partial(T,S)}{\partial(L,F)} = \frac{\partial(S,F)}{\partial(T,S)} \\ &= \frac{\partial(S,F)}{\partial(T,L)}\frac{\partial(T,L)}{\partial(T,S)} = \left.\frac{\partial(S,F)}{\partial(T,L)}\Big/\frac{\partial S}{\partial L}\right|_T.\end{aligned}$$

The Jacobian in this formula is positive as you can show it explicitly:

$$\frac{\partial(S,F)}{\partial(T,L)} = \frac{\partial(S,F)}{\partial(S,L)}\frac{\partial(S,L)}{\partial(T,L)} > 0, \tag{19.106}$$

since both factors are diagonal elements.

For the entropic (resp., energetic) case it is negative (resp., positive). For a polymer chain, to increase L under constant F, you must calm down the 'kids' (cool the chain), so S decreases. For a metal rod, to increase L under constant F, you must increase the directional disorder of the interatomic forces, so S increases.

(4) From $dE = TdS + FdL = 0$ obviously

$$\left.\frac{\partial S}{\partial L}\right|_E = -\frac{F}{T} < 0. \tag{19.107}$$

Or you can do as follows as well:

$$\left.\frac{\partial S}{\partial L}\right|_E = \frac{\partial(S,E)}{\partial(L,E)} = \frac{\partial(S,E)}{\partial(L,S)}\frac{\partial(L,S)}{\partial(L,E)} = -\left.\frac{\partial E}{\partial L}\right|_S\Big/\left.\frac{\partial E}{\partial S}\right|_L = -\frac{F}{T}. \tag{19.108}$$

E9.2 [Fluctuation of enthalpy]
Calculate the fluctuation of enthalpy $\langle \delta H^2\rangle$. Notice that $\delta H = T\delta S + V\delta P$.

Solution.

$$\langle \delta H^2\rangle = T^2\langle \delta S^2\rangle + V^2\langle \delta P^2\rangle, \tag{19.109}$$

because δS and δP are statistically independent. Following Einstein, we know the density distribution function of fluctuations:

$$\propto \exp[\delta^2 S/k_B] = \exp\left\{-\frac{1}{2k_BT}[\delta S\delta T - \delta P\delta V]\right\}. \tag{19.110}$$

We choose δS and δP as basic fluctuations:

$$-\frac{1}{2k_BT}[\delta S\delta T - \delta P\delta V] = -\frac{1}{2k_BT}\left[\left.\frac{\partial T}{\partial S}\right|_P (\delta S)^2 - \left.\frac{\partial V}{\partial P}\right|_S (\delta P)^2 + \cdots\right], \tag{19.111}$$

where the remaining terms are irrelevant. Therefore, the Gaussianness of the distribution tells us

$$\langle \delta S^2\rangle = k_BT\left.\frac{\partial S}{\partial T}\right|_P = k_BC_P, \tag{19.112}$$

$$\langle \delta P^2\rangle = -k_BT\bigg/\left.\frac{\partial V}{\partial P}\right|_S = k_BT/V\beta_S, \tag{19.113}$$

where β_S is the adiabatic compressibility. Therefore,

$$\langle \delta H^2\rangle = k_BT(TC_P + V/\beta_S). \tag{19.114}$$

E9.3. [Independent spin system in magnetic field]
A graduate textbook[326] discusses the entropy and temperature relation for a non-interacting spins (just the model we discussed in Section 17) as follows; Under magnetic field B, the system entropy reads

$$S(E,B) = -Nk_B\left[\frac{N+E/\mu B}{2N}\log\frac{N+E/\mu B}{2N} + \frac{N-E/\mu B}{2N}\log\frac{N-E/\mu B}{2N}\right], \tag{19.115}$$

where the author identifies $E = -MB$.

The author says "let us introduce a result from thermodynamics" and writes a nonsense

$$\left.\frac{\partial S}{\partial E}\right|_{M,N} = \frac{1}{T}. \tag{19.116}$$

(1) Correct the errors.
(2) After correction, obtain the B-$\tilde{H}$ relation. Here, $\tilde{H} = E - MB = -MB$, where E is the true internal energy of the system (distinct from the fake internal energy E in the quoted book).[327]

[326] Reichl's *A modern course of statistical physics* pp12-13
[327] $\tilde{H}$ corresponds to the enthalpy for a fluid system.

(3) Show that adiabatic reducing of the external magnetic field cools the spins.

Solution.
(1) Since E (whatever it is) is fixed (because M is fixed), this derivative is meaningless.

As you know the internal energy of the system is zero, and the 'generalized enthalpy' $\tilde{H} = E - MB = -MB$, so, if you wish to use something like internal energy, (19.115) should read

$$S(\tilde{H}, B) = -Nk_B \left[\frac{N + \tilde{H}/\mu B}{2N} \log \frac{N + \tilde{H}/\mu B}{2N} + \frac{N - \tilde{H}/\mu B}{2N} \log \frac{N - \tilde{H}/\mu B}{2N} \right], \tag{19.117}$$

The Gibbs relation is $d\tilde{H} = TdS - MdB$, so a meaningful counterpart of (19.116) reads

$$\left.\frac{\partial S}{\partial \tilde{H}}\right|_{B,N} = \frac{1}{T}. \tag{19.118}$$

In the quoted book $dE = TdS + BdM$ is used to get (19.116), but an external magnetic field is applied, so the proper thermodynamic potential is $\tilde{H}$.

(2) Explicitly computing (19.118), we obtain (you have only to differentiate the factors outside log)

$$\frac{1}{T} = -\frac{k_B}{2\mu B} \left[\log \frac{N + \tilde{H}/\mu B}{2N} - \log \frac{N - \tilde{H}/\mu B}{2N} \right] = \frac{k_B}{2\mu B} \log \frac{N - \tilde{H}/\mu B}{N + \tilde{H}/\mu B}. \tag{19.119}$$

That is, ($x \equiv \tilde{H}/\mu NB$)

$$(1 + x)e^{2\beta\mu B} = (1 - x) \;\Rightarrow\; x = \frac{1 - e^{2\beta\mu B}}{1 + e^{2\beta\mu B}} = -\tanh(\beta\mu B), \tag{19.120}$$

or

$$\tilde{H} = -\mu NB \tanh(\beta\mu B) = -MB. \tag{19.121}$$

(3) Adiabaticity means S constant, so $\tilde{H}/\mu B$ (actually $-M/\mu$) must be constant as well. Therefore, (19.121) means $\tanh(\mu B/k_B T)$ is constant. If you reduce B, then T must decrease. However, note that M does not change, so it is not 'demagnetization.' This argument may be used to explain the cooling of the spin system itself, BUT if you wish to use a spin system as a coolant, you need real demagnetization (See at the end of **17.17**).

20 Chemical potential

Summary
∗ To discuss open systems we must extend the first law of thermodynamics by including the mass action $dZ' = \sum \mu dN$.
∗ When exchange of a chemical is allowed between various parts of the system, the equilibrium condition is the identity of its chemical potentials among the parts.
∗ The chemical potential generally has the form $\mu = \mu^{\ominus} + k_BT \log a$, where activity a is related to the concentration of the chemical.
∗ Algebraic expression of chemical reactions gives the reaction equilibrium condition $\sum \nu\mu = 0$, which leads to the concept of equilibrium constant.

Key words
mass action, chemical potential, Gibbs-Duhem relation, phase equilibrium, Clapeyron-Clausius equation, osmotic pressure, van't Hoff's law, Raoult's law, colligative properties, chemical reaction, signed stoichiometric coefficients, law of mass action, equilibrium constant, van't Hoff's equation

What you should be able to do
∗ Be able to explain what the chemical potential is, and understand various equilibrium conditions in terms of chemical potentials.
∗ Be able to understand the shifting direction of the reaction when T or P is altered.

20.1 Open systems

So far we have discussed isolated systems, thermally isolated systems, and systems whose work coordinates are buffered (e.g., thermostatted systems). These *closed systems* are not allowed to exchange substances between the systems themselves and their surrounding world.

Now, we will discuss *open systems* for which exchange of their component chemicals between themselves and their environments is allowed. We must extend the first law in the following form

$$\Delta E = Q + W + Z, \tag{20.1}$$

where Z is called the *mass action*, which describes the energetic contribution of materials exchange.

20.2 Mass action and chemical potential

To begin with, for simplicity, we assume only one chemical may be exchanged. We need one variable N to specify its amount in the system (in moles or in numbers[328]). We prepare a semipermeable rigid membrane that allows the passage of this chemical. Setting up a device as illustrated in Fig. 20.1 and injecting this chemical (only) into the system (or sucking up from the system), we can measure the necessary work (necessary mass action) $d'Z$ to inject dN molecules into the system. This is written as

$$d'Z = \mu dN. \tag{20.2}$$

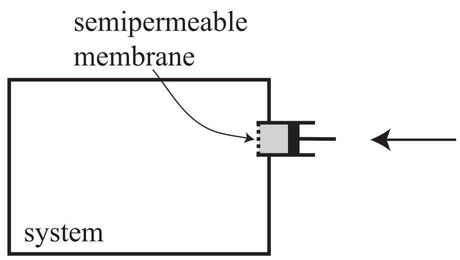

Figure 20.1: How to measure a chemical potential; however, this is only a very schematic figure. Since ordinary work coordinates and entropy must be kept constant, it is practically almost impossible to use this approach. Practically, we use (20.14) under T, P (and other intensive conjugate variables to work coordinates) constant.

Here, it is explicitly noted that Z is not a state function, and μ is called the *chemical potential* of this chemical.

If we have more than one chemicals whose amounts we can change independently,[329] we can appropriately generalize the above setup and write

$$d'Z = \sum_i \mu_i dN_i, \tag{20.3}$$

where N_i denotes the amount of the ith chemical and μ_i the corresponding chemical potential.

Intuitively, the chemical potential of a chemical of a system is the measure of the system's capability to export the chemical.

[328]But in these lecture notes, N always implies the number of particles, and we will not use moles unless clearly stated. Thermodynamics only handles the situation that the atomic nature of the material is not discernible, but here we adopt an eclectic attitude.

[329]What is independently changed and what not may not be a simple question, but usually, common-sense tells us the right answer. For example, if you want to inject water into the system, inevitably, you inject OH^-, H_3O^+, etc. as well, but they are 'slaved' to the total amount of water when T and P are fixed (chemical equilibrium). Therefore, we may conclude that only 1 component matters, and this answer is in agreement with our common sense conclusion.

20.3 Gibbs relation

Including the mass action, the full form of the Gibbs relation reads (cf **9.27**)

$$dE = TdS - PdV + \mu dN + xdX + \cdots. \tag{20.4}$$

or

$$dS = \frac{1}{T}dE + \frac{P}{T}dV - \frac{\mu}{T}dN - \frac{x}{T}dX + \cdots. \tag{20.5}$$

Needless to say, if you have several independently modifiable chemicals, we must replace μdN with a sum over these chemicals $\sum_i \mu_i dN_i$. Be careful about the signs.

Other thermodynamic potentials read

$$dA = -SdT - PdV + \mu dN + xdX + \cdots, \tag{20.6}$$

$$dG = -SdT + VdP + \mu dN + xdX + \cdots. \tag{20.7}$$

20.4 Gibbs-Duhem relation

If the system size is increased by a fraction $\delta\lambda$ by joining a small fraction of the

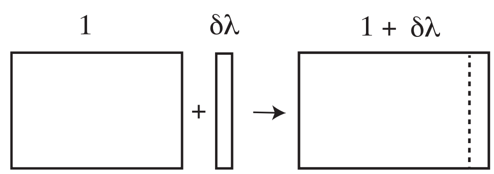

Figure 20.2: A fraction $\delta\lambda$ of the original system is added. Then, the increase of the extensive quantity X is $\delta X = X\delta\lambda$ (i.e., $X \to X + X\delta\lambda$).

identical system in the identical equilibrium state (Fig. 20.2), all the extensive quantities are multiplied by $1 + \delta\lambda$. However, all the conjugate intensive quantities are intact. Therefore, (20.4) applied to this situation reads

$$\delta E = E\delta\lambda = (TS - PV + \mu N + xX + \cdots)\delta\lambda, \tag{20.8}$$

or

$$E = TS - PV + \mu N + xX + \cdots. \tag{20.9}$$

This implies

$$dE = (TdS - PdV + \mu dN + xdX + \cdots) + (SdT - VdP + Nd\mu + Xdx + \cdots), \tag{20.10}$$

but (20.4) is true, so we must conclude that

$$SdT - VdP + Nd\mu + Xdx + \cdots = 0. \tag{20.11}$$

This relation is called the *Gibbs-Duhem relation*. This tells us how the chemical potential changes as a function of T, P, etc., if there is only one chemical species:

$$d\mu = -\frac{S}{N}dT + \frac{V}{N}dP - \frac{X}{N}dx + \cdots . \tag{20.12}$$

20.5 Gibbs free energy in terms of chemical potentials

If we combine (20.9) with the definition of the Gibbs free energy, we obtain

$$G = \mu N + xX + \cdots . \tag{20.13}$$

Usually, there are many chemicals and no other work coordinates than V, so this becomes

$$G = \sum_i \mu_i N_i . \tag{20.14}$$

If there is only one chemical, notice that the Gibbs relation (20.7) is just (20.12).

(20.13) can be more directly obtained by the same approach as is used to derive (20.9). We know

$$dG = -SdT + VdP + \mu dN + xdX. \tag{20.15}$$

By the grafting process in Fig. 20.2, $G \to G + G\delta\lambda$, since G is extensive, but since T and P are intact (intensive!). Therefore, (20.15) reads

$$G\delta\lambda = \mu N\delta\lambda + xX\delta\lambda, \tag{20.16}$$

which is just (20.13).

20.6 Equilibrium condition with chemical exchange

Suppose two systems I and II are joined to exchange heat, volume and chemicals while the whole system is in isolation (or thermally isolated and no work nor mass action is provided from outside). Then, the equilibrium condition must be the maximization of the total entropy. Let S_X be the entropy of system X. Then, $S = S_{\mathrm{I}} + S_{\mathrm{II}}$. If we assume thermal and pressure equilibration have already been attained, the remaining equilibrium condition is

$$\delta S = \sum_i \left(\frac{\mu_{i\mathrm{I}}}{T}\delta N_{i\mathrm{I}} + \frac{\mu_{i\mathrm{II}}}{T}\delta N_{i\mathrm{II}} \right) = 0. \tag{20.17}$$

Assuming that there is no chemical reaction changing N_i's, we must conclude $\delta N_{i\mathrm{I}} + \delta N_{i\mathrm{II}} = 0$. Therefore, the equilibrium condition is

$$\mu_{i\mathrm{I}} = \mu_{i\mathrm{II}} \tag{20.18}$$

for each i that can be exchanged between the two subsystems.

20.7 Phase equilibria

We will discuss phase transitions[330] in detail toward the end of these lecture notes, but let us discuss some elementary and important aspects of phase co-existence associated with first order phase transitions (= discontinuous phase transitions).[331]

If two phases coexist (just as ice floating on liquid water), we may regard different phases as different compartments I and II in contact with each other through the interphase (phase boundary). Let us study the condition for the equilibrium of these two phases (*phase equilibrium* of these two phases) of a pure substance under constant T and P. The equilibrium condition is the minimum of the Gibbs free energy of the whole system. Since there is only one chemical component,

$$0 = \delta G = \mu_{\mathrm{I}} \delta N_{\mathrm{I}} + \mu_{\mathrm{II}} \delta N_{\mathrm{II}}, \tag{20.19}$$

Therefore, if the system is materially closed, $\delta N = \delta N_{\mathrm{I}} + \delta N_{\mathrm{II}} = 0$, so we must conclude

$$\mu_{\mathrm{I}} = \mu_{\mathrm{II}}. \tag{20.20}$$

This is the phase equilibrium condition, which may be rewritten as

$$\Delta \mu = 0, \tag{20.21}$$

where Δ implies the change due to phase transition.

20.8 Clapeyron-Clausius equation

It is often interesting to know what happens, e.g., to the boiling point if the pressure is reduced (cf. vacuum distillation). To this end we must understand how the chemical potential changes. By the same logic used to derive the Gibbs-Duhem relation, we arrive at

$$d\mu = vdP - sdT, \tag{20.22}$$

where $v = V/N$ and $s = S/N$. These densities depend on the phases, but T and P are common to the coexisting phases, so (20.21) reads

$$\Delta v \, dP = \Delta s \, dT, \tag{20.23}$$

[330] What is the phase transition? We will discuss the topic in depth later. Here, you have only to consider familiar examples such as melting of ice or boiling of water.

[331] There are two major classes of phase transitions, continuous and discontinuous. In the former, there is no jump in any extensive quantities across the transition, but something strange can happen (say, their derivatives = susceptibilities diverge). In contrast, for discontinuous phase transitions at least one extensive quantity changes discontinuously at the phase transition point. For example, when ice melts, the density changes.

where dT and dP are changes along the phase coexistence line (the arrow in Fig. 20.3), and $\Delta v = v_{\mathrm{I}} - v_{\mathrm{II}}$ and $\Delta s = s_{\mathrm{I}} - s_{\mathrm{II}}$.

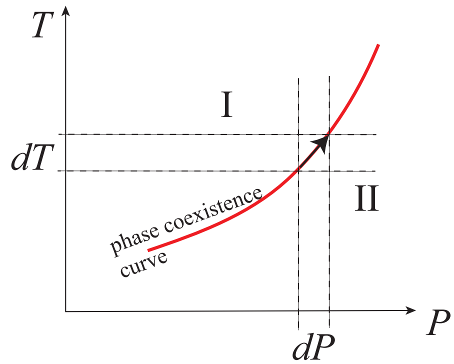

Figure 20.3: What happens to the phase coexistence temperature if the phase coexistence pressure is changed by dP? Here, the red curve describes the phase transition line between phase I and phase II.

(20.23) implies

$$\left.\frac{dP}{dT}\right|_{\text{coexist}} = \frac{\Delta s}{\Delta v} = \frac{s_{\mathrm{I}} - s_{\mathrm{II}}}{v_{\mathrm{I}} - v_{\mathrm{II}}}, \tag{20.24}$$

which is called the *Clapeyron-Clausius equation*. Here, you may also interpret v as the molar volume (volume/one mole) and s as the molar entropy. Since the entropy change Δs is related to the latent heat $\Delta h = h_{\mathrm{I}} - h_{\mathrm{II}}$ as $\Delta s = \Delta h/T$ with the phase transition temperature T, we can also write

$$\left.\frac{dP}{dT}\right|_{coexist} = \frac{\Delta h}{T\Delta v}. \tag{20.25}$$

20.9 Chemical potential of ideal gas: thermodynamics

Thus, we have learned that chemical potentials are fundamentally important. What can thermodynamics say about the chemical potential? From (20.22), if the temperature is fixed

$$d\mu = \frac{V}{N}dP. \tag{20.26}$$

Therefore, if we know the equation of state, we can say something about the chemical potential. For example, for an ideal gas we have

$$d\mu = \frac{k_BT}{P}dP. \tag{20.27}$$

That is,

$$\mu(T, P) = \mu(T, P^{\ominus}) + k_BT\log(P/P^{\ominus}). \tag{20.28}$$

Here $\ominus$ denotes some standard state. In practice, we often write

$$\mu(T, P) = \mu^{\ominus}(T) + k_B T \log P, \tag{20.29}$$

where $\mu^{\ominus}(T)$ is called the standard chemical potential.

20.10 Chemical potential of ideal gas: statistical mechanics

Let us compute the chemical potential of the ideal gas statistical mechanically. We have computed the Helmholtz free energy, so we may obtain

$$\mu = \left.\frac{\partial A}{\partial N}\right|_{T,V}. \tag{20.30}$$

We know

$$Z = \frac{1}{N!}\left[\left(\frac{2\pi m k_B T}{h^2}\right)^{3/2} V\right]^N = \frac{1}{N!}\left[\frac{\sqrt{2\pi}}{\lambda_T} L\right]^{3N} = \left[\frac{e n_Q V}{N}\right]^N, \tag{20.31}$$

where we have used Stirling's formula and $n_Q = (\sqrt{2\pi}/\lambda_T)^3$ with $\lambda_T = (h^2/m k_B T)^{1/2}$, the thermal de Broglie wavelength.

We obtain

$$A = N k_B T \log(N/V n_Q) - N k_B T, \tag{20.32}$$

so

$$\mu = k_B T \log \frac{N}{V n_Q} = k_B T \log \frac{n}{n_Q} = k_B T \log \frac{P}{k_B T n_Q}, \tag{20.33}$$

where n is the number density. This indeed has the form (20.29).

20.11 Chemical potentials of components of ideal gas mixture

The chemical potential of the ith component of the ideal gas mixture can be obtained with the aid of Dalton's law of partial pressures:

$$\mu_i(T, P) = \mu_i^{\ominus}(T) + RT \log P_i, \tag{20.34}$$

where P_i is the partial pressure of the ith gas.

20.12 Chemical potential of ideal solutions

Let us model the solvent/solution as a lattice model: each lattice point of the system is occupied either by a solvent molecule or by a solute molecule (Fig. 20.4).

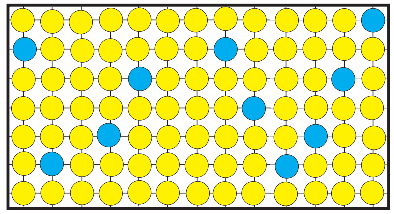

Figure 20.4: Lattice solution: N solvent molecules (yellow) and n solute molecules (blue).

We ignore the interactions among molecules (other than the volume exclusion due to occupying the lattice points); we call such a solution an *ideal solution*. N solvent molecules are mixed with n solute molecules to make a solution containing an $x = n/(N+n)$ mole fraction of solute. Let us discuss a dilute solution $0 < x \ll 1$.

Let the chemical potential of a pure solvent be $\mu_0(T,P)$ and that of a pure solute $\mu_s(T,P)$. Then, the initial Gibbs free energy (before mixing) is $G = N\mu_0 + n\mu_s$. After mixing, the Gibbs free energy of the total system will change:

$$\Delta G = \Delta E + P\Delta V - T\Delta S, \tag{20.35}$$

but if we assume that the solution is ideal, its volume and energy do not depend on the concentration of the solute, so we may assume ΔE and ΔV are both zero. Therefore,

$$\Delta G = -T\Delta S. \tag{20.36}$$

That is, G changes only due to the mixing entropy.

We model the solution as a lattice gas mixture as illustrated above, so we have

$$\Delta S = k_B \log \binom{N+n}{n} = -Nk_B \log(1-x) - nk_B \log x \tag{20.37}$$

immediately from Boltzmann's formula. Therefore, the Gibbs free energy after mixing is,

$$G = N\mu_0 + n\mu_s + Nk_BT\log(1-x) + nk_BT\log x. \tag{20.38}$$

Although we can immediately read off the chemical potentials after mixing, we honestly differentiate G to get the chemical potentials:

$$\mu_{\text{solv}} = \left.\frac{\partial G}{\partial N}\right|_{T,P} = \mu_0 + k_BT\log(1-x). \tag{20.39}$$

Analogously, we have

$$\mu_{\text{solute}} = \mu_s + k_BT\log x. \tag{20.40}$$

20.13 Raoult's law

In the above we interpreted the two components as a solvent and a solute, but we could interpret the mixture as the mixed liquid consisting of two liquids I and II. After mixing, how can we confirm that the chemical potentials of the components can be written as

$$\mu_{\mathrm{I}} = \mu_{\mathrm{I}0} + k_B T \log x_{\mathrm{I}}, \tag{20.41}$$

$$\mu_{\mathrm{II}} = \mu_{\mathrm{II}0} + k_B T \log x_{\mathrm{II}}, \tag{20.42}$$

where x_{I} (x_{II}) is the mole fraction of component I (II), the temperature is T, and the chemical potential of pure substances (at the pressure we are working) are denoted with suffix 0?

We have only to study the partial pressure of the corresponding gas components in the vapor in equilibrium with the mixed liquid. We assume that the vapors are ideal gases and their chemical potentials have the forms of (20.29) or (20.34). Let us write the chemical potentials of individual pure gases at T and under the atmospheric pressure as $\mu^{\ominus}_{\mathrm{I}G}$, $\mu^{\ominus}_{\mathrm{II}G}$. If we write the vapor pressure of pure liquids as $P_{\mathrm{I}0}$, $P_{\mathrm{II}0}$ (in atm), we have[332]

$$\mu_{\mathrm{I}0} = \mu^{\ominus}_{\mathrm{I}G} + k_B T \log P_{\mathrm{I}0}, \tag{20.43}$$

$$\mu_{\mathrm{II}0} = \mu^{\ominus}_{\mathrm{II}G} + k_B T \log P_{\mathrm{II}0}. \tag{20.44}$$

If the partial pressures in the vapor are P_{I} and P_{II}, then their chemical potentials read $\mu_{\mathrm{I}G}$ and $\mu_{\mathrm{II}G}$

$$\mu_{\mathrm{I}G} = \mu^{\ominus}_{\mathrm{I}G} + k_B T \log P_{\mathrm{I}}, \tag{20.45}$$

$$\mu_{\mathrm{II}G} = \mu^{\ominus}_{\mathrm{II}G} + k_B T \log P_{\mathrm{II}}. \tag{20.46}$$

The coexistence condition of the gas mixture and the liquid mixture is $\mu_{\mathrm{I}} = \mu_{\mathrm{I}G}$ and $\mu_{\mathrm{II}} = \mu_{\mathrm{II}G}$, so we have

$$\mu^{\ominus}_{\mathrm{I}G} + k_B T \log P_{\mathrm{I}0} + k_B T \log x_{\mathrm{I}} = \mu^{\ominus}_{\mathrm{I}G} + k_B T \log P_{\mathrm{I}}, \tag{20.47}$$

$$\mu^{\ominus}_{\mathrm{II}G} + k_B T \log P_{\mathrm{II}0} + k_B T \log x_{\mathrm{II}} = \mu^{\ominus}_{\mathrm{II}G} + k_B T \log P_{\mathrm{II}}. \tag{20.48}$$

Consequently, we have arrived at *Raoult's law*:

$$P_{\mathrm{I}} = x_{\mathrm{I}} P_{\mathrm{I}0}, \;\; P_{\mathrm{II}} = x_{\mathrm{II}} P_{\mathrm{II}0}. \tag{20.49}$$

That is, the partial vapor pressure of a component is identical to its pure vapor pressure × its mole fraction in the solution.[333]

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[332] Here, pressures measured in a particular unit (in atm) appears as it is in the logarithm, so you must respect the unit when you use the formulas.

[333] François-Marie Raoult (1830-1901). He also pointed out the melting point depression for the first time (1878). This was a key to demonstrating that electrolytes indeed dissociate.

If we combine this and Dalton's law of partial pressure, we may conclude that the amount of a gas dissolved in a solvent is proportional to the gas pressure (*Henry's law*).[334]

20.14 Osmotic pressure

The osmotic pressure π is the required 'extra' pressure to prevent flowing in of solvent molecules through the semipermeable membrane that blocks solute molecules (see Fig. 20.5). That is, the pressure of the solution side must be increased as $P \to P+\pi$. This result is, as we have already seen, an important ingredient of Einstein's theory of the Brownian motion[335] **7.10**.

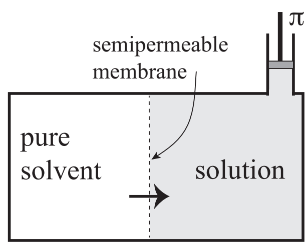

Figure 20.5: The horizontal arrow indicates the tendency of solvent molecules to invade.

Since both sides of the membrane must have the same chemical potentials for the solvent molecules, because they can go through the membrane (see (20.39)):

$$\mu_{\text{solv}}(P+\pi, T) = \mu_0(P+\pi, T) + k_B T \log(1-x) = \mu_0(P, T), \tag{20.50}$$

so

$$-\mu_0(P+\pi, T) + \mu_0(P, T) = k_B T \log(1-x) \simeq -k_B T x. \tag{20.51}$$

As we have already seen in the above $d\mu = (V/N)dP$ under constant temperature, so the above equation reads (Taylor expansion!)

$$-(V/N)\pi = -k_B T(n/N) \Rightarrow \pi V = n k_B T. \tag{20.52}$$

---

[334]William Henry (1774-1836). The law was published in 1803. [1803: William Symington demonstrates his Charlotte Dundas, the "first practical steamboat", in Scotland; Beethoven: Symphony No. 3 "Eroica" (Thielemann, VPO)]

[335]There we wished to know the force acting on the solute molecules (suspended particles). We can relate the osmotic pressure and this force as follows.

Suppose the pressure is in balance when a mere piston is placed between the solution and the pure solvent. Now, we replace the piston with a rigid membrane that blocks only solute molecules. This means the force (pressure) due to the solute particles is sustained by the membrane. Thus, the pressure contributed by the solvent to the outside of the solution is reduced by this pressure which is equal to π, allowing the solvent molecules to flow in from the pure solvent side. That is, the force corresponding to π is acting on the solute molecules.

This is called *van't Hoff's law*, which Einstein used in his Brownian motion theory (actually, he derived this equation by himself).

20.15 Colligative properties

A very similar question is the melting-point depression or the boiling point elevation due to solute (see Discussion 10).

Raoult's law, van't Hoff's law, Henry's law, boiling-point elevation, melting-point depression, etc. are all independent of the chemical nature of the solute and are due to the $\log(1-x)$ or $\log x$ term in the chemical potential (i.e., only due to the particle number ratio), so we may understand them in a unified fashion. Therefore, these phenomena are traditionally said to exhibit the *colligative*[336] *properties*.

20.16 Chemical reactions

Here, an elementary exposition of equilibrium chemical reactions is given. Without (irreversible) chemical reactions no atomism was possible. Furthermore, the idea of detailed balance originated from chemical reactions. Also to understand chemical reactions is becoming increasingly important even for physicists because we living organisms are chemical machines.

Since the general formulas may be cumbersome, in this lecture, we use the following reaction to illustrate the general formulas:

$$\mathrm{N_2} + 3\mathrm{H_2} \leftrightarrow 2\mathrm{NH_3}. \tag{20.53}$$

This formula implies that one molecule (or one mole of nitrogen reacts with 3 molecules (or 3 moles) of hydrogen to produce two molecules (or 2 moles) of ammonia. This does not mean that four molecules react at once; it is a summary of an appropriate set of elementary reactions.[337]

The left hand side of (20.53) is called the *original system* (or *reactant system*) and the right hand side the *product system*. The coefficients 2, 3 and (not explicitly written) 1 (for nitrogen) are called *stoichiometric coefficients*.

If we use the *sign convention* that the stoichiometric coefficients for the product system are all positive, and those for the original system all negative, we may write the reaction in an algebraic form

$$-\,\mathrm{N_2} - 3\mathrm{H_2} + 2\mathrm{NH_3} = 0. \tag{20.54}$$

[336] ligated together

[337] As the actual *elementary reactions* in the gas phase, such a reaction as (20.53) is very unusual, because elementary reactions are unimolecular decay or binary collision type reactions.

Thus, generally any reaction may be written as

$$\sum \nu_i C_i = 0, \tag{20.55}$$

where ν_i are *signed stoichiometric coefficients* for chemical C_i; $\nu_i > 0$ (resp., $\nu_i < 0$) implies i is a product (resp., a reactant).

20.17 Activity of chemical

For a gas mixture with the partial pressure P_i of chemical i, we may write its chemical potential per mole[338] as

$$\mu_i = \mu_i^{\ominus} + RT \log P_i. \tag{20.56}$$

Here, $\mu_i^{\ominus}$ is the chemical potential for, e.g., $P_i = 1$ (in, say, MPa, atm, etc.[339]). In solutions the chemical potential of a solute i in a solution is written as

$$\mu_i = \mu_i^{\ominus}(T, P) + RT \log a_i, \tag{20.57}$$

where a_i is called the *activity* of chemical i, which is close to the mole fraction x_i when the solution is dilute.

20.18 Equilibrium condition for reactions: the law of mass action

The equilibrium condition for the reaction (20.55) reads

$$0 = \sum_i \nu_i \mu_i = \sum_i \nu_i \left[\mu_i^{\ominus}(T, P) + RT \log a_i\right]. \tag{20.58}$$

Or, (assuming the constant TP condition)

$$-\Delta G^{\ominus} \equiv -\sum_i \nu_i \mu_i^{\ominus}(T, P) = RT \log \left(\prod_i a_i^{\nu_i}\right). \tag{20.59}$$

The left hand side does not depend on the chemical composition of the system, so we introduce the *chemical equilibrium constant* $K(T, P)$ according to

$$K(T, P) = e^{-\Delta G^{\ominus}/RT} = \frac{\cdots a_p^{\nu_p} \cdots}{\cdots a_r^{-\nu_r} \cdots}, \tag{20.60}$$

[338] Up to this point we studied everything per molecule, so k_B appeared in the expression of chemical potentials, but in the chemical reaction part of this lecture, the chemical potentials per mole will be used, so k_B is everywhere replaced with R.

[339] Since a dimensional quantity appears in the logarithm, when you use such formulas, you must stick to the unit being used.

where the numerator have all the products, and the denominator all the reactants. (20.60) is called the *law of mass action*. Note that all the exponents in the above formula are positive. Large K implies that the reaction favors the product system in equilibrium (the reaction shifts to the right). The equilibrium constant for the reaction (20.53) is given by

$$K(T,P) = \frac{[\mathrm{NH_3}]^2}{[\mathrm{N_2}][\mathrm{H_2}]^3}. \tag{20.61}$$

Here, $[X]$ generally describes the partial pressure (fugacity) of chemical X in the gas phase reaction or the molarity or mole fraction (or activity) in the solution.

In principle, the chemical equilibrium constant may be statistical-mechanically computed. However, except for ideal gasses, it is prohibitively hard to compute the needed chemical potentials, so, for almost all interesting examples of chemical reactions, theoretical calculations are useless.

20.19 Shift of chemical equilibrium

If we differentiate the equilibrium constant with respect to T, we can obtain the *heat of reaction*, that is, ΔH (enthalpy change) due to reaction. The Gibbs-Helmholtz relation **13.16** (or its analog for the Gibbs free energy) tells us

$$\left.\frac{\partial \log K}{\partial T}\right|_P = \frac{\Delta H^\ominus}{RT^2}, \tag{20.62}$$

where $\Delta H^\ominus$ is the enthalpy change for the 'standard state.' This is called *van't Hoff's equation*. Similarly,

$$\left.\frac{\partial \log K}{\partial P}\right|_T = -\frac{\Delta V^\ominus}{RT}, \tag{20.63}$$

where $\Delta V^\ominus$ is the volume change due to reaction for the 'standard state'. In reactions the change Δ always implies (product system) − (original system).

(20.62) tells us that if the reaction is exothermic (exoergic, i.e., $\Delta H^\ominus < 0$), then increasing the temperature shifts the reaction to reduce the heat generation (i.e., K decreases and the reaction tends to shift back from the product system to the original reactant system). This is an example of *Le Chatelier's principle* (Lecture 17) asserting that "the response to a perturbation is in the direction to reduce its effect." (20.63) is also its example. Needless to say, these are manifestations of the stability of our world.

Q20.1 [Gibbs relation for densities]
Show that the Gibbs relation for densities (extensive quantities per volume): $e = E/V$ (internal energy density), $s = S/V$ (entropy density), $n = N/V$ (number density), $\overline{x} = X/V$, etc. reads

$$de = Tds + \mu dn + xd\overline{x}. \tag{20.64}$$

Solution.

From (20.9), we get

$$e = Ts - P + \mu n + x\overline{x}. \tag{20.65}$$

On the hand, dividing the Gibbs-Duhem relation (20.11) with V, we get

$$sdT - dP + nd\mu + \overline{x}dx = 0 \tag{20.66}$$

Therefore, differentiating (20.65) and using (20.66), we get

$$de = Tds + \mu dn + xd\overline{x}. \tag{20.67}$$

How about the Gibbs relation per unit mass or per mole?

Q20.2 [Impurity effect]
Let us continue the lattice gas example to understand the effect of impurities on the phase transition temperatures.

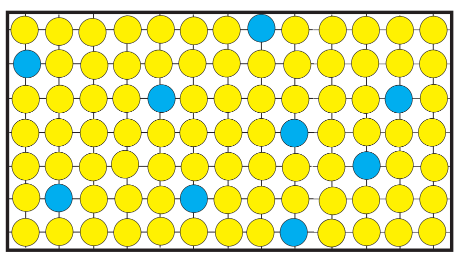

Figure 20.6: Lattice gas model we already discussed.

We know the chemical potential of the solvent molecules (majority) reads

$$\mu_L = \mu_L^{\ominus} + k_B T \log(1 - x). \tag{20.68}$$

Here, x is the mole fraction of the solute molecules (blue particles in Fig. 20.6) the solution. $\mu_L^{\ominus}$ is the chemical potential of the pure solvent liquid. Let us write the chemical potential of the pure solid phase of the solvent as $\mu_S^{\ominus}$.
(1) If we cool the solution, a solid phase of the solvent molecules emerges. When solidification occurs, impurity molecules (i.e., solute molecules) are largely excluded from the emerging solid. Let us idealize (not a bad approximation) the solid phase to be pure. Let T_m be the melting point of the pure substance. This implies

$$\mu_L^{\ominus}(T_m, P) = \mu_S^{\ominus}(T_m, P). \tag{20.69}$$

What is the equilibrium coexistence temperature of the pure solid and the solution with a mole fraction x of impurity molecules? You have only to compute the melting temperature shift ΔT to order x. Assume that the latent heat of melting is L (per molecule).
(2) We may assume that the vapor of the solvent at T may be approximated as an ideal gas. At T its pressure is P. Now, we add the solute molecules as impurity to this solvent. You may assume that the solute molecules cannot escape the liquid phase, so the vapor phase still consists of pure solvent molecules. What is the pressure change ΔP due to the addition of the mole fraction x of the impurity molecules?
(3) You must have obtained $\Delta P/P = -x$ from (2), assuming the gas volume is much larger than the liquid volume so the latter may be ignored. $|\Delta P|$ is 2850 Pa, when 23.3 g of a substance is solved in 100 g of water at 100 °C. What is the molecular weight of this substance?

Solution.
(1) Let us assume that at temperature $T_m + \Delta T$ the equilibrium between the solvent crystal and the solution holds:

$$\mu_S^\ominus(T_m + \Delta T, P) = \mu_L^\ominus(T_m + \Delta T, P) + k_B(T_m = \Delta T)\log(1 - x). \tag{20.70}$$

That is, to order x, we may Taylor-expand the above condition as

$$\frac{\partial[\mu_S^\ominus(T_m, P) - \mu_L^\ominus(T_m, P)]}{\partial T_m}\Delta T = -k_B T_m x \tag{20.71}$$

Denoting extensive quantities per molecule with lower case letters corresponding to the standard notation, Gibbs' relation gives $d\mu = -sdT + vdP$, so the above equation reads (the 'pure sign' $\ominus$ is omitted)

$$[s_L(T_m, P) - s_S(T_m, P)]\Delta T = -k_B T_m x \tag{20.72}$$

From the latent heat L

$$s_L(T_m, P) - s_S(T_m, P) = L/T_m \tag{20.73}$$

Thus, we have reached

$$\Delta T = -\frac{k_B T_m^2}{L} x < 0 \tag{20.74}$$

That is, the melting point is lowered by the amount proportional to the impurity concentration. This is called the *melting-point depression*.
(2) Let us denote the ideal gas chemical potential as $\mu_G(T, P)$. From the general form, we may write

$$\mu_G(T, P) = \mu_G^\ominus(T) + k_B T \log P. \tag{20.75}$$

Therefore, the equilibrium between the pure solvent and its vapor requires at pressure P

$$\mu_L^\ominus(T, P) = \mu_G^\ominus(T) + k_B T \log P, \tag{20.76}$$

and the equilibrium between the solution and its vapor requires at pressure $P + \Delta P$

$$\mu_L^{\ominus}(T, P + \Delta P) + k_B T \log(1 - x) = \mu_G^{\ominus}(T) + k_B T \log(P + \Delta P). \tag{20.77}$$

Subtracting (20.76) from (20.77), we obtain

$$\mu_L^{\ominus}(T, P + \Delta P) - \mu_L^{\ominus}(T, P) + k_B T \log(1 - x) = k_B T \log(1 + \Delta P/P). \tag{20.78}$$

Taylor-expanding this to order x, we get

$$\left.\frac{\partial \mu_L}{\partial P}\right|_T \Delta P - k_B T x = \frac{k_B T}{P} \Delta P. \tag{20.79}$$

The partial derivative here gives the volume (per molecule) of the solvent liquid, which may be neglected relative to the gas volume $k_B T/P$. After this approximation we get the famous equation

$$\Delta P = -xP. \tag{20.80}$$

(3) Let M be the molecular weight of the solute. Then, since the ambient pressure is 1 atm (as seen from the boiling point of the water)

$$x = \frac{23.3/M}{100/18 + 23.3/M} = \frac{|\Delta P|}{P} \tag{20.81}$$

or

$$\frac{23.3}{M} = \frac{(100/18)|\Delta P|/P}{1 - |\Delta P|/P} \simeq \frac{100}{18} \frac{|\Delta P|}{P} = \frac{100}{18} \frac{2850}{1.013 \times 10^5}. \tag{20.82}$$

Hence, $M \simeq 149$.

Q20.3 [Chemical equilibria]
Let us consider the reaction to synthesize ammonia:

$$N_2 + 3H_2 \longrightarrow 2NH_3. \tag{20.83}$$

Its equilibrium constant may be written in terms of partial pressures as

$$K = \frac{P_{NH_3}^2}{P_{N_2} P_{H_2}^3} = 1.5 \times 10^{-5}, \tag{20.84}$$

if the (partial) pressures are in atm (at 500 °C).
(1) If you wish to synthesize ammonia, is it more or less advantageous to increase the total pressure of the reaction vessel? You must justify your answer (perhaps quoting the relevant equation(s)).
(2) Suppose the atomic ratio of N and H is 1:3 (i.e., the stoichiometric ratio). If 90%

of reactants are converted into ammonia in equilibrium, what is the total pressure P of the mixture? You may treat the gases as ideal gases.

Solution.

(1) This is le Chatelier. Since the volume decreases if the reaction proceeds, increasing pressure should shift the reaction to the ammonia side. Or more precisely, we use

$$\left.\frac{\partial \log K}{\partial P}\right|_T = -\frac{\Delta V}{RT}, \tag{20.85}$$

where ΔV is the volume change due to the reaction. In this case it is negative, so increasing P increases K, that is, the reaction shifts two the right.

(2) We need the final mole fractions of the chemicals. If $100x\%$ of N_2 has been converted into ammonia and there was 1 mole of nitrogen gas, the total number of molecules in moles is

$$1 - x + 3(1 - x) + 2x = 4 - 2x. \tag{20.86}$$

Therefore, the partial pressures after equilibration read

$$P_{N_2} = P\frac{1-x}{4-2x}, P^3_{H_2} = P\frac{3-3x}{4-2x}, P^2_{NH_3} = P\frac{2x}{4-2x}. \tag{20.87}$$

Hence,

$$K = \frac{[2x/(4-2x)]^2}{P^2[(1-x)/(4-2x)][(3-3x)/(4-2x)]^3} = \frac{16x^2(2-x)^2}{27P^2(1-x)^4} \tag{20.88}$$

For $x = 0.9$

$$P^2 = 5808/K = 3.87 \times 10^8, \tag{20.89}$$

$P = 1.97 \times 10^4$ atm.

21 Grand canonical ensemble and ideal quantum systems

Summary
$*$ Grand canonical partition function/ensemble is introduced.
$*$ Noninteracting quantum systems are discussed with the aid of grand partition function.
$*$ Pressures of fermions and bosons are compared.
$*$ $PV = 2E/3$ for 'any' ideal gas.

Key words
grand canonical partition function, grand canonical ensemble, fermion, boson, Bose-Einstein distribution, Fermi-Dirac distribution

What you should be able to do
$*$ Be able to explain why PV is directly obtained from the grand canonical partition function.
$*$ Intuitively understand low temperature noninteracting fermion and boson systems.
$*$ In particular, compare the pressures of boson and fermion systems intuitively.
$*$ Be able to derive the one particle density of states $D_t(\varepsilon)$. Note $D_t \propto \sqrt{\varepsilon}$.

21.1 Grand canonical ensemble/partition function: motivation

We now introduce another ensemble. We know microcanonical, canonical, and generalized canonical ensembles (e.g., pressure ensembles). The fourth law **9.5** tells us

$$A = E - TS = -PV + \mu N. \tag{21.1}$$

Can you directly derive this, following the logic used in Lecture 20 to demonstrate the Gibbs-Duhem relation (i.e., mimic the fine letters in **20.5**)? Therefore, (21.1) implies

$$PV = -A + \mu N = ST - E + \mu N, \tag{21.2}$$

That is,

$$\frac{PV}{T} = S - \frac{E}{T} + \frac{\mu}{T}N. \tag{21.3}$$

This is a Legendre transformation of entropy, so there must be an ensemble that directly gives PV/T or PV/k_BT.

Compare the following formulas:

$$S = k_B \log w(E, V, X), \tag{21.4}$$

$$-\frac{A}{T} = S - \frac{E}{T} \quad = \quad k_B \log Z(T, V, X). \tag{21.5}$$

We know with the aid of Boltzmann's principle

$$Z(T, V, X) = \int dE\, w(E, V, X) e^{-E/k_B T} = \int dE\, e^{[S(E) - E/T]/k_B}. \tag{21.6}$$

Thus, we can easily mimic this to get

$$\frac{PV}{T} = S - \frac{E - \mu N}{T} = k_B \log \Xi(T, V, \mu) \tag{21.7}$$

with

$$\Xi(T, V, \mu) = \int dE \sum_N w(E, V, N) e^{-(E - \mu N)/k_B T} = \sum_{N=0}^{\infty} Z(T, V, N) e^{\beta \mu N}. \tag{21.8}$$

Ξ is called the *grand (canonical) partition function*, which describes the system thermostatted and chemostatted with a reservoir at temperature T and chemical potential μ. Recall that μ is the needed work to push one molecule into the system, so by adjusting μ you can regulate the average number of particles in the system. If a system is macroscopic, the fluctuation of the total number of particles is irrelevant, so you may use μ to control N.

21.2 Grand canonical ensemble/partition function: summary

Let us summarize:

$$\frac{PV}{T} = -\frac{A}{T} + \frac{\mu N}{T} = k_B \log \Xi(T, V, \mu) \tag{21.9}$$

with

$$\Xi(T, V, \mu) = \sum_{N=0}^{\infty} Z(T, V, N) e^{\beta \mu N} = \sum_{\text{microstates}} e^{\beta(H - \mu N)}, \tag{21.10}$$

where the summation over 'microstates' means all the possible microstates allowed to the system irrespective of the total number of particles in the system.

The ensemble equivalence holds here as well: If $N \gg \log N$, then you can use any ensemble you wish. For example, if you have about a few thousand particles confined in a trap, you may use the grand canonical formalism above to describe the system.

The Gibbs relation reads

$$d\left(\frac{PV}{T}\right) = -Ed\frac{1}{T} + \frac{P}{T}dV + Nd\frac{\mu}{T}. \tag{21.11}$$

This has a (statistical-mechanically) more convenient form:

$$d \log \Xi = -Ed\beta + \beta P dV + N d(\beta \mu). \tag{21.12}$$

21.3 Example: adsorption

Let us solve an example problem (which is made deliberately slightly complicated) to become familiar with the use of chemical potentials and the grand canonical formalism. Suppose there is a gas mixture consisting of two distinct molecular species A and B. The mixture is an ideal gas and the partial pressure of X is P_X ($X = A$ or B). The gas is in equilibrium with an adsorbing metal surface on which there are N adsorption sites. Molecule X adsorbed at a site is with energy ε_X (which is often negative) relative to the one in the gas phase, where $X = A$ or B. Each surface site can accommodate at most one A molecule, and at most two B molecules. One adsorbed A atom has 2 different (internal) states (with the same energy), and one adsorbed B molecule has 1 state, but if two B molecules are adsorbed to the same site, then they can together have 5 states with the same energy (the caption of Fig. 21.1 summarizes the system). We wish to know the surface concentration of the atoms when the surface is in equilibrium with the gas mixture. You may assume the gas phase is huge, so you need not worry about its composition change due to adsorption. That is, the gas phase is a chemical reservoir.

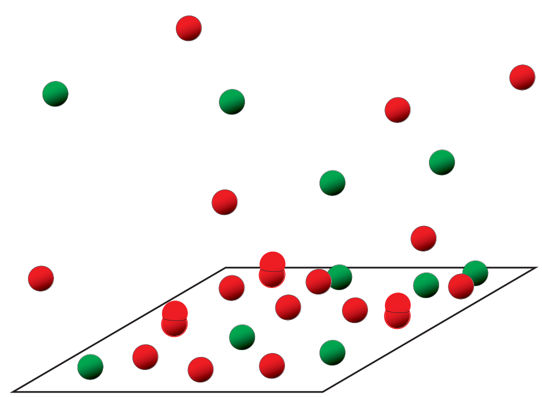

Figure 21.1: Adsorption of gas particles on a metal surface: A: green (2 internal states when adsorbed), B: red (if singly adsorbed, with single internal state; if doubly adsorbed, with 5 internal states).

We wish to know the average number of A and B atoms on the metal surface.

Since we do not know how many particles are on the surface, it must be convenient to use the grand canonical ensemble. Assuming the chemical potentials of A and B as μ_A and μ_B, respectively, write down the partition function of the metal surface:

$$\Xi = \left[1 + 2e^{-\beta(\varepsilon_A - \mu_A)} + e^{-\beta(\varepsilon_B - \mu_B)} + 5e^{-2\beta(\varepsilon_B - \mu_B)}\right]^N . \tag{21.13}$$

The needed chemical potentials can be computed with the aid of the ideal gas statistical mechanics as we did in the preceding lecture. We have done that calculation, so let us copy the needed results:

$$\mu_A = k_BT \log(\beta P_A/n_{QA}), \;\; \mu_B = k_BT \log(\beta P_B/n_{QB}). \tag{21.14}$$

Here, n_{QX} is the 'quantum density' depending on T and the mass (see above (20.32)), and $P_{QX} = n_{QX} k_B T$ may be called the 'quantum pressure.' We know (we ignore the volume (or the area) change)

$$d \log \Xi = -E d\beta + N_A d(\beta\mu_A) + N_B d(\beta\mu_B), \tag{21.15}$$

so we obtain

$$N_A = N \frac{2e^{-\beta(\varepsilon_A - \mu_A)}}{1 + 2e^{-\beta(\varepsilon_A - \mu_A)} + e^{-\beta(\varepsilon_B - \mu_B)} + 5e^{-2\beta(\varepsilon_B - \mu_B)}} \tag{21.16}$$

and

$$N_B = N \frac{e^{-\beta(\varepsilon_B - \mu_B)} + 10e^{-2\beta(\varepsilon_B - \mu_B)}}{1 + 2e^{-\beta(\varepsilon_A - \mu_A)} + e^{-\beta(\varepsilon_B - \mu_B)} + 5e^{-2\beta(\varepsilon_B - \mu_B)}}. \tag{21.17}$$

21.4 Microstates for non-interacting indistinguishable particle systems

Let us consider a system consisting of non-interacting particles. Suppose the states of a single particle are numbered as $i = 1, 2, \cdots$. If we assume that all the particles are indistinguishable, then to specify a microstate of a system consisting of such particles, we have only to count the number n_i of particles in the i-th one particle state (n_i is also called the *occupation number* of the ith one particle state; do NOT confuse the microstates of the whole system and the one particle states). Or, we have only to make a table of the occupation numbers $\{n_1, n_2, \cdots\}$; we may identify this table and the microstate.

To study the thermodynamics of such a system, we should use the grand canonical ensemble, because we have not specified the total number of particles.

21.5 Grand partition function of indistinguishable particle system

Let ε_i be the energy of the i-th one particle state. The total energy $\mathcal{E}$ and the total number of particles N of the microstate $\{n_1, n_2, \cdots\}$ can be written as

$$\mathcal{E} = \sum_{i=1} \varepsilon_i n_i, \tag{21.18}$$

and

$$N = \sum_{i=1} n_i. \tag{21.19}$$

Then, the grand canonical partition function must be

$$\Xi(\beta, \mu) = \sum_{n_1, n_2, \cdots} \mathrm{e}^{-\beta\mathcal{E} + \beta\mu N}. \tag{21.20}$$

Using the microscopic descriptions of $\mathcal{E}$ and N ((21.18) and (21.19)), we can rearrange the summation as

$$\Xi = \prod_i \Xi_i, \tag{21.21}$$

where

$$\Xi_i \equiv \sum_{n_i} \exp[-\beta(\varepsilon_i - \mu)n_i]. \tag{21.22}$$

This quantity may be called the grand canonical partition function for the ith one particle state.

21.6 Bosons and fermions

In the world it seems that there are only two kinds of particles:

bosons: there is no upper bound for the occupation number of a single one-particle state;

fermions: the occupation number of a single one-particle state can be at most 1 (the Pauli exclusion principle).

This is an empirical fact. Electrons, protons, ^{3}He, etc., are fermions. Mesons, ^{4}He, D, etc., are bosons.

There is the so-called *spin-statistics relation* that the particles with half odd integer spins are fermions, and those with integer spins are bosons. The rule applies also to compound particles such as hydrogen atoms. Thus, H and T are bosons, but their nuclei are fermions. D and ^{3}He are fermions. ^{4}He is a boson, and so is its nucleus.

For a neutral system consisting of $+$ and $-$ charged particles (e.g., the usual electron-nucleus system) it is proved that at least $+$ or $-$ species must be all fermions for the system to be stable. Here, 'stable' means that there is a positive number B such that the system energy E satisfies $E > -NB$, where N is the number of particles in the system. That is, for the world to be stable, we desperately need fermions.

21.7 Ideal boson systems

For bosons, any number of particles can occupy the same one particle state, so the occupation number of a particular one particle state can be any of 0, 1, 2, $\cdots$. Therefore,

$$\Xi_i = \sum_{n=0}^{\infty} \mathrm{e}^{-\beta(\varepsilon_i - \mu)n} = \left(1 - \mathrm{e}^{-\beta(\varepsilon_i - \mu)}\right)^{-1}. \tag{21.23}$$

The mean occupation number of the i-th state is given by

$$\langle n_i \rangle = \sum_{n=0}^{\infty} n_i \mathrm{e}^{-\beta(\varepsilon_i - \mu)n} / \Xi_i, \tag{21.24}$$

so we conclude

$$\langle n_i \rangle = \left.\frac{\partial \log \Xi_i}{\partial \beta\mu}\right|_{\beta} = k_B T \left.\frac{\partial \log \Xi_i}{\partial \mu}\right|_{T} = \frac{1}{\mathrm{e}^{\beta(\varepsilon_i - \mu)} - 1}. \tag{21.25}$$

This distribution is called the *Bose-Einstein distribution*.

If the (one-particle) ground-state energy is zero, then the ground state occupancy is

$$\langle n_{\text{ground}} \rangle = \frac{1}{e^{-\beta\mu} - 1}, \tag{21.26}$$

but this should not be negative, so $\mu \leq 0$. That is, notice that the chemical potential must be *smaller* than the (one-particle) ground state energy to maintain the positivity of the average occupation number.

21.8 Ideal fermion systems

For fermions, at most one particle can occupy the same one particle state, the occupation number of a particular one particle state is 0 or 1. Therefore,

$$\Xi_i = \sum_{n=0}^{1} \mathrm{e}^{-\beta(\varepsilon_i - \mu)n} = 1 + \mathrm{e}^{-\beta(\varepsilon_i - \mu)}. \tag{21.27}$$

The mean occupation number of the i-th state is given by

$$\langle n_i \rangle = \sum_{n=0}^{1} n_i \mathrm{e}^{-\beta(\varepsilon_i - \mu)n} / \Xi_i, \tag{21.28}$$

so we conclude

$$\langle n_i \rangle = \left.\frac{\partial \log \Xi_i}{\partial \beta\mu}\right|_{\beta} = k_B T \left.\frac{\partial \log \Xi_i}{\partial \mu}\right|_{T} = \frac{1}{\mathrm{e}^{\beta(\varepsilon_i - \mu)} + 1}. \tag{21.29}$$

This distribution is called the *Fermi-Dirac distribution*.

Notice that usually the ground state energy is chosen as the origin of energy, so

$$\langle n_{\text{ground}} \rangle = \frac{1}{e^{-\beta\mu} + 1}. \tag{21.30}$$

It is important to recognize the qualitative features of this Fermi-Dirac distribution function (see Fig. 21.2). The distribution has a cliff of width of order $k_B T$. In the $T \to 0$ limit, it has a vertical cliff at $\varepsilon = \mu$, which is called the *Fermi level*.[340] Notice that $\mu > 0$ is required, if the temperature is low enough.

[340] Do not forget that μ for a fixed N is temperature dependent. The energy of the highest occupied state at $T = 0$ is called the *Fermi energy*.

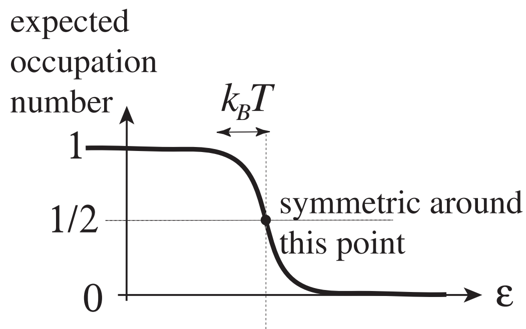

Figure 21.2: The cliff has a width of order k_BT. μ is called the *Fermi level*. The symmetry noted in the figure is the so-called *particle-hole symmetry*

21.9 Classical limit

The distribution functions of the occupation numbers are quite different from the classical distribution function obtained by Maxwell and Boltzmann. The difference should be due to the quantum interference among particles (or particle wave functions) when the number density is not low. Therefore, in order to obtain the classical limit, we must take the occupation number 0 limit to avoid quantum interference among particles. The chemical potential μ is a measure of the "strength" of the chemostat to push particles into the system. Thus, we must make the chemical potential extremely small: $\mu \searrow -\infty$.

In this limit both Bose-Einstein (21.26) and Fermi-Dirac distributions (21.30) reduce to the Maxwell-Boltzmann distribution as expected:

$$\langle n_i \rangle \to \mathcal{N} \mathrm{e}^{-\beta\varepsilon_i}, \tag{21.31}$$

where $\mathcal{N} = e^{\beta\mu}$ is the normalization constant determined by the total number of particles in the system.

Notice that $\mu \to -\infty$ is far away from the situations where quantum effects are important; $\mu \simeq 0$ for bosons and $\mu > 0$ for fermions.

21.10 Intuitive pictures

Before going to the equations of state, let us try to build our intuition. Suppose there are only three one-particle states with energies 0, ε and 3ε, and there are three particles. Make a table of all the microstates of the three-particle system for bosons and for fermions.

Fermions first:

microstate	0	ε	3ε	total energy
1	1	1	1	4ε

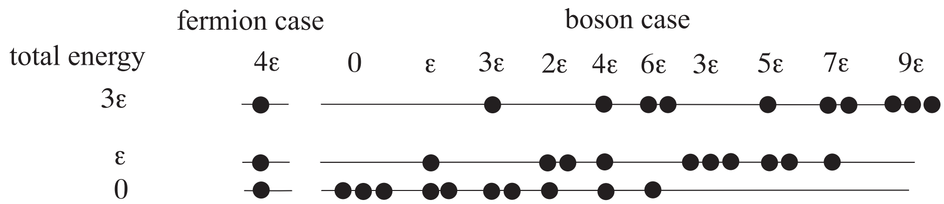

Figure 21.3: identical particles in three one particle states; fermion (leftmost) and boson cases.

Bosons:

microstate	0	ε	3ε	total energy
1	3	0	0	0
2	2	1	0	ε
3	2	0	1	3ε
4	1	2	0	2ε
5	1	1	1	4ε
6	1	0	2	6ε
7	0	3	0	3ε
8	0	2	1	5ε
9	0	1	2	7ε
10	0	0	3	9ε

Suppose there are 100 identical spinless[341] bosons or fermions whose s-th one-particle state has an energy $\varepsilon_s = s\varepsilon$ ($s \in \boldsymbol{N}$). These particles do not interact. For the boson case, at $T = 0$ all the particles are in the lowest energy one-particle state (see Fig. 21.4). For fermions, all the low-lying one particle states are completely filled up to some energy level that corresponds to μ. Notice that the ground state energy of the fermion and boson systems are quite different.

The low-lying excited microstates are also in Fig. 21.4 (right). For the boson case all the particles have equal chance to be excited, but in the case of fermions, only the particles near the Fermi level can be excited (and excited particles leave *holes*). This should tell you something about the specific heat of these systems (later).

21.11 Pressure of ideal systems

The distinction between fermions and bosons show up clearly in pressure:

$$\frac{PV}{k_B T} = \log \Xi = \mp \sum_i \log\left(1 \mp e^{-\beta(\varepsilon_i - \mu)}\right). \tag{21.32}$$

If T, V, μ are the same, then the pressure of the system consisting of the particles with the same single-particle energy states (i.e., the the same density of states) shows the following ordering (BE = Bose-Einstein, MB = Maxwell-Boltzmann, FD

[341]'Spinless' implies that these particles do not have any internal degrees of freedom.

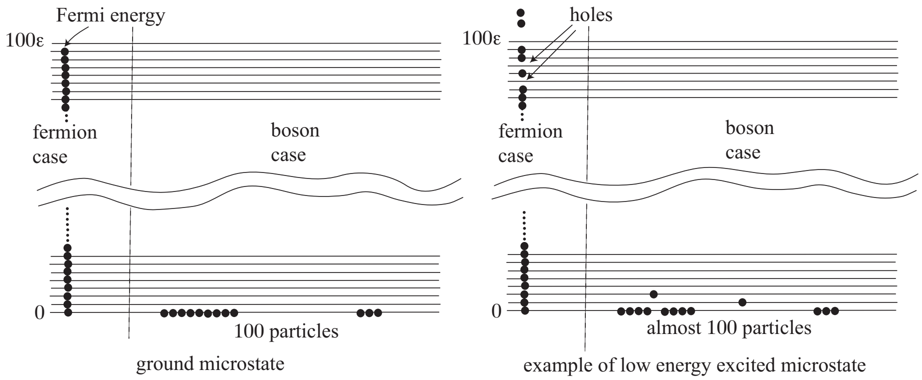

Figure 21.4: Ground states and low-lying excited levels for fermions (left in each panel) and bosons (right). Do not confuse one particle states and microstates. Here, the lowest energy (ground state) microstate is described on the left, and one example of low-energy excited microstate is illustrated on the right.

= Fermi-Dirac):

$$P_{BE} > P_{MB} > P_{FD}. \tag{21.33}$$

To see $P_{BE} > P_{FD}$ we use (21.32). Let $x = e^{-\beta(\varepsilon_i - \mu)}$ and we compare $-\log(1-x)$ and $\log(1+x)$ (see Fig. 21.5). This figure must be enough. This is also easily seen from $1/(1-x) = 1 + x + x^2 + \cdots > 1 + x$ for $x \in (0, 1)$.

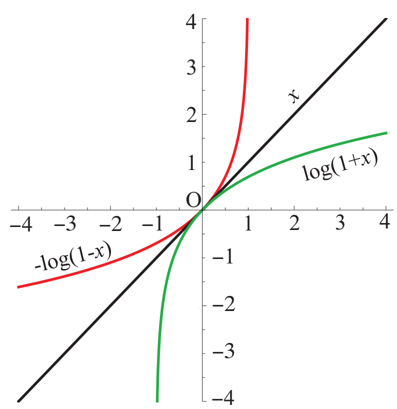

Figure 21.5: $\log(1+x)$ is always below x. Now, $-\log(1-x)$ is obtained from $\log(1+x)$ by making mirror images $x \to -x$ and then $y \to -y$. Obviously, $x < -\log(1-x)$.

21.12 Pressure under constant N (the usual case)

In contrast, if T, V, N are the same (the usually more interesting case than the above case), then (usually $P_{FD} \gg P_{MB}$)

$$P_{FD} > P_{MB} > P_{BE}. \tag{21.34}$$

To show this requires some trick, so a formal demonstration is below with fine letters, but intuitively this can be understood by the extent of effective particle-particle attraction as is illustrated in Fig. 21.6. The figure not only suggests the pressures, but also suggests the extent of particle density fluctuations. The particle density fluctuations in a boson system are larger than those in a fermion system.

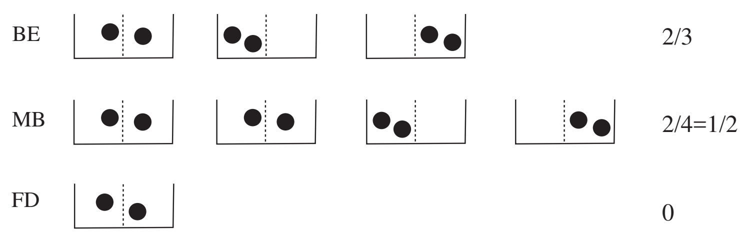

Figure 21.6: Two-particle two box illustration of statistics. The fractions in the right denote the relative weights of the states for which effective attraction can be seen. (BE = Bose-Einstein, MB = Maxwell-Boltzmann, FD = Fermi-Dirac)

As seen from the 'effective attraction weights' in the above figure, the fermion system exhibits the largest pressure; fermions avoid each other (Pauli's exclusion principle), so they hit the wall more often

(21.34) may be demonstrated as follows: Classically, $PV = Nk_BT$, so we wish to demonstrate (N and $\langle N \rangle$ need not be distinguished, since we consider macrosystems)

$$\log \Xi_{FD} > \langle N \rangle > \log \Xi_{BE}. \tag{21.35}$$

Let us see the first inequality:[342] Writing $x_j = e^{-\beta(\varepsilon_j - \mu)}$, we have

$$\log \Xi_{FD} - \langle N \rangle = \sum_j \left[\log(1 + x_j) - \frac{x_j}{1 + x_j} \right]. \tag{21.36}$$

We are done, because for $x > 0$[343]

$$\log(1 + x) - \frac{x}{1 + x} > 0. \tag{21.37}$$

Similarly, we can prove the second inequality in (21.35).

21.13 Universal *P*-*E* relation: introduction

Let $D(\varepsilon)d\varepsilon$ denote the number of single particle states whose energy is between ε and $\varepsilon + d\varepsilon$. $D(\varepsilon)$ is called the one-particle state density (or *density of states* of the one-particle system). If we know this, the pressure (21.32) can be rewritten as

$$PV = \mp k_BT \int d\varepsilon\, D(\varepsilon) \log \left(1 \mp e^{-\beta(\varepsilon - \mu)}\right). \tag{21.38}$$

[342] The reader might wonder why we cannot use Ξ_{MB} to demonstrate the formula; the reason is that μ in this grand partition function and that in Ξ_{FD} or Ξ_{BE} are distinct. Remember that we keep N; inevitably μ depends on statistics, so we cannot easily compare the Boltzmann factor $e^{\beta(\varepsilon-\mu)}$ in each term.

[343] Consider the derivatives.

In the present case $D(\varepsilon)$ is the density of states for a particle confined in a 3D box of volume V, which we will denote by $D_t(\varepsilon)$, where the suffix t implies the translational degrees of freedom.

We know for a classical ideal gas

$$PV = \frac{2}{3}E, \tag{21.39}$$

where E is the internal energy. 'Miraculously,' this is true for non-interacting fermions and bosons (and their mixtures as well). The formulas for PV and E are quite different from the classical case. Here,

$$E = \int d\varepsilon\, D_t(\varepsilon)\varepsilon\langle n(\varepsilon)\rangle = \int d\varepsilon\, D_t(\varepsilon)\frac{\varepsilon}{e^{\beta(\varepsilon-\mu)} \mp 1}. \tag{21.40}$$

21.14 Density of one-particle states

To demonstrate this, we need $D_t(\varepsilon)$. First, a quick way is explained to derive the formula appropriate for a statistical mechanics course. We count the number of microscopic states for a single particle up to some energy ε. To do this we use the classical-quantum mechanics correspondence: the number of quantum states in the phase volume element $d\boldsymbol{p}d\boldsymbol{q}$ is given by $d\boldsymbol{p}d\boldsymbol{q}/h^3$. Then, the total number of quantum states for a single particle whose energy is less than or equal to ε must be give by

$$\frac{1}{h^3}\int_{\boldsymbol{q}\in V} d\boldsymbol{q}\int_{|\boldsymbol{p}|<\sqrt{2m\varepsilon}} d\boldsymbol{p} = \int_0^{\varepsilon} d\varepsilon\, D_t(\varepsilon), \tag{21.41}$$

that is,

$$\int_0^{\varepsilon} d\varepsilon\, D_t(\varepsilon) = \frac{4\pi}{h^3}V\int_0^{\sqrt{2m\varepsilon}} p^2 dp. \tag{21.42}$$

Differentiating this with ε, we get

$$D_t(\varepsilon) = \frac{4\pi}{h^3}V\frac{\sqrt{2m}}{2\sqrt{\varepsilon}}(\sqrt{2m\varepsilon})^2 = 2\pi V\left(\frac{2m}{h^2}\right)^{3/2}\varepsilon^{1/2}. \tag{21.43}$$

You can easily extend this approach to higher or lower dimensional spaces, and to the cases with other p-ε relations (dispersion relations). $D_t(\varepsilon) \propto \varepsilon^{1/2}$ is important (worth memorizing) for the case with $\varepsilon \propto p^2$ in 3-space.

That is, $D_t(\varepsilon) = \gamma V\varepsilon^{1/2}$, where $\gamma = 2\pi(2m/h^2)^{3/2}$ is a constant. This can be obtained by a dimensional analytical idea as well. $D_t(\varepsilon)h^3 d\varepsilon$ must have the dimension of the phase volume whose dimension is L^3 times [momentum]^3, so $D_t(\varepsilon)h^3 \propto$

$V\sqrt{\varepsilon}^3/\varepsilon = V\varepsilon^{1/2}$.

Note the following relation that can easily be seen from $\int \varepsilon^{1/2} d\varepsilon = (2/3)\varepsilon^{3/2} = (2\varepsilon/3)\varepsilon^{1/2}$

$$\int_0^\varepsilon d\varepsilon D_t(\varepsilon) = \frac{2}{3}\varepsilon D_t(\varepsilon). \tag{21.44}$$

21.15 Universal *P*-*E* relation: demonstration

Let us return to our problem. The pressure can be rewritten as (the fundamental theorem of calculus)

$$PV = \mp k_B T \int d\varepsilon \left[\int_0^\varepsilon d\varepsilon' D_t(\varepsilon')\right]' \log\left(1 \mp e^{-\beta(\varepsilon-\mu)}\right). \tag{21.45}$$

Performing an integration by parts, we get

$$PV = \mp k_B T \left[\int_0^\varepsilon d\varepsilon' D_t(\varepsilon') \log\left(1 \mp e^{-\beta(\varepsilon-\mu)}\right)\right]_0^\infty \pm k_B T \int d\varepsilon \, \left[\int_0^\varepsilon d\varepsilon' D_t(\varepsilon')\right] \frac{d}{d\varepsilon} \log\left(1 \mp e^{-\beta(\varepsilon-\mu)}\right). \tag{21.46}$$

The first term vanishes (you must check this[344*]), so ((21.44) will be used)

$$\begin{aligned} PV &= \pm k_B T \int d\varepsilon \, \left[\int_0^\varepsilon d\varepsilon' D_t(\varepsilon')\right] \frac{d}{d\varepsilon} \log\left(1 \mp e^{-\beta(\varepsilon-\mu)}\right) && (21.47)\\ &= \pm \frac{2}{3} k_B T \int d\varepsilon \, \varepsilon D_t(\varepsilon) \frac{d}{d\varepsilon} \log\left(1 \mp e^{-\beta(\varepsilon-\mu)}\right) && (21.48)\\ &= \pm \frac{2}{3} k_B T \int d\varepsilon \, \varepsilon D_t(\varepsilon) \frac{\pm \beta e^{-\beta(\varepsilon-\mu)}}{1 - \mp e^{-\beta(\varepsilon-\mu)}} && (21.49)\\ &= \frac{2}{3} \int d\varepsilon \, D_t(\varepsilon) \frac{\varepsilon}{e^{\beta(\varepsilon-\mu)} \mp 1} = \frac{2}{3} E. && (21.50) \end{aligned}$$

Now, a bomb making question. There is an isolated metal container of volume V and energy E with N fermions whose chemical potential is $\mu = 10$ eV. These fermions are adiabatically converted into bosons. Can we use this mechanism to make a bomb? Notice that since E and V are unchanged, the pressure does not change. [Hint: You must know 1 eV is roughly equivalent to 10^5 K.]

[344*] $\varepsilon \to 0$ for the boson case is only slightly tricky, but $\varepsilon^{1/2} \log \varepsilon \to 0$ saves the day.

Q21.1 [Langmuir isotherm]
In a big box is an ideal gas A whose mass is m per molecule. Inside the box is a surface with N absorption sites that can accommodate at most one A molecules per site. When one A is absorbed, its energy is $-\varepsilon$ ($\varepsilon > 0$, i.e., ε lower than the free state) and has z internal states with the same energy.

When the pressure of the box is P, and the temperature is T, what is the fraction θ of the surface occupied by A? Or, more concretely, find the factor X in the following formula

$$\theta = \frac{P}{P + P_Q/X}, \tag{21.51}$$

where $P_Q = n_Q k_B T$ with $n_Q = (2\pi m k_B T/h^2)^{3/2}$. The formula (21.51) is called the *Langmuir isotherm*.

Solution.
(1) We regard the gas phase as a chemical reservoir, whose chemical potential μ may be calculated (or found in the lecture notes) later. Under this chemical potential the grand canonical partition function of the absorbing surface can be written as

$$\Xi = \prod_{i=1}^{N} \Xi_i, \tag{21.52}$$

where Ξ_i is the 'grand canonical partition function for the ith absorption center.' We may write

$$\Xi_i = 1 + ze^{-\beta(-\varepsilon-\mu)} = 1 + ze^{\beta(\varepsilon+\mu)}. \tag{21.53}$$

The expectation value of the total number M of the absorbed A molecules is N times expected number of A at a single absorption center:

$$M = \frac{\partial \log \Xi}{\partial \beta\mu} = N\frac{ze^{\beta(\varepsilon+\mu)}}{1 + ze^{\beta(\varepsilon+\mu)}}. \tag{21.54}$$

Now, let us obtain (or copy) μ:

$$\mu = k_B T \log \frac{P}{k_B T n_Q}, \tag{21.55}$$

or

$$e^{\beta\mu} = \frac{P}{k_B T n_Q} \equiv \frac{P}{P_Q}, \tag{21.56}$$

where $n_Q = (2\pi m k_B T/h^2)^{3/2}$. Therefore, $\theta = M/N$ reads

$$\theta = \frac{z\alpha(P/P_Q)}{1 + z\alpha(P/P_Q)} = \frac{P}{P + P_Q/z\alpha}, \tag{21.57}$$

where $\alpha = e^{\beta\varepsilon}$. That is,

$$X = ze^{\beta\varepsilon}. \tag{21.58}$$

Q21.2 [Bosons and fermions: rudiments]
There is a system in which each particle can assume only three states with energies 0, ε and ε ($\varepsilon > 0$, i.e., excited states are degenerate). There are two identical particles without spin.
(1F) When the particles are fermions, write down the canonical partition function (I recommend you to make a table of all the microstates).
(2F) Find the probability of finding N $(= 0, 1, 2)$ particles in the ground state.
(3F) Compute the average occupation number N_0 of the ground state. Are the limits $T \to \infty$ and $T \to 0$ reasonable?
(1-3B) Repeat the same problems assuming that the particles are bosons.
(4) In the high temperature limit what is the most important observation?

Solution.
Here 'degenerate' means that the energies happen to be identical but the states are clearly distinguishable like the three $2p$ orbits in the hydrogen atom.
(1F) To compute the canonical partition function, you must itemize all the microstates.

microstate	0	ε	ε	total energy
1	1	1	0	ε
2	1	0	1	ε
3	0	1	1	2ε

Hence,

$$Z = 2e^{-\beta\varepsilon} + e^{-2\beta\varepsilon}.$$

(2F) Let us write the desired probabilities as $P(N)$.

$$P(1) = \frac{2e^{-\beta\varepsilon}}{2e^{-\beta\varepsilon} + e^{-2\beta\varepsilon}} = \frac{2}{2 + e^{-\beta\varepsilon}}, \quad P(0) = \frac{e^{-2\beta\varepsilon}}{2e^{-\beta\varepsilon} + e^{-2\beta\varepsilon}} = \frac{1}{e^{\beta\varepsilon} + 2}, \ P(2) = 0.$$

(3F)

$$\langle N_0 \rangle = P(1) = \frac{2}{2 + e^{-\beta\varepsilon}}$$

$T \to \infty$: $N_0 = 2/3$ (yes, all the states are equally probable).
$T \to 0$: $N_0 = 1$ (yes, the lowest level must surely be occupied).
(1B) To compute the canonical partition function, you must itemize all the microstates.

microstate	0	ε	ε	total energy
1	1	1	0	ε
2	1	0	1	ε
3	0	1	1	2ε
4	2	0	0	0
5	0	2	0	2ε
6	0	0	2	2ε

Hence,

$$Z = 1 + 2e^{-\beta\varepsilon} + 3e^{-2\beta\varepsilon}.$$

(2B)

$$P(1) = (2/Z)e^{-\beta\varepsilon}, \;\; P(0) = (3/Z)e^{-2\beta\varepsilon}, \;\; P(2) = 1/Z.$$

(3B)

$$N_0 = \frac{2 + 2e^{-\beta\varepsilon}}{1 + 2e^{-\beta\varepsilon} + 3e^{-2\beta\varepsilon}}.$$

$T \to \infty$: $N_0 = 2/3$ (yes, all the states are equally probable, and must be the same as the fermion case).
$T \to 0$: $N_0 = 2$ (yes, all the particles must be there).
(4) Both agree as noted above.

Q21.3 [**Bose gas pressure**]
If we compare the pressure P_{BE} of an ideal boson gas and that P_{MB} of an ideal classical gas under the same V, T and N, $P_{MB} > P_{BE}$. Mimicking the Fermi-Dirac case (i.e., $P_{FD} > P_{MB}$) explained in the lecture notes, demonstrate this inequality.

Solution.
$\beta P_{MB} V = N$, so we wish to compare $\beta P_{BE} V$ and N (since μ's are not the same for the two cases, we cannot immediately comparer the pressure formulas).

$$\beta P_{BE} V = -\sum_i \log(1 - e^{-\beta(\varepsilon_i - \mu)}), \tag{21.59}$$

and

$$N = \sum_i \frac{1}{e^{\beta(\varepsilon_i-\mu)} - 1} = \sum_i \frac{e^{-\beta(\varepsilon_i-\mu)}}{1 - e^{-\beta(\varepsilon_i-\mu)}}. \tag{21.60}$$

Here, you must use consistently the formula for bosons.

Let us compare the corresponding summand terms in P and N, writing $x = e^{-\beta(\varepsilon_i - \mu)}$. Let

$$f(x) = \frac{x}{1-x} + \log(1-x). \tag{21.61}$$

$f(0) = 0$.

$$f'(x) = \frac{1}{1-x} + \frac{x}{(1-x)^2} - \frac{1}{1-x} = \frac{x}{(1-x)^2}, \tag{21.62}$$

which is positive for $x > 0$. Therefore, $f(x) > 0$, if $x > 0$. QED.

Q21.4 [**Boson-fermion mixed gas**]. There is a mixture of $N/3$ non-interacting fermions and $2N/3$ non-interacting bosons in a container of volume V. The total internal energy is E. What is the total pressure P of the mixture? [Hint: Dalton's law of partial pressures applies. You must clearly state your logic to support your answer.]

Solution.
Let P_F and P_B be the respective partial pressures, and E_F and E_B internal energies of the respective components. Then,

$$P_F V = \frac{2}{3} E_F, \;\; P_B V = \frac{2}{3} E_B,$$

so

$$(P_F + P_B)V = \frac{2}{3}(E_F + E_B) \;\Rightarrow\; PV = \frac{2}{3} E,$$

which is due to additivity of internal energy and the law of partial pressures. Hence, $P = 2E/3V$.

Discussion 10

We will discuss chemical potential and grand canonical approach

D10.1 [Chemical potential of ideal gas]
Consider a fluid whose Gibbs relation is $dE = TdS - PdV + \mu dN$ so the Gibbs free energy $G = E - TS + PV$ reads $G = \mu N$. Thus, you should be able to get μ directly with the aid of the so-called pressure ensemble, the ensemble with T-P constant. You may have been fed up with this ensemble, but obtain μ, using the partition function Y and $N\mu = -k_BT \log Y$. The answer must be the same as the result given in (20.33).

Solution.
Actually, this problem was almost done in **1**(3) of Discussion 8. We know the canonical partition function:

$$Z(T,V) = \frac{1}{N!}\left[\left(\frac{2\pi m k_B T}{h^2}\right)^{3/2}\right]^N V^N, \tag{21.63}$$

so we get

$$Y(T,P) = \left[\left(\frac{2\pi m}{h^2}\right)^{3/2} \frac{(k_BT)^{5/2}}{P}\right]^N. \tag{21.64}$$

Therefore,

$$N\mu = -k_BT\log Y = Nk_BT\log\frac{P/k_BT}{(2\pi m k_BT/h^2)^{3/2}}, \tag{21.65}$$

or

$$\mu = k_BT\log\frac{n}{n_Q}, \tag{21.66}$$

where n is the number density and

$$n_Q = (\sqrt{2\pi}/\lambda_T)^3 \tag{21.67}$$

with the thermal de Broglie wavelength $\lambda_T = h/\sqrt{mk_BT}$. This is just (20.33).

D10.2 [Colligative properties review]

The properties of dilute mixtures with or without phase transitions may be understood in terms of the chemical potentials based on the ideal gas law and mixing entropy. In short, information-theoretically calculated entropy can explain the core physics of the so-called colligative properties (Raoult, van't Hoff (or osmotic pressure), Henry's law, transition temperature shifts, etc.). Thus, the basic form of the chemical potential in the gas phase is

$$\mu(T, P) = \mu^{\ominus}(T) + k_B T \log P, \tag{21.68}$$

where P may be the partial pressure in a mixture. In the liquid phase

$$\mu(T, x) = \mu^{\ominus}(T) + k_B T \log x, \tag{21.69}$$

where x is the mole fraction. Both P and x in ideal systems are related to the probability (or the relative probability) to find the relevant particle.

An important feature of (21.69) is that μ can be indefinitely small ($\searrow -\infty$) if $x \searrow 0$. Thus, if a reaction can produce a molecule that does not exist in the system, extremely large drop of ΔG may be realized by the reaction.
(0)* What is the implication of this observation?
(i) In the hydrolysis of ATP: ATP $\longrightarrow$ADP + Pi, inorganic phosphate ion Pi is produced. If the concentration of Pi is very low, then this reaction can drive difficult reactions irreversibly. For example, if a codon correctly matches with the anticodon this reaction occurs and the correct translation of the codon to the corresponding amino acid is secured. Explain.
(ii) [As discussed in the lecture] We could produce indefinitely large mechanical work from this type of reaction. This is a correct thermodynamic conclusion, but still sounds too good. This highlights a major distinction among thermal, chemical, and electromechanical energies. Explain.

Traditionally, the chemical physics properties studied within these 'information theoretical chemical potential' are called colligative properties. Representative problems we can at least approximately answer within this framework look as:

(1) If 2 g of a non-volatile extract from pitch is dissolved in 100 g of benzene, the vapor pressure of benzene at 300 K is reduced to 99.1 mmHg from 100 mmHg. What is the average molecular weight of this extract?

(2) How many weight % of methanol is required to prevent water from freezing at 260 K?

(3) 1.23 g of a kind of globular protein is in 100 cm^3 aqueous solution. The osmotic pressure of this solution is 7.43 cm of water column. What is the molecular weight of this protein?

The colligative properties may be treated in a unified fashion as follows:
I and II denote two distinct but coexisting phases/systems. For a chemical that may go between I and II freely the equilibrium condition is

$$\mu_{\mathrm{I}}^0(T_{\mathrm{I}}', P_{\mathrm{I}}') = \mu_{\mathrm{II}}^0(T_{\mathrm{II}}', P_{\mathrm{II}}') + k_B T_{\mathrm{II}}' \log y. \tag{21.70}$$

Here, superfix 0 means the pure state and y denotes the mole fraction in II of the chemical being exchanged. We assume without 'impurity' (minority)

$$\mu_{\mathrm{I}}^0(T_{\mathrm{I}}, P_{\mathrm{I}}) = \mu_{\mathrm{II}}^0(T_{\mathrm{II}}, P_{\mathrm{II}}). \tag{21.71}$$

Combining these two, we obtain

$$\mu_{\mathrm{I}}^0(T_{\mathrm{I}}', P_{\mathrm{I}}') - \mu_{\mathrm{I}}^0(T_{\mathrm{I}}, P_{\mathrm{I}}) = \mu_{\mathrm{II}}^0(T_{\mathrm{II}}', P_{\mathrm{II}}') - \mu_{\mathrm{II}}^0(T_{\mathrm{II}}, P_{\mathrm{II}}) + k_B T_{\mathrm{II}}' \log y. \tag{21.72}$$

The rest is to adapt this to various situations.

Vapor pressure change
These are about the pressure of the vapor (gas phase) coexisting with mixture liquid. Thus, I = G, II = L, $T = T'$ is everywhere the same, so let us drop it from μs. Using (21.68) for the gas phase, we see

$$k_B T \log P_{\mathrm{G}}'/P_{\mathrm{G}} = k_B T \log y \tag{21.73}$$

or $P_{\mathrm{G}}' = yP_{\mathrm{G}}$.[345] This may be understood as:
Raoult's law: the partial pressure P_{G}' of one component in a liquid mixture is given by its mole fraction y times the vapor pressure P_{G} of the component when it is pure, or
Henry's law: the amount y of a gas component resolved in the liquid phase is proportional to the partial pressure of the component in the gas phase.

Osmotic pressure (van't Hoff's law)
I is the pure liquid, and II the mixture under $P_{\mathrm{II}}' = P + \pi$ (slightly pressurized). There is no temperature change (let us drop $T = T'$). Without impurity $P_{\mathrm{I}} = P_{\mathrm{II}} = P$. Let $y = 1 - x$, where x is the mole fraction of the impurity in II. Thus, (21.72) reads

$$\mu^0(P) = \mu^0(P + \pi) + k_B T \log(1 - x), \tag{21.74}$$

where μ^0 is the pure liquid chemical potential.

We know generally (you must be able to derive this from the Gibbs relation),

$$d\mu = vdP - sdT, \tag{21.75}$$

[345] Here, we use the fact that the liquid phase volume change due to the pressure change is negligible.

where v is the molar volume/molecule (for a pure liquid $v = V/N$) and s the molar entropy per molecule.[346] Therefore, we get

$$\pi = nk_BT, \tag{21.77}$$

where $n = xN_A/V$ (the number density).[347]

You could change the temperatures of I and II (instead of P). What will you have to do to stop the movement of the solvent from I to II (which should be at higher temperature, I or II)?

Phase transition point shift

Impurities in the liquid phase are often excluded from the coexisting gas or solid phase. In such cases, II = L and I may be G or S phase. Under constant pressure, we are interested in the shift in the coexistence temperature. Combining (21.72) and (21.75) with $y = 1 - x$, $T_{\rm I} = T_{\rm II} = T$ (the pure substance phase transition point) and $T'_{\rm I} = T'_{\rm II} = T + \Delta T$ (the phase transition point of the mixture), we get (to order x)

$$-s_{\rm I}\Delta T = -s_{\rm II}\Delta T - k_BTx \tag{21.78}$$

Melting-point depression: I = S, II = L. Then, $s_{\rm II} - s_{\rm I} = L/N_AT$, where L is the melting heat (enthalpy change due to the phase transition per mole). Therefore,

$$\Delta T = -\frac{k_BT^2}{L/N_A}x, \text{ which is} < 0. \tag{21.79}$$

Boiling-point elevation: I = G, II = L. Then, $s_{\rm I} - s_{\rm II} = L/N_AT$, where L is the evaporation heat (enthalpy change due to the phase transition per mole). Therefore,

$$\Delta T = \frac{k_BT^2}{L/N_A}x, \text{ which is} > 0. \tag{21.80}$$

Now, let us answer the above-mentioned representative questions.

(1) If 2 g of a non-volatile extract from pitch is dissolved in 100 g of benzene (C_6H_6), the vapor pressure of benzene at 300 K is reduced to 99.1 mmHg from 100 mmHg. What is the average molecular weight of this extract?

(2) How many weight % of methanol (CH_3OH) is required to prevent water from freezing at 260 K? The melting heat of ice is 334 J/g, and that of methanol is 99

[346]Here, chemical potentials are per molecule. That is why k_B appears. Chemical potentials per mole reads

$$\mu(T, x) = \mu^{\ominus}(T) + RT\log x. \tag{21.76}$$

[347]This same equation reads $\pi V = cRT$ where c is the molarity with appropriate choice of the units.

J/g.

(3) 1.23 g of a kind of globular protein is in 100 cm^3 solution. The osmotic pressure of this solution is 7.43 cm of water column at 25 °C. What is the molecular weight of this protein?

(1) is the Raoult question. (2) is the melting point depression. (3) is a van't Hoff question.

Solution.
(1) The molecular weight of benzene is 78. If the average molecular weight of the extract is M, the impurity mole fraction x is

$$x = \frac{2/M}{2/M + 100/78} = \frac{156}{156 + 100M} \tag{21.81}$$

This means

$$M = \frac{156(1-x)}{100x}. \tag{21.82}$$

We may use Raoult's law:

$$100(1-x) = 99.1. \tag{21.83}$$

Therefore

$$x = \frac{100 - 99.1}{100} = 0.009. \tag{21.84}$$

Thus

$$M = \frac{156(1 - .009)}{0.9} = 171.8. \tag{21.85}$$

(2) We wish to shift the freezing point of the mixture by $-\Delta T = 13$ K. (21.79) implies

$$x = \frac{L\Delta T}{RT^2}, \tag{21.86}$$

where $L = 334$ J/g $= 6012$ J/mole, and $T = 273$ K. Therefore,

$$x = \frac{6012 \times 13}{8.314 \times 273^2} = \frac{78256}{619634} = 0.126. \tag{21.87}$$

This means that the methanol-water mole ratio is $0.126/(1-0.126) = 0.144$. Therefore, the weight ratio $W_m/W_w = 0.144 \times 32/18 = 0.256$. Thus, the weight % is $W_m/(W_m + W_w) = 0.256/1.256 = 20$ %.

(3) π is 7.43 cm Water column $= 7.43 \times 10^{-2} \times 9.8 \times 10^3 = 7.28 \times 10^2$ Pa (here 10^3 is the density of water in kg/m^3). (21.77) implies the amount n of the protein in moles in volume 100 cm^3 is given by

$$n = \pi V/RT = \frac{728 \times 100 \times 10^{-6}}{8.314 \times 298} = 0.294 \times 10^{-4}. \tag{21.88}$$

That is, 1.23 g corresponds to this amount in moles, so the molecular weight is 4.14×10^4.

D10.3 [**More practical melting point depression problems**]
(1) The melting point of water should be depressed by the absorbed air. What do you think is its order, 0.1 K, 0.01 K or 0.001 K? At 273 K under 1 atm, the solubility of nitrogen in water is 23.5 ml/l, and that of oxygen is 48.9 ml/l.
Solution.
The melting point depression is given by (21.79); in our context, $T = 273$ K, $L = 6012$ J/mole as calculated already, so

$$|\Delta T| = \frac{8.314 \times 273^2}{6012} x = 103x, \tag{21.89}$$

where x is the mole fraction. Accurate calculation needs the law of partial pressure as well as Henry's law, but we see that N_2 and O_2 contribute about the same, so we may estimate

$$x = \frac{30 \times 10^{-3}/22.4}{1000/18} = \frac{1.3 \times 10^{-3}}{55}. \tag{21.90}$$

Thus, it is of the order of 0.001 K.

(2) If m g of a substance is dissolved in 100 g of benzene, its melting point is decreased by 1.7 K. If the same amount is dissolved in water the melting point of water is decreased by 1.2 K. The melting heat of benzene is 127 J/g. Its melting point is 5.5 °C. How do you explain these two facts consistently?

Solution.
For benzene

$$|\Delta T| = \frac{8.314 \times 278.5^2}{127 \times 78} x = 65.1x, \tag{21.91}$$

Therefore, in benzene, $x = 0.0265 = y/(100/78 + y)$ or $y = (0.0265 \times 100/78)/(1 - 0.0265) = 0.0349$.

For water, we know (21.89), so $x = 0.01165 = y/(100/18 + y)$ or $y = (0.01165 \times 100/18)/(1 - 0.01165) = 0.0655$.

The most natural interpretation is that this substance dissociates into two pieces in water, but not so in a not so polar solvent.

D10.4 [**Miscible vs immiscible**][348]
There are two liquids A and B whose vapor pressures are given as $P_{\mathrm{A}}^0(T)$ and $P_{\mathrm{B}}^0(T)$, respectively. Assume that these chemicals do not react each other, and in the gas

[348] Already discussed in a lecture.

phase they make an ideal gas mixture.
(1) Suppose that these liquids mix well and make an ideal mixture. Then, Raoult's law holds. If the mole fraction of A in the liquid phase is x, what is the vapor pressure of this mixture at temperature T?
(2) Suppose that these liquids does not mix at all. Still you can put them in a single vessel and heat. What is the vapor pressure of this mixture at temperature T?
(3) What can you say about the boiling points of case (1) and case (2)? The boiling points are $T_{\rm A}$ and $T_{\rm B}$, respectively, for these pure liquids.

Solution.
(1) According to Raoult's law,

$$P_{\rm mix}(T) = xP_{\rm A}^0(T) + (1-x)P_{\rm B}^0(T). \tag{21.92}$$

(2) Both liquids contribute $P_{\rm A}^0(T)$ and $P_{\rm B}^0(T)$ independently, so

$$P_{\rm nonmix}(T) = P_{\rm A}^0(T) + P_{\rm B}^0(T). \tag{21.93}$$

(3) Notice that

$$\min\left[P_{\rm A}^0(T), P_{\rm B}^0(T)\right] \le P_{\rm mix}(T) \le \max\left[P_{\rm A}^0(T), P_{\rm B}^0(T)\right] \le P_{\rm nonmix}(T). \tag{21.94}$$

Boiling occurs when the total vapor pressure of the system reaches a given pressure (say, 1 atm). Therefore,

$$\max(T_{\rm A}, T_{\rm B}) \ge T_{\rm mix}(T) \ge \min(T_{\rm A}, T_{\rm B}) \ge T_{\rm nonmix}. \tag{21.95}$$

Therefore, if these liquids mix well, its boiling point is between T_A and T_B, but if they do not, the boiling point of the 'juxtaposed liquids' is less than any of T_A or T_B.

D10.5 [Simple adsorption problem].
Consider a two dimensional lattice with N sites, each of which can adsorb at most one particle of chemical A. The energy of the adsorbing site is reduced by ε (> 0) when a particle is adsorbed (or you can say an adsorbed chemical A particle has its energy reduced by ε relative to its non-adsorbed states).
(1) At temperature T, n particles are adsorbed on the lattice. Using the canonical formalism, find the chemical potential μ of the adsorbed particles in terms of the covering fraction θ of the lattice by the adsorbed particles. Notice that if n is fixed, E is fixed, so canonical and microcanonical ensemble approaches are virtually the same. You can (but need not) follow the following steps:
(i) Compute the canonical partition function $Z(n)$, and then calculate the Helmholtz free energy $A(n)$ of the lattice with n particles on it (thus, the total $E = -n\varepsilon$).
(ii) Then, utilizing the Gibbs relation, compute the chemical potential (per particle)

μ.
(2) Write down the grand canonical partition function for this lattice system, assuming that the particle chemical potential is (general) μ. Then, compute the adsorbed number n of particles, and confirm the consistency of your answer and that for (1).
(3) The 2D lattice system is immersed in a big tank of a solution of chemical A in an inert solvent. The chemical potential of the solute (particles of chemical A) is given by

$$\mu_A = \mu_A^{\ominus}(T) + k_BT \log x, \tag{21.96}$$

where x is the mole fraction of chemical A in the solution. Find the equilibrium fraction θ of the lattice points covered by the particles.
(4) What happens to this coverage, if you raise the temperature? You may assume that ε is sufficiently large (i.e., adsorption is energetically favorable). Can you comment on the relation between your observation and Le Chatelier's principle? (Or better, guess the result first and then confirm your guess.) Assume that resolving chemical A into the solvent is energetically neutral, so $\mu_A^{\ominus}$ is T independent.

Solution.
(1) The canonical partition function reads (for $E = -n\varepsilon$)

$$Z(n) = \binom{N}{n} e^{n\beta\varepsilon}, \tag{21.97}$$

because we do not know where these n particles are adsorbed. The Helmholtz free energy reads

$$A(n) = -k_BT \log \binom{N}{n} - n\varepsilon = Nk_BT \left[\frac{n}{N}\log\frac{n}{N} + \left(1-\frac{n}{N}\right)\log\left(1-\frac{n}{N}\right)\right] - n\varepsilon. \tag{21.98}$$

Since $dA = -SdT + \mu dn + \cdots$,

$$\mu = \left.\frac{\partial A}{\partial n}\right|_T = -\varepsilon + k_BT\log\frac{n}{N-n} = -\varepsilon + k_BT\log\frac{\theta}{1-\theta}, \tag{21.99}$$

where the covering fraction θ is used.
(2)

$$\Xi = \sum_{n=0}^{N} \binom{N}{n} e^{n\beta(\varepsilon+\mu)} = \left(1 + e^{\beta(\varepsilon+\mu)}\right)^N. \tag{21.100}$$

Of course, we can write this down immediately, because each lattice point has two states with the number of particles 0 and 1 (and energy 0 and $-\varepsilon$, respectively). Therefore, recalling

$$d\left(\frac{PV}{k_BT}\right) = d\log\Xi = -Ed\beta + \beta PdV + Nd(\beta\mu), \tag{21.101}$$

we have (N in the above formula is the generic notation for the number of particles in the system, which is n in the present case)

$$n = \frac{\partial \log \Xi}{\partial \beta\mu} = N\frac{e^{\beta(\varepsilon+\mu)}}{1+e^{\beta(\varepsilon+\mu)}}. \tag{21.102}$$

That is,

$$\theta = \frac{e^{\beta(\varepsilon+\mu)}}{1+e^{\beta(\varepsilon+\mu)}}. \tag{21.103}$$

From this we get

$$e^{\beta(\varepsilon+\mu)} = \frac{\theta}{1-\theta}, \tag{21.104}$$

which agrees with the above result.

(3) The solute chemical potential in the solution and that of adsorbed particles (21.99) must be identical in equilibrium:

$$\mu_A^{\ominus} + k_BT\log x = -\varepsilon + k_BT\log\frac{\theta}{1-\theta}. \tag{21.105}$$

We can solve θ from this, BUT the following formula must be obtained almost immediately

$$\theta = \frac{xe^{\beta(\varepsilon+\mu_A^{\ominus})}}{1+xe^{\beta(\varepsilon+\mu_A^{\ominus})}}, \tag{21.106}$$

because replacing μ in the formula for θ above (21.103) with $\mu_A^{\ominus} + k_BT\log x$ must be the answer.

The result is reasonable: if x is increased, the coverage should increase; if ε is increased, then the adsorbed particles become more stable, so the coverage again increases.

(4) The adsorbing process of the particle is an exoergic process, because ε is released upon adsorption. Therefore, Le Chatelier tells us that θ must be a decreasing function of T. Let us confirm this. $\theta/(1-\theta)$ is an increasing function of θ, and

$$xe^{\beta(\varepsilon+\mu^{\ominus})} = \theta/(1-\theta). \tag{21.107}$$

Therefore, increasing T reduces β, which reduces $\theta/(1-\theta)$. Hence, θ decreases as expected.

D10.6 [Small system in terms of grand-canonical formalism].
There are 100 identical spinless bosons whose n-th one-particle state has an energy $\varepsilon_n = n\varepsilon$ ($n \in \boldsymbol{N}$; $n = 0$ is the one-particle ground state). These particles do not interact. When the system is in equilibrium with the particle reservoir (chemostat)

of temperature T and chemical potential μ, on the average 99 particles occupy the one-particle ground state ($n = 0$), and one particle occupies the one-particle first excited state ($n = 1$). The other one-particle states are negligibly occupied.
(1) Find the chemical potential μ in terms of ε (or compute μ/ε).
(2) Is the second excited state occupied only negligibly? Compute $\langle n_2\rangle$. $\langle n_2\rangle/\langle n_1\rangle$ is not terribly small, so you might think that the problem is not self-consistent. Give your comment on this observation.

Solution.
(1) Since

$$\langle n_0\rangle = \frac{1}{e^{-\beta\mu}-1} = 99, \tag{21.108}$$

$$\langle n_1\rangle = \frac{1}{e^{\beta(\varepsilon-\mu)}-1} = 1, \tag{21.109}$$

we have

$$-\beta\mu = \log(100/99) = 0.010050335, \tag{21.110}$$

$$\beta(\varepsilon-\mu) = \log 2 = 0.693147. \tag{21.111}$$

Hence, $\beta = 0.683097/\varepsilon$ and $\mu = -0.010050335/(0.683097/\varepsilon) = -0.0147\varepsilon$. Clearly recognize that μ is negative (does not exceed the ground state energy)!
(2) $\beta(2\varepsilon-\mu) = 2\beta(\varepsilon-\mu) - (-\beta\mu) = 2 \times 0.693147 - 0.010050335 = 1.37624$, so $\langle n_2\rangle = 0.338$. Actually, $\langle N\rangle$ is about 0.5 articles more than 100. This is inevitable because $\log 100/100 = 0.05$, so a few % error is actually expected. We must admit that for an $N = 100$ closed system, to use the open-system formalism is not terribly accurate.

D10.7 [Near ground microstates].
In a system one particle state has energies 0, ε, 2ε, $\cdots$ (equally spaced and not degenerate as illustrated in Fig 20.4 in the Lecture Notes), where $\varepsilon = 0.01$ eV.[349]
(1) There are 1000 particles in the system. What is the energy of the lowest energy microstate (= ground microstate, i.e., the ground state of the whole system) from the origin of the one particle state energy for (1F) fermions and for (1B) bosons? (Ignore the internal states of the particles.)
(2) Itemize all the excited microstates (of the whole system, needless to say) whose excitation energies are less than or equal to 3ε (from the ground microstate) for fermions (2F) and for bosons (2B).
(3) The above system with 1000 fermions is initially at $T = 0$. Suppose all the fermions are converted into bosons adiabatically (that is, with E being kept constant). Is the temperature of the resultant boson system in equilibrium higher than

[349] 1 eV corresponds to 12,000 K.

5,000 K?

(4) [Can you make a fermion bomb?][350] There is a fermion gas at room temperature with the Fermi energy 10 eV. The gas is in an adiabatic container. The fermions are actually metastable, and are converted into stable bosons without any energy input. The reader may assume the particles do not interact. If the transformation from fermions to bosons is carried out adiabatically, so that the particles experience no sudden forces, can the resulting bose gas explode the container?

Solution.
(1F) 0, ε, $\cdots$ up to 999ε one particle states are singly occupied, so the total energy must be $(1+2+\cdots+999)\varepsilon = 999 \times 1000/2)\varepsilon = 499,500\varepsilon$.
(1B) Obviously 0.
(2F) Let us make a microstate table. In this case let us make an occupation table. The double horizontal line is the Fermi energy at $T = 0$. See Fig. 20.4.

1P level							
1003ε	×	×	×	×	×	×	×
1002ε	×	×	×	×	○	×	×
1001ε	×	×	○	×	×	○	×
1000ε	○	○	×	○	×	×	×
999ε	×	○	×	○	×	○	○
998ε	○	×	○	○	○	×	○
997ε	○	○	○	×	○	○	○
996ε	○	○	○	○	○	○	○
ΔE	ε	2ε	2ε	3ε	3ε	3ε	0

No holes below 997ε.

(2B) Let us make a microstate table:

total energy	ε	2ε	3ε
ε	1	0	0
2ε	2	0	0
	0	1	0
3ε	3	0	0
	1	1	0
	0	0	1

All other particles are in the one particle ground state.

(3) Good physicists' answer: as you can see from Fig. 21.4 in the lecture notes, if fermions are converted to bosons, then the 'tower' of fermions at $T = 0$ crumbles down to a 'dust cloud' with the particle energy about 5 eV. Since this is about 60 kK, obviously, the resultant boson system is extremely hot $\gg 5000$ K.

We can confirm this as follows. We use that the resultant classical system is less

[350] the core part of UIUC Qual Spring 2002; notice the year.

hot than the boson system (bosons 'attract each other' (see Fig. 21.6 in the lecture notes), so they tend to be 'attracted' toward more populated one particle states than less. Therefore, we need a higher temperature to have the same average energy as the classical case.

Now, let us solve the classical case.

$$Z_N = \sum_{\sum_k n_k = N} \frac{N!}{n_0! n_1! n_2! \cdots n_k! \cdots} e^{-\beta \sum_k k\varepsilon n_k} = \left(\sum_k e^{-k\beta\varepsilon} \right)^N = (1 - e^{-\beta\varepsilon})^{-N}, \tag{21.112}$$

where n_k is the number of particles occupying the one particle ground state with energy $k\varepsilon$. The summation over k is from 0 to ∞. Therefore, with the aid of the Gibbs-Helmholtz formula, we get

$$E = -\frac{\partial \log Z_N}{\partial \beta} = \frac{N\varepsilon}{e^{\beta\varepsilon} - 1}. \tag{21.113}$$

$E = 4995$ eV, so

$$e^{\beta\varepsilon} - 1 = N\varepsilon/E = 10/4995 \simeq 0.002 \tag{21.114}$$

or $\beta\varepsilon = \log 1.002 \sim 0.002$. That is, $1/\beta = \varepsilon/0.002 = 5$ eV (as you can immediately see $1/\beta \simeq E/N$, the average energy as we have already guessed). Thus, $T \sim 60,000$ K. The temperature of the bose system cannot be lower than this, so surely $T > 5000$ K. [The resultant temperature is so high that you might wish to do relativistic calculation....]

(4) As you see this is very closely related to (3). Notice that the pressure does not change, because the internal energy does not change, so explosion due to the change of pressure is impossible. However, the temperature increases a lot, because the Fermi energy is 10 eV (corresponding to 120 kK) and most containers would evaporate. Notice that this is a 3D system, so higher energy levels are more degenerate, so the 'tower' looks like a cone standing on its apex, so much worse than (3). Since the content is already under high pressure before the conversion, explosion is inevitable.

Exercise 10

E10.1. [Easy colligative property questions]
(1) 12.3 g of an unknown substance (with negligible vapor pressure) is dissolved in 100 g of water. Its vapor pressure is 743 mmHg at 100 °C. What is its molecular weight M?

(2) A 1 l solution containing 25 g of a substance at 0°C exhibits the osmotic pressure 2.34 atm. What is the osmotic pressure of the solution containing 31 g/l of the same substance (with the same solvent) at 30°C?

Solution.
(1) This is a Raoult's law problem. The mole fraction y of water is

$$y = \frac{100/18}{100/18 + 12.3/M} = \frac{5.56}{5.56 + 12.3/M} = 743/760 = 0.9776. \tag{21.115}$$

Therefore,

$$5.56 = 0.9776(5.56 + 12.3/M) \;\Rightarrow\; 0.1245 = 12.3/M \;\Rightarrow\; M = 98.8. \tag{21.116}$$

(2) van't Hoff's law tells us that

$$\pi = cRT, \tag{21.117}$$

where c is the molarity. Thus, $\pi \propto mT$, where m is the mass of the solute.

$$\frac{\pi}{2.34} = \frac{31 \times 303}{25 \times 273} \;\Rightarrow\; \pi = 1.3762 \times 2.34 = 3.22 \text{ atm}. \tag{21.118}$$

E10.2. [Steam distillation][351]
According to the Clapeyron-Clausius equation, the vapor pressure of a liquid obeys

$$\frac{dP}{dT} = \frac{\Delta H}{T\Delta V}, \tag{21.119}$$

where ΔH denotes the evaporation heat, and ΔV is the volume increase by evaporation. Usually, the vapor is approximated as an ideal gas and the liquid volume is ignored, so $\Delta V = V_{\text{vapor}} = RT/P$ is used. Therefore, the original Clapeyron-Clausius equation may be written as

$$\frac{dP}{dT} = \frac{P\Delta H}{RT^2}. \tag{21.120}$$

(1) Show that this implies $P = ce^{-\Delta H/RT}$, where c is a positive constant, if we may assume ΔH is constant.

[351]'DIY steam distillation of mint oil from mint herb' is described step by step here [in Japanese].

(2) There are two immiscible liquids A and B with the vapor pressure (in atm) (T in K)

$$P_{\mathrm{A}}(T) = 942293e^{-5135/T}, \; P_{\mathrm{B}}(T) = 605380e^{-5364/T}. \tag{21.121}$$

What is the boiling point of the A, B mixture? [You can use graphic method to solve this. For example, you can use `http://dlippman.imathas.com/graphcalc/graphcalc.html`]
(3) What is the mole fraction of B in the vapor phase? [In this example, A is actually water.]

Solution.
(1) We have only to integrate the Clapeyron-Clausius equation (21.120):

$$\frac{d\log P}{dT} = \frac{\Delta H}{RT^2} \;\Rightarrow\; \log\frac{P}{P_0} = \frac{\Delta H}{R}\left(\frac{1}{T_0} - \frac{1}{T}\right). \tag{21.122}$$

Thus,

$$P = P_0 e^{(\Delta H/RT^0 - \Delta H/RT)} = ce^{-\Delta H/RT}. \tag{21.123}$$

(2) Since A and B do not mix, the vapor phase pressure is just the sum of their vapor pressures as discussed in Disc.**4** or in a lecture,

$$P(T) = P_{\mathrm{A}}(T) + P_{\mathrm{B}}(T) = 942293e^{-5135/T} + 605380e^{-5364/T}. \tag{21.124}$$

The graphs we need are seen in Fig. 21.7:

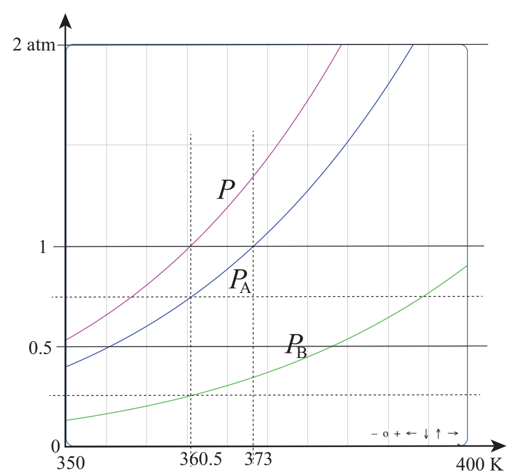

Figure 21.7: $P_{\mathrm{A}}(T)$, $P_{\mathrm{B}}(T)$ and $P(T)$

Therefore, $P = 1$ is realized at $T = 360.5$ K.

(3) From the graph the partial pressures in the vapor can be read off as $P_{\mathrm{A}} = 0.75$, and $P_{\mathrm{B}} = 0.25$. Thus 0.25 is the answer.

E10.3 [**Adsorption question**]
Consider a surface with N adsorption centers, each of which can accommodate at most one particle. The energy of the adsorbing site is reduced by ε (> 0, that is the one particle energy is $-\varepsilon$) when a particle is adsorbed. On the surface there is a conversion reaction between A and B, which is Δ (> 0) more stable than A. B cannot detach from the surface. The surface is placed in a large tank filled with gas of A with chemical potential μ.
(1) Write down the grand canonical partition function for the adsorbing surface.
(2) Find the total coverage fraction θ (i.e., the number of sites occupied by A or B divided by N).
(3) What do you expect to happen to the chemical potential of A, if you change Δ while fixing the total coverage θ?

Solution.
(1) At each adsorption center, there are 3 states: empty, A or B. Therefore, the 'grand canonical partition function for a site' reads

$$1 + e^{\beta(\varepsilon+\mu)} + e^{\beta(\varepsilon+\Delta)}, \tag{21.125}$$

so the grand canonical partition function for the surface reads

$$\Xi = \left(1 + e^{\beta(\varepsilon+\mu)} + e^{\beta(\varepsilon+\Delta)}\right)^N. \tag{21.126}$$

(2) The number of A is

$$\frac{\partial \log \Xi}{\partial \beta\mu} = N\frac{e^{\beta(\varepsilon+\mu)}}{1 + e^{\beta(\varepsilon+\mu)} + e^{\beta(\varepsilon+\Delta)}}. \tag{21.127}$$

The number of B is analogously obtained as

$$\frac{\partial \log \Xi}{\partial \beta\mu} = N\frac{e^{\beta(\varepsilon+\Delta)}}{1 + e^{\beta(\varepsilon+\mu)} + e^{\beta(\varepsilon+\Delta)}}. \tag{21.128}$$

Therefore,

$$\theta = \frac{e^{\beta(\varepsilon+\mu)} + e^{\beta(\varepsilon+\Delta)}}{1 + e^{\beta(\varepsilon+\mu)} + e^{\beta(\varepsilon+\Delta)}}. \tag{21.129}$$

(3) If θ is constant, then

$$e^{\beta(\varepsilon+\mu)} + e^{\beta(\varepsilon+\Delta)} \tag{21.130}$$

must be constant. Therefore, increasing Δ must be compensated by reducing μ. That is, we must reduce the tendency of A to be adsorbed on the surface, because adsorbed A implies more B.

E10.4. [Elementary ideal quantum particles]
The one particle state energies are equally spaced (with spacing ε) for a particle.

(1) There are $N = 1232$ identical fermions in the system and its ground state has energy $E_0 = 2311$ eV (relative to the one-particle ground state).
(i) What is the spacing ε and the Fermi level μ_F of the system?
(ii) What is the specific heat of the system at very low temperatures? You may assume $\beta\varepsilon \gg 1$.
(2) Now, let us assume these particles are identical bosons and ε is the same.
(i) What is the the specific heat of the system at very low temperatures?
(ii) The system is expanded and ε becomes smaller. What do you expect to happen to the specific heat of the system?

Solution.
See **D10.7**.
(1)
(i) The many-body ground state is realized by filling all the one-particle states from the one-particle ground state 0 to 1231th level. Therefore, the total energy must be

$$0 + \varepsilon + 2\varepsilon + \cdots + 1231\varepsilon = \frac{1231 \times 1232}{2}\varepsilon = 758296\varepsilon = 2311. \tag{21.131}$$

Therefore, $\varepsilon = 3.048 \times 10^{-3}$ eV.
(ii) At very low temperatures the canonical partition function reads (here, the energy origin is chosen to be the many-body ground state energy E_0)

$$Z = 1 + e^{-\beta\varepsilon} + 2e^{-2\beta\varepsilon} + \cdots. \tag{21.132}$$

Actually, we may ignore the second term and beyond. Therefore, the internal energy relative to the many-body ground state energy is

$$E - E_0 = -\frac{\partial \log Z}{\partial \beta} = \frac{\varepsilon(e^{-\beta\varepsilon} + \cdots)}{1 + e^{-\beta\varepsilon} + \cdots}. \tag{21.133}$$

The specific heat is

$$C(T) = \frac{dE}{dT} = \frac{d}{dT}\frac{\varepsilon}{e^{\beta\varepsilon} + 1} = \frac{\varepsilon^2 T^{-2} e^{\beta\varepsilon}}{(e^{\beta\varepsilon} + 1)^2} \simeq \frac{\varepsilon^2}{T^2} e^{-\beta\varepsilon}. \tag{21.134}$$

Notice that this is, as expected, the Schottky type specific heat due to the energy gap just above the (many-body) ground state.

(2)
(i) At very low temperatures the canonical partition function reads

$$Z = 1 + e^{-\beta\varepsilon} + 2e^{-2\beta\varepsilon} + \cdots \tag{21.135}$$

Therefore, the answer is just the same as (1)(ii).
(ii)

$$\frac{dC}{d\varepsilon} = \frac{1}{T^2}(2\varepsilon - \beta\varepsilon^2)e^{-\beta\varepsilon}, \tag{21.136}$$

so if $k_BT < \varepsilon/2$ (See Fig. 13.1 in the lecture notes; the peak is $T_P = \varepsilon/2k_B$ as noted there), C decreases as a function of ε for fixed T. Therefore, if ε is decreased, for $T < T_P$ $C(T)$ increases. If ε is decreased, then the peak T_P shifts to the lower temperature (and the peak becomes steeper), so for $T < T_P$ $C(T)$ for fixed T increases, but on the other side $C(T)$ decreases.

22 Ideal quantum gases at very low temperatures

Summary
$*$ Elementary low temperature behaviors of non-interacting particle systems are discussed.
$*$ We will guess low temperature behaviors of E, S, μ for free fermions.

Key words
Fermi energy, Bose-Einstein condensation, condensate

What you should be able to do
$*$ You should be able to calculate various quantities for $T = 0$ fermion.
$*$ For E, μ $T \neq 0$ corrections start with the terms of order T^2. You must be able to explain why.
$*$ Understand why $C_V \propto T$ for fermions close to $T = 0$.
$*$ Remember the shape and rough scales of the derivative of the Fermi-Dirac distribution.
$*$ Understand why Bose-Einstein condensation occurs.

22.1 Noninteracting fermion at $T = 0$

The equation of state reads $PV = 2E/3$, so let us compute the internal energy at $T = 0$. The one particle states are completely filled up to the chemical potential $\mu(0)$ at $T = 0$, which is determined by

$$N = \int_0^{\mu(0)} d\varepsilon\, D_t(\varepsilon) = \gamma_0 V \int_0^{\mu(0)} \varepsilon^{1/2} d\varepsilon = \frac{2}{3}\gamma V \mu(0)^{3/2}. \tag{22.1}$$

Here, $D_t(\varepsilon) = \gamma_0 V \varepsilon^{1/2}$ with $\gamma_0 = 2\pi(2m/h^2)^{3/2}$ (recall **21.14**). We do not need details, but

$$\mu(0) \propto n^{2/3} \tag{22.2}$$

is worth remembering, where n is the number density.

The internal energy at $T = 0$ is given by

$$E(0) = \int_0^{\mu(0)} d\varepsilon\, D_t(\varepsilon)\varepsilon = \gamma_0 V \int_0^{\mu(0)} \varepsilon^{3/2} d\varepsilon = \frac{2}{5}\gamma_0 V \mu(0)^{5/2} = \frac{3}{5} N\mu(0). \tag{22.3}$$

The last formula should be obtainable by dimensional analysis except for the numerical factor. This implies

$$PV = \frac{2}{5} N\mu(0). \tag{22.4}$$

Notice that this is usually very large. You might have realized that at $T = 0$, $E = -PV + \mu(0)N$, so our familiar $E = 2PV/3$ gives us everything we wish.

22.2 Fermi energy and fermion pressure

$\mu(0) = \varepsilon_F$ is called the Fermi energy, and it is a materials constant. For ordinary metals, it is a few eV $\approx 5 \times 10^4$ K. If V is 10^{-3} m^3 for 1 mole of electrons, then $P \approx (6 \times 10^{23})(5 \times 10^4 \times 1.62 \times 10^{-19})/10^{-3} \approx 5 \times 10^{11}$ Pa.

22.3 Low temperature specific heat of electrons (fermions)

Let us intuitively discuss the electronic heat capacity of metals at low temperatures. We may assume that the Fermi-Dirac distribution is (almost) a step function. We can infer from the width of the 'avalanche region' of the cliff of the Fermi-Dirac distribution that the number of excitable electrons is $\sim Nk_BT$ at the temperature around T. We know generally that the specific heat is proportional to the number of the excitable degrees of freedom, so $C_V \propto T$ at lower temperatures. Thus, at sufficiently low temperatures this dominates the heat capacity of metals (where T^3 coming from the lattice vibration **16.12** is much less than T).

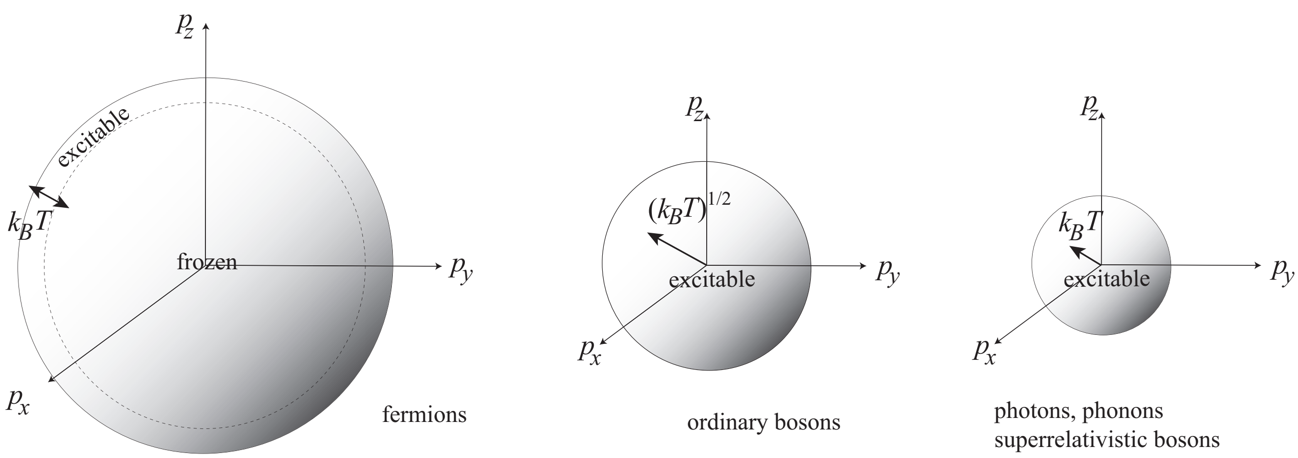

Figure 22.1: C_V is proportional to the number of degrees of freedom that may be excited at temperature T. For photons and phonons all the particles occupying the one particle states up to the energy $\sim k_BT$ can be excited, so in 3-space the specific heat is proportional to T^3 (this is also true for superrelativistic bosons). For fermion systems, among the occupied one particle states, only the particles within the width $\sim k_BT$ near the top of the occupied states can be excited, so $C_V \propto T$. These ideas may be used in any dimensional space.

22.4 Low temperature approximation for fermions

To get this result more quantitatively, we need a way to estimate the contribution of the cliff width. Let us look at the formula for N:

$$N = \int_0^\infty D(\varepsilon)\frac{1}{e^{\beta(\varepsilon-\mu)}+1}. \tag{22.5}$$

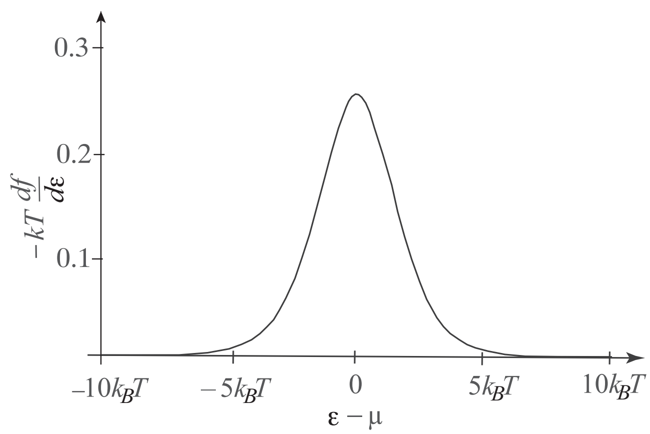

Figure 22.2: The derivative of the Fermi distribution. Its width is about $5k_BT$ and the height is $\beta/4$.

Let $f(\varepsilon) = 1/(e^{\beta(\varepsilon-\mu)}+1)$. Since we know $-f'(\varepsilon)$ is concentrated sharply around $\varepsilon = \mu$ (Fig. 22.2), we wish to exploit this fact:

$$\begin{aligned}\int_0^\infty \left[\int_0^\varepsilon D(\varepsilon')d\varepsilon'\right]' f(\varepsilon)d\varepsilon &= \int_0^\varepsilon D(\varepsilon')d\varepsilon' f(\varepsilon)\Big|_{\varepsilon=0}^{\infty} - \int_0^\infty d\varepsilon \left[\int_0^\varepsilon D(\varepsilon')d\varepsilon'\right] f'(\varepsilon)\\ &= -\int_0^\infty d\varepsilon\left[\int_0^\varepsilon D(\varepsilon')d\varepsilon'\right] f'(\varepsilon).\end{aligned} \tag{22.6}$$

Now, f' is localized around μ, so we need the quantity in [ ] only near $\varepsilon = \mu$. Therefore, let us Taylor-expand it as follows:

$$\begin{aligned}&-\int_0^\infty \left[\int_0^\mu D(\varepsilon')d\varepsilon' + D(\mu)(\varepsilon-\mu) + \frac{1}{2}D'(\mu)(\varepsilon-\mu)^2 + \cdots\right] f'(\varepsilon)d\varepsilon\\ &\qquad = \int_0^\mu D(\varepsilon')d\varepsilon' - \frac{1}{2}D'(\mu)\int_0^\infty (\varepsilon-\mu)^2 f'(\varepsilon)d\varepsilon + \cdots.\end{aligned} \tag{22.7}$$

Detailed calculation is not given here, but it is clear that the correction is of order T^2; the integral in the second term has the dimension of energy squared, so it must be proportional to $(k_BT)^2$. If we wish to compute E in the above calculation, D is replaced by εD, but the expansion method is exactly the same, so the correction term is proportional to T^2. That is, although we do not go through any detailed calculation, we can conclude with a certain positive number α (because E must increase with T) that

$$E(T) = E(0) + \frac{1}{2}\alpha T^2 + \cdots . \tag{22.8}$$

Therefore, as we have expected above, $C_V = \alpha T$ for sufficiently small T.

22.5 Low temperature entropy of fermion systems

We know

$$\left.\frac{\partial S}{\partial T}\right|_V = \frac{C_V}{T} = \alpha. \tag{22.9}$$

This implies that under V, N constant condition $S(T) = S(0) + \alpha T$, but $S(0) = 0$ is assumed usually, so we conclude that for sufficiently small T

$$S(T) = C_V. \tag{22.10}$$

22.6 Low temperature behavior of chemical potential

Now, let us study the T dependence of μ. You may probably guess that $\mu(T) = \mu(0) - O[T^2]$ from the above calculation. We know $\mu = G/N = (E - ST + PV)/N = (5E/3 - ST)/N$ for noninteracting systems. Therefore, we confirm our guess:

$$N\mu = \frac{5}{3}\left(E(0) + \frac{1}{2}\alpha T^2\right) - \alpha T^2 = \frac{5}{3}E(0) - \frac{1}{6}\alpha T^2. \tag{22.11}$$

What happens if the spatial dimension is 1? It is an increasing function of T for sufficiently low T.

22.7 Difficulty of continuum approximation at low temperatures for bosons

Next, let us study the free boson system. Let us take the ground state energy of the system to be the origin of energy. Then, the chemical potential cannot be positive. The total number of particles in the system of free bosons is given by

$$N = \sum_i \frac{1}{e^{\beta(\varepsilon_i - \mu)} - 1}. \tag{22.12}$$

If T is sufficiently small, the first term corresponding to the single-particle ground state can become very large (see Fig. 22.3), so in general it is dangerous to approximate (22.12) by integral with the aid of a smooth density of state as in the fermion case (in case of fermions, each term cannot be larger than 1, so there is no problem at all in this approximation).

Let us look at the difficulty in approximating (22.12) by an integration in 3-space. In this case the density of states has the form $D_t(\varepsilon) = \gamma V \varepsilon^{1/2}$ with some positive constant γ (see **21.14**). Let us write the continuous approximation to (22.12) as N_1:

$$N_1(T,\mu) \equiv \gamma V \int_0^\infty d\varepsilon \, \frac{\varepsilon^{1/2}}{e^{\beta(\varepsilon-\mu)} - 1}. \tag{22.13}$$

N_1 is a function of T and μ. It is an increasing function of T, and also an increasing function of μ. For a given T, if we can choose μ (which must be negative) satisfying $N = N_1$, then we can describe the system with a continuous approximation of the grand canonical ensemble with this μ.

Now, let us decrease the temperature. Then, N_1 decreases, so to keep $N_1 = N$ we must increase μ. However, we cannot indefinitely increase μ; $\mu = 0$ is the upper limit. Is there any guarantee that before reaching this limit, $N = N_1(T,\mu)$ may always be satisfied?

Since $N_1(T,\mu) \le N_1(T,0)$,

$$\gamma V \int_0^\infty d\varepsilon \, \frac{\varepsilon^{1/2}}{e^{\beta(\varepsilon-\mu)} - 1} \le \gamma V (k_B T)^{3/2} \int_0^\infty dz \frac{z^{1/2}}{e^z - 1}. \tag{22.14}$$

The integral on the right-hand side is finite. That is, with a positive constant A we may write

$$N_1(T,\mu) \le AVT^{3/2}. \tag{22.15}$$

The equality holds when $\mu = 0$. N_1 can be made indefinitely close to 0 by reducing T. However, the system should have N bosons independent of T, so there must be a temperature T_c at which

$$N = N_1(T_c, 0) \tag{22.16}$$

and for $T < T_c$

$$N > N_1(T, 0). \tag{22.17}$$

This is the difficulty of continuum approximation for low temperature bosons in 3-space.

22.8 (Bose-)Einstein condensation

The temperature T_c is called the *(Bose-)Einstein condensation temperature*; below this the continuous approximation breaks down. Notice that T_c is determined by (22.16) and

$$T_c \propto n^{2/3}. \tag{22.18}$$

Since the system must have N particles, the remaining $N_0 = N - N_1$ must occupy some one particle state. The only possibility is the ground state which is not properly taken into account by the continuous approximation.

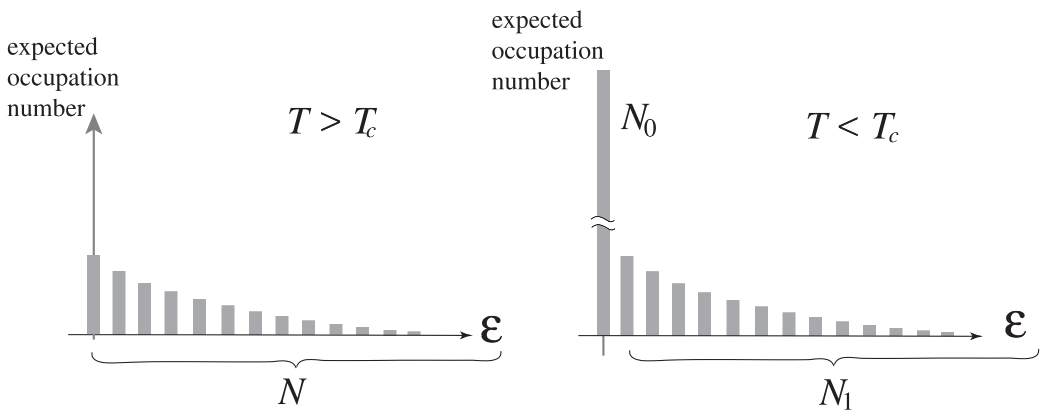

Figure 22.3: If $T < T_c$, where T_c is the Bose-Einstein condensation temperature, then the ground state is occupied by $N_0 = O[N]$ particles, so the approximation of (22.12) by an integral becomes grossly incorrect.

A macroscopic number N_0 $(= N - N_1)$ of particles fall into the lowest energy one particle state (see Fig. 22.3). This phenomenon is called a *(Bose-)Einstein condensation*. Notice that except for the ground state no other one particle states are occupied by macroscopic numbers of particles under any condition. Only the one-particle ground state can be occupied by a macroscopic number of particles below T_c. Here, 'macroscopic' implies that N_0/N is a positive number in the large system size limit ($N \to \infty$ limit, the thermodynamic limit).

22.9 Non-condensate population

From (22.14), we know that N_1 is an increasing function of μ, but we cannot increase μ indefinitely; μ must be non-positive. Hence, at or below a certain particular temperature T_c μ vanishes. That is, at $T = T_c$ the equality must hold in (22.14), so T_c is fixed by the condition (22.16), that is,

$$N = C(k_B T_c)^{3/2} \int_0^\infty dz \frac{z^{1/2}}{e^z - 1}. \tag{22.19}$$

Below T_c we have

$$N_1 = C(k_B T)^{3/2} \int_0^\infty dz \frac{z^{1/2}}{e^z - 1}. \tag{22.20}$$

Therefore, we get for $T \le T_c$ (Fig. 22.4)

$$N_1 = N \left(\frac{T}{T_c}\right)^{3/2}. \tag{22.21}$$

Thus the condensate population reads for $T \le T_c$.

$$N_0 = N \left[1 - \left(\frac{T}{T_c}\right)^{3/2}\right]. \tag{22.22}$$

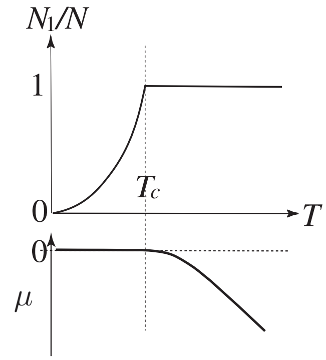

Figure 22.4: The ratio N_1/N of non-condensate atoms has a singularity at the Bose-Einstein condensation point T_c. The lower panel describes the chemical potential.

22.10 Bose-Einstein condensation does not occur in 2- and 1-spaces

No Bose-Einstein condensation occurs in one and two dimensional free spaces, because N_1 is not bounded from above. For example, in 2-space

$$N_1 = \int_0^\infty D_2(\varepsilon)\frac{1}{e^{\beta(\varepsilon-\mu)}-1}d\varepsilon, \tag{22.23}$$

where $D_2(\varepsilon)$ is the density of states of a single particle in 2-space. Let us repeat our quick derivation:

$$\int_0^\varepsilon d\varepsilon D_2(\varepsilon) = \frac{V}{h^2}\int_{\boldsymbol{p}^2/2m\le\varepsilon} d\boldsymbol{p} = \frac{2\pi V}{h^2}\int_0^{\sqrt{2m\varepsilon}} pdp, \tag{22.24}$$

so

$$D_2(\varepsilon) = \frac{2\pi V}{h^2}\sqrt{2m\varepsilon}\frac{d\sqrt{2m\varepsilon}}{d\varepsilon} = cV, \tag{22.25}$$

where c is a constant. Therefore,

$$N_1 \propto V\int_0^\infty \frac{1}{e^{\beta(\varepsilon-\mu)}-1}d\varepsilon. \tag{22.26}$$

We know N_1 must be an increasing function of μ and the largest possible μ is zero for bosons, so

$$\int_0^\infty \frac{1}{e^{\beta(\varepsilon-\mu)}-1}d\varepsilon \le \int_0^\infty \frac{1}{e^{\beta\varepsilon}-1}d\varepsilon. \tag{22.27}$$

The integral on the right-hand side blows up from the contribution close to $\varepsilon = 0$; there $1/(e^{\beta\varepsilon}-1) \simeq 1/\beta\varepsilon$, so the integral diverges logarithmically. Therefore, for any N and T, we can find $\mu < 0$ such that $N = N_1$. Thus, there is no Bose-Einstein condensation.

Why don't you check the 1D case?

22.11 Continuum approximation is always valid for E and P

Notice that the integral expression for E or PV is still all right, because for these quantities the ground state does not contribute at all.[352]

22.12 Low temperature heat capacity of bose systems

The Bose-Einstein condensate (i.e., N_0) does not contribute to internal energy, so we may use the continuum approximation to compute the internal energy. Below T_c we may set $\mu = 0$, so

$$E = \int_0^\infty d\varepsilon D(\varepsilon) \frac{\varepsilon}{e^{\beta\varepsilon} - 1}. \tag{22.28}$$

In 3-space, we know $D(\varepsilon) = \gamma V \varepsilon^{1/2}$ with γ being a positive constant. Therefore, for $T < T_c$

$$E = \gamma V \int_0^\infty d\varepsilon\, \varepsilon^{1/2} \frac{\varepsilon}{e^{\beta\varepsilon} - 1} = \gamma V \beta^{-5/2} \int_0^\infty d(\beta\varepsilon) \frac{(\beta\varepsilon)^{3/2}}{e^{\beta\varepsilon} - 1} \propto V T^{5/2}. \tag{22.29}$$

(More easily, we can simply count the power of ε. Here, we have $d\varepsilon$, $\varepsilon^{1/2}$ and ε, so $\varepsilon^{5/2}$ is the 'dimension of the integral.' The only relevant quantity with the dimension of energy is $k_B T$, so this integral must be proportional to $T^{5/2}$.) From this the low temperature heat capacity is

$$C_V \propto \left(\frac{T}{T_c}\right)^{3/2}. \tag{22.30}$$

This goes to zero with T as required by the third law **16.5**.

Notice that C_V is proportional to the number of degrees of freedom excitable at around T (recall Fig. 22.1).

[352] Accurately speaking, a careful calculation shows that the ground-state contributions to E and P are of order $\log N$, which we may ignore. If not, the grand canonical formalism cannot be applied in any case.

Q22.1 [Density of state]
Find the density of states $D(\varepsilon)$ (for the translational degrees of freedom) of a single particle in the volume V in 2-space with the super-relativistic dispersion relation $\varepsilon = c|\boldsymbol{p}|$.

Solution.
Here, I give the most general solution with (fairly detailed) explanation: in d-space with the dispersion relation $\varepsilon = \alpha|\boldsymbol{p}|^\gamma$, where α is a positive constant. Our strategy is always the same. If we can study the classical phase volume, dividing it with h^d in d-space, we can obtain the number of states for a single particle. The single-particle states with energy not exceeding ε corresponds to those with the momenta satisfying $|\boldsymbol{p}| \leq (\varepsilon/\alpha)^{1/\gamma}$ Therefore, the number of the single-particle states with energy less than ε may be written in two ways:

$$\int_0^\varepsilon d\varepsilon\, D(\varepsilon) = \frac{1}{h^d}\int_{\boldsymbol{q}\in V} d^d\boldsymbol{q} \int_{|\boldsymbol{p}|\leq(\varepsilon/\alpha)^{1/\gamma}} d^d\boldsymbol{p}.$$

The right-hand side may be rewritten by computing the position-coordinate integral (that gives V) and by introducing the polar coordinate system

$$\int_0^\varepsilon d\varepsilon\, D(\varepsilon) = \frac{1}{h^d} V \int_0^{(\varepsilon/\alpha)^{1/\gamma}} S_{d-1}p^{d-1}dp,$$

where S_{d-1} is the volume of $d-1$-unit sphere, whose general form may be found in my graduate course notes. To obtain $D(\varepsilon)$, we simply differentiate the above identity:[353]

$$D(\varepsilon) = \frac{V}{h^d}S_{d-1}(\varepsilon/\alpha)^{(d-1)/\gamma}\frac{d(\varepsilon/\alpha)^{1/\gamma}}{d\varepsilon} = \frac{V}{h^d}S_{d-1}\frac{\varepsilon^{(d-1)/\gamma}}{\alpha^{d/\gamma}}\frac{d\varepsilon^{1/\gamma}}{d\varepsilon} = \frac{S_{d-1}V}{\gamma h^d}\frac{\varepsilon^{d/\gamma-1}}{\alpha^{d/\gamma}}.$$

For $d = 3$ and $\gamma = 2$ (the usual particle in 3-space), $S_2 = 4\pi$, $\alpha = 1/2m$ and we recover the formula we know well

$$D(\varepsilon) = 2\pi\frac{V}{h^3}(2m)^{3/2}\varepsilon^{1/2}.$$

For the problem case $d = 2$, $\gamma = 1$, $S_1 = 2\pi$, and $\alpha = c$, so

$$D(\varepsilon) = 2\pi\frac{V}{h^2}\frac{\varepsilon}{c^2}.$$

Of course, this has 'almost' been given when we studied Planck's formula.

Q22.2 [Ideal bosons in 2-harmonic trap]

[353] $f(x) = g(x)$ means $f'(x) = g'(x)$ if the first equality is an identity (and differentiable) in x.

There is a 2-harmonic trap $U = (1/2)\alpha x^2$,[354] where x is the distance from the origin, and α is a positive constant. We know the single particle energy levels in this trap are denoted as

$$\varepsilon = \hbar\omega(1 + n_1 + n_2), \tag{22.31}$$

where $n_1, n_2 \in \boldsymbol{N} = \{0, 1, 2. \cdots\}$, and ω is a positive constant.
(1) The density of states $D(\varepsilon)$ is the number of states with energy between ε and $\varepsilon + d\varepsilon$. Here, however, to make the one particle ground state to be with zero energy, let us subtract the zero-point energy in the following. Therefore, we know

$$\int_0^\varepsilon d\varepsilon' \, D(\varepsilon') = \sum_{n_1+n_2 \in [0, \varepsilon/\hbar\omega]} 1. \tag{22.32}$$

Noting that the sum on the right-hand side is essentially the area of the shaded triangle in the following figure, obtain $D(\varepsilon)$.

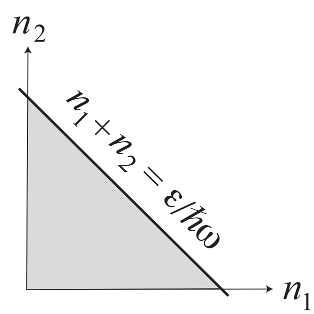

Figure 22.5: The relation between n_1, n_2 and $\varepsilon/\hbar\omega$. Here, the zero-point energy ($\hbar\omega$) has been subtracted from ε.

(2) Is there a Bose-Einstein condensation in this 2D trap? [Hint. Compute N_1 and study whether it is finite or not for $\mu = 0$. Mimic our argument in 3D free space.]

Solution.
(1) As explained, the right-hand side must be the area of the triangle, so

$$\int_0^\varepsilon d\varepsilon' \, D(\varepsilon') = \frac{1}{2}\left(\frac{\varepsilon}{\hbar\omega}\right)^2.$$

Differentiating this with ε, we obtain

$$D(\varepsilon) = \frac{\varepsilon}{(\hbar\omega)^2} \propto \varepsilon.$$

(2) **Warning**: $\mu = 0$ below T_c is when we choose the ground state energy to be zero. We have already removed the zero-point energy, so we can consider $\mu = 0$.

[354] This can be realized on graphene.

Let us compute (the expectation value of) the total number N_1 of particles in the excited states for $\mu = 0$:

$$N_1 = \int_0^\infty d\varepsilon\, D(\varepsilon) \frac{1}{e^{\beta\varepsilon} - 1} \propto \int_0^\infty d\varepsilon\, \frac{\varepsilon}{e^{\beta\varepsilon} - 1} = k_B T \int_0^\infty dz\, \frac{z}{e^z - 1}.$$

This integral is finite: the dangerous contribution comes from small z, because for large z the integrand is exponentially small. For small z the integrand tends to a constant, so the integral is finite, and N_1 can be indefinitely small for sufficiently small T. Therefore, $N_0 = N - N_1$, the condensate population, must be macroscopic. That is, we can expect a Bose-Einstein condensation.

Q22.3 [Isoenergetic compression]
There are $2N$ non-interacting fermions in a container of volume V. While the volume is isoenergetically halved (that is $V \to V/2$ while E is kept constant), two fermions react to make a single boson. After the reaction completed, all the fermions are converted into non-interacting bosons (i.e., N bosons in volume $V/2$ with internal energy E). Assume that the chemical potential of the initial fermion system is 0.7 eV and its temperature is $T = 0$. Is the final temperature higher than 5×10^3 K? You MUST justify your answer, since guessing the answer may not be very hard. [Hint: the 'bomb question.']

Solution.
The total energy of the original system would be estimated from the $T = 0$ formula as $E = (3/5)2N\mu(0)$. After the reaction we have N bosons. We know for given T, N and V, $P_{MB} > P_{BE}$, but if E, N and V are the same $P_{MB} = P_{BE} = (2/3)E/V$. From $P_{MB}(V/2) = Nk_BT_{MB} = (2/3)E$, we have

$$T_{MB} = \frac{2E}{3Nk_B} = \frac{2}{3}\frac{6N\mu}{5Nk_B} = \frac{4\mu}{5k_B}.$$

This is equal to 0.56 eV$/k_B \simeq 6000$ K $> 5 \times 10^3$ K. That is, classical gas would have about this temperature.

To estimate the boson system temperature is actually rather delicate, but the following argument tells us that the final temperature is definitely higher than 5×10^3 K. The pressure of any gas is an increasing function of T. If the temperature is the same, that is, if T, N, and V are the same, $P_{MB} > P_{BE}$, but in our case they are identical, so the actual temperature of the final bosonic system must be higher than T_{MB}.

Q22.4 [Ideal quantum system volume change] Watch out for trivial questions Assume that the particles do not interact, and answer the following questions for **both** ideal bosons and ideal fermions (both without any internal degree of freedom).

(1) The volume V is increased under constant internal energy. Does the temperature decrease? Assume that the initial temperature is sufficiently low (below T_c for

bosons).
(2) The volume V is increased under constant entropy. Does the temperature decrease?
(3) The volume V is increased under constant temperature. Does the pressure decrease?

Solution.
(1) If the volume is increased, the level spacings decrease.
(F) For fermions, if this happens at a very low temperature, then particles must be excited to go beyond the Fermi energy. Thus, T increases. More quantitatively, let us 'head-on' consider

$$\left.\frac{\partial T}{\partial V}\right|_E = \frac{\partial(T,E)}{\partial(V,E)} = \frac{\partial(T,E)}{\partial(V,T)}\frac{\partial(V,T)}{\partial(V,E)} = -\frac{1}{C_V}\left.\frac{\partial E}{\partial V}\right|_T. \tag{22.33}$$

Using the Gibbs relation, we get

$$\left.\frac{\partial E}{\partial V}\right|_T = T\left.\frac{\partial S}{\partial V}\right|_T - P, \tag{22.34}$$

but

$$\left.\frac{\partial S}{\partial V}\right|_T = \frac{\partial(S,T)}{\partial(V,T)} = \frac{\partial(S,T)}{\partial(V,P)}\frac{\partial(V,P)}{\partial(V,T)} = \left.\frac{\partial P}{\partial T}\right|_V \tag{22.35}$$

with the aid of a Maxwell's relation. Using $P = 2E/3V$,

$$\left.\frac{\partial S}{\partial V}\right|_T = \frac{2C_V}{3V}. \tag{22.36}$$

Thus,

$$\left.\frac{\partial E}{\partial V}\right|_T = \frac{2}{3V}(TC_V - E). \tag{22.37}$$

For free fermions, we know E at low temperatures has a big T-independent chunk E_0, so for sufficiently low temperatures, this derivative must be negative. Hence, (22.33) must be positive.
(B) We know classically T is constant, so we could guess that for bosons T must decrease. Since the level spacings shrink generally, the gap between the ground state and the first excited state also shrinks. This destabilizes the condensate (makes them easier to 'evaporate' into non-condensate state). Thus, the total energy increases. Therefore, you must cool the system to keep E. That is, T goes down as expected. Needless to say, under this condition the contribution from the non-condensate is opposite, but its low-lying energy states are much less populated than the ground state below T_c, so you must cool the system. More quantitatively, the boson case is easy: Since we may assume $\mu = 0$, we know

$$E = TS - PV = TS - \frac{2}{3}E \;\; \Rightarrow \;\; E = \frac{3}{5}TS. \tag{22.38}$$

Expanding V reduces the condensate, so S increases. Hence, T must be decreased under constant E. In this case we can do better: we can explicitly obtain E from integration

$$E = \int d\varepsilon\, D_t(\varepsilon) \frac{\varepsilon}{e^{\beta\varepsilon} - 1} \propto VT^{5/2}, \tag{22.39}$$

so T must be decreased as $V^{-5/2}$. We could use (22.37) which is also correct for free bosons as well. We know $C_V \propto T^\theta$ for some $\theta > 0$ (of course, we know $\theta = 3/2$, but we do not need the exact value), so

$$TC_V - E = \frac{\theta}{1+\theta} TC_V > 0, \tag{22.40}$$

which is the opposite of fermions.
(2) Since the entropy is constant, we may imagine a situation in which the particles move with the energy levels. However, the level spacings decrease, so excitation would be easier with the initial temperature. To keep S we must maintain the shape of the occupation number distribution. In particular, the condensate population in case of (B) and the cliff shape in case of (F) must be maintained. Hence, T must be decreased. To be quantitative, we need

$$\left.\frac{\partial T}{\partial V}\right|_S = \frac{\partial(T,S)}{\partial(V,S)} = \frac{\partial(T,S)}{\partial(V,P)} \frac{\partial(V,P)}{\partial(V,S)} = -\frac{\partial(V,P)}{\partial(V,S)} \tag{22.41}$$

$$= -\frac{\partial(V,T)}{\partial(V,S)} \frac{\partial(V,P)}{\partial(V,T)} = -\frac{T}{C_V} \left.\frac{\partial P}{\partial T}\right|_V = -\frac{2T}{3V} < 0. \tag{22.42}$$

Here. our favorite $P = 2E/3V$ has been used.
(3) $(\partial P/\partial V)_T < 0$ thermodynamically!.

Q22.5 [1D Fermion system]
Consider a 1D ideal fermion system.
(1) Find the density of one particle states, assuming that the volume (length) is V.
(2) Obtain PV/E.
(3) Assuming that $E = E_0 + \alpha T^2/2$ for sufficiently small T, compute the entropy for sufficiently small T.
(4) Find the chemical potential μ to order T^2 using α.

Solution.
(1) Let us use our usual short cut:

$$\int_0^\varepsilon d\varepsilon D_t(\varepsilon) = \frac{V}{h} \int_{-\sqrt{2m\varepsilon}}^{\sqrt{2m\varepsilon}} dp = \frac{V}{h} 2\sqrt{2m\varepsilon} = \frac{2\sqrt{2m}V}{h} \varepsilon^{1/2}. \tag{22.43}$$

Therefore,

$$D_t(\varepsilon) = \frac{\sqrt{2m}V}{h} \varepsilon^{-1/2}. \tag{22.44}$$

(2) This implies (or comparing (22.43) and (22.44))

$$\int_0^\varepsilon d\varepsilon\, D_t(\varepsilon) = 2\varepsilon D_t(\varepsilon), \tag{22.45}$$

so

$$PV = \mp k_B T \int_0^\varepsilon d\varepsilon (2\varepsilon D_t(\varepsilon))' \log(1 \mp e^{-\beta(\varepsilon-\mu)}) = 2\int_0^\varepsilon d\varepsilon\, D_t(\varepsilon) \frac{\varepsilon}{e^{\beta(\varepsilon-\mu)} \mp 1} = 2E. \tag{22.46}$$

(3) From the formula for E, we get $C_V = \alpha T$. We know

$$\left.\frac{\partial S}{\partial T}\right|_V = \frac{C_V}{T} = \alpha, \tag{22.47}$$

so $S = C_V = \alpha T$, since $S(0) = 0$ (the third law; this is just the same as in 3-space).
(4) We know

$$N\mu = E - TS + PV = 3E - \alpha T^2 = 3E_0 + \frac{1}{2}\alpha T^2 = N\mu_0 + \frac{1}{2}\alpha T^2. \tag{22.48}$$

Notice that μ increases with T. This is the opposite of the case in 3-space.

If you repeat the above calculation in 2-space, you will realize that to order T^2, the chemical potential is independent of T.

Warning: In the above we used a fundamental thermodynamic relation $E = TS - PV + \mu N$. You might think that since we discuss systems with constant N, honestly speaking we are using the canonical ensemble, so the basic Gibbs relation is $dE = TdS - PdV$, so $E = TS - PV$ must be correct. Since $PV = 2E/3$, you might write $E = 2TS/5$. The RHS vanishes in the $T \to 0$ limit. However, for the fermion system, we say $E = E_0 + O[T^2]$, and E_0 is huge, usually. How come?

If you use the grand canonical ensemble, you must stick to it to be consistent. The energy zero is the zero of one particle state in this formalism (not the ground state energy of the whole system). This causes the discrepancy E_0, which is the ground state energy of the whole system relative to the ground state energy of a single particle (for the boson case, there is no discrepancy). That is, with $E = E_0 + O[T^2]$ you must use $E = TS - PV + \mu N$. $PV = 2E/3$ is derived with the aid of the grand canonical formalism, so this E contains E_0. The discrepancy occurs only when we discuss the fermion system.

An obvious lesson is that whenever you use E instead of δE, you must stick to your initial choice of the energy origin.

Q22.6 [Bosons below T_c]

Consider a non-interacting boson system below T_c in 3-space. Its internal energy E is proportional to $T^{5/2}$.
(1) Show this with the aid of statistical mechanics.

(2) Show this using thermodynamics, knowing that $PV = 2E/3$.
[Hint. Simply mimic what we did for the Stefan-Boltzmann law. You need not rederive the formulas derived in the lectures.]

Solution.
(1)

$$E = \int_0^\infty d\varepsilon\, D(\varepsilon)\frac{\varepsilon}{e^{\beta\varepsilon}-1} \propto \int_0^\infty d\varepsilon\, \varepsilon^{1/2}\frac{\varepsilon}{e^{\beta\varepsilon}-1} = \beta^{-5/2}\int_0^\infty d(\beta\varepsilon)\,(\beta\varepsilon)^{1/2}\frac{\beta\varepsilon}{e^{\beta\varepsilon}-1},$$

so indeed $E \propto T^{5/2}$.
(2) We use $E = TS - PV$, because $\mu = 0$. Therefore, we have

$$S = \frac{5E}{3T}.$$

Differentiating this wrt E under constant V, we get

$$-\frac{2}{3T} = -\frac{5}{3T^2}\left.\frac{\partial T}{\partial E}\right|_V E.$$

or

$$\frac{dE}{E} = \frac{5}{2}\frac{dT}{T}.$$

That is, $E \propto T^{5/2}$.

Q22.7 [Superrelativistic condensation?]
Consider bosons whose dispersion relation is ultrarelativistic, i.e., $\varepsilon = c|\boldsymbol{p}|$ (as photons).
(1) In 3-space, this system exhibits a Bose-Einstein condensation. What is the number density n dependence of the critical temperature T_c? (Find θ in $T_c \propto n^\theta$.)
(2) Is there any Bose-Einstein condensation in 2-space for these bosons? [Needless to say, you must justify your opinion.]

Solution.
(1) Let us compute the noncondensate population N_1 in 3D:

$$N_1 = \int d\varepsilon\, D_t(\varepsilon)\frac{1}{e^{\beta\varepsilon}-1}. \tag{22.49}$$

We need the density of (one particle states) D_t. Let us use a shortcut (or you can copy the needed result from somewhere in the lecture notes):

$$\int_0^\varepsilon D_t(\varepsilon)d\varepsilon = \frac{V}{h^3}\int_{|\boldsymbol{p}|<\varepsilon/c} d^3\boldsymbol{p} = \frac{V}{h^3}\frac{4\pi}{3}\frac{\varepsilon^3}{c^3}. \tag{22.50}$$

That is,

$$D_t(\varepsilon) = \frac{4\pi V}{h^3c^3}\varepsilon^2. \tag{22.51}$$

Therefore,

$$N_1 = \int d\varepsilon\, D_t(\varepsilon) \frac{1}{e^{\beta\varepsilon} - 1} \propto VT^3 \tag{22.52}$$

Therefore, at the critical temperature $n \propto T_c^3$, or $\theta = 1/3$.
(2) Let us compute the noncondensate population N_1 in 2D. We need the density of state in 2D:

$$\int_0^{\varepsilon} D_t(\varepsilon) d\varepsilon = \frac{V}{h^2} \int_{|\boldsymbol{p}|<\varepsilon/c} d^2\boldsymbol{p} = \frac{V}{h^2} \pi \frac{\varepsilon^2}{c^2}. \tag{22.53}$$

That is,

$$D_t(\varepsilon) = \frac{2\pi V}{h^2 c^2} \varepsilon. \tag{22.54}$$

Now the continuous expression of the number of particles is

$$N_1 = \int d\varepsilon\, D_t(\varepsilon) \frac{1}{e^{\beta(\varepsilon-\mu)} - 1} \le \int d\varepsilon\, D_t(\varepsilon) \frac{1}{e^{\beta\varepsilon} - 1}. \tag{22.55}$$

The question is whether this is finite or not. Since $D_t \propto \varepsilon$, and for small ε,

$$\frac{1}{e^{\beta\varepsilon} - 1} \sim \frac{k_B T}{\varepsilon}. \tag{22.56}$$

Therefore, there is no divergence of the integral due the small portion of ε. The integrand is exponentially small for large ε, N_1 is bounded from above by a constant proportional to VT^2. Therefore, there must be a Bose-Einstein condensation at sufficiently low temperatures.

Discussion 11

We will mainly discuss low temperature ideal quantum systems. The explanations of the problems may be read independently (so the same comments and formulas are often repeated).

D11.1 [Zeeman splitting][355]
An electron in the outer shell of an ion has magnetic moment of one Bohr magneton μ_B. In a magnetic field B,[356] this outer shell state splits into two energy levels with $E = E_0 \pm \mu_B B$ (down or up states; the up state is more stable, because it is parallel to B). The magnetization $M = \mu_B(n_u - n_d)$, where n_u (resp., n_d) is the occupation number of the up (resp., down) state. You can assume that electrons do not interact with each other.
(1) Find $\langle M \rangle$ and $\langle N \rangle$ with a grand canonical ensemble,[357] assuming that there are N ions.
(2) Give the average magnetization when the outer shell contains exactly one electron, and compare it with the result for $\mu = E_0$ in (1).
Solution
(1) Notice that even if we prepare one chemostat for electrons, there are different interpretations of GCS.
(i) For each ion there are two states. You could imagine these two states could be 'connected to the chemostat' separately. Then, the grand-canonical partition function is (that is, each level may be occupied by at most one electron)

$$\Xi = \left(1 + e^{-\beta(E_0 - \mu_B B - \mu)}\right)^N \left(1 + e^{-\beta(E_0 + \mu_B B - \mu)}\right)^N. \tag{22.57}$$

(ii) If each ion is occupied by at most one electron, the GCE reads

$$\Xi = \left(1 + e^{-\beta(E_0 - \mu_B B - \mu)} + e^{-\beta(E_0 + \mu_B B - \mu)}\right)^N. \tag{22.58}$$

From these

$$\beta PV = \log \Xi. \tag{22.59}$$

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[356]Actually the field is in the z-direction, and B is its z-component.

[357][This is a comment for those who are extremely careful about logic.] What is written here is the way the usual books ask the question, but, strictly speaking, it is not the usual GCE explained in the books (and in my lecture notes), because B is also fixed (M is not fixed), so $E - ST - \mu N - MB$ is the Legendre transformation, instead of the usual $E - ST - \mu N$. It is, HOWEVER, still $PV = ST + \mu N + BM - E$ is the corresponding thermodynamic potential.

What is the conclusion of this precise argument? You must be careful when you use the Gibbs relation. If B is fixed instead of M $-d(PV) = -SdT - PdV - Nd\mu - MdB$ rather than $-d(PV) = -SdT - PdV - Nd\mu + BdM$.

In practice, you may regard the GCE as the ensemble for which all the extensive quantities but V are allowed to change by fixing their corresponding conjugate intensive variables.

The corresponding Gibbs relation reads

$$d(\beta PV) = -Ed\beta + \beta PdV + Nd(\beta\mu) + Md(\beta B). \tag{22.60}$$

Therefore:
For (i)

$$\langle N\rangle/N = \frac{\partial \log \Xi}{\partial \beta\mu} = \frac{1}{e^{\beta(E_0-\mu_B B-\mu)}+1} + \frac{1}{e^{\beta(E_0+\mu_B B-\mu)}+1}, \tag{22.61}$$

$$\langle M\rangle/N = \frac{\partial \log \Xi}{\partial \beta B} = \frac{\mu_B}{e^{\beta(E_0-\mu_B B-\mu)}+1} - \frac{\mu_B}{e^{\beta(E_0+\mu_B B-\mu)}+1}. \tag{22.62}$$

For (ii)

$$\langle N\rangle/N = \frac{\partial \log \Xi}{\partial \beta\mu} = \frac{e^{-\beta(E_0-\mu_B B-\mu)} + e^{-\beta(E_0+\mu_B B-\mu)}}{1+e^{-\beta(E_0-\mu_B B-\mu)} + e^{-\beta(E_0+\mu_B B-\mu)}}, \tag{22.63}$$

$$\langle M\rangle/N = \frac{\partial \log \Xi}{\partial \beta B} = \frac{e^{-\beta(E_0-\mu_B B-\mu)} - e^{-\beta(E_0+\mu_B B-\mu)}}{1+e^{-\beta(E_0-\mu_B B-\mu)} + e^{-\beta(E_0+\mu_B B-\mu)}}, \tag{22.64}$$

(2)
Interpretation (i): For $\langle N\rangle/N = 1$ we must solve $x = e^{\beta(E_0-\mu)}$ from

$$1 = \frac{1}{1+x/y} + \frac{1}{1+xy} = \frac{2+x(y+1/y)}{1+x(y+1/y)+x^2}, \tag{22.65}$$

where $y = e^{\beta\mu_B B}$. Therefore, for any y $x = 1$ is the solution. That is, $E_0 = \mu$ is the condition. Under this condition,

$$\langle M\rangle = \mu_B\left(\frac{1}{1+1/y} - \frac{1}{1+y}\right) = \mu_B\frac{y-1}{y+1} = \mu_B\frac{e^{\beta\mu_B B}-1}{e^{\beta\mu_B B}+1} = \mu_B \tanh\frac{\beta\mu_B B}{2}. \tag{22.66}$$

Interpretation (ii): For $\langle N\rangle/N = 1$ we must solve $x = e^{\beta(E_0-\mu)}$ from

$$1 = \frac{y+1/y}{x+y+1/y}, \tag{22.67}$$

so again $x = 0$ or $E_0 = \mu$ is the condition. Therefore,

$$\langle M\rangle = \mu_B\frac{y-1/y}{y+1/y} = \mu_B\frac{e^{\beta\mu_B B}-e^{-\beta\mu_B B}}{e^{\beta\mu_B B}+e^{-\beta\mu_B B}} = \mu_B \tanh\beta\mu_B B. \tag{22.68}$$

Thus, this agrees with the (micro)canonical case we have already encountered in the notes.

What is the lesson? If many ions are embedded in a medium that may allow the exchange of electrons (and electron-electron interaction on the same ion negligible)

(i) may well be realistic. However, if ions are isolated (ii) is realistic (as we have confirmed).

Semi-quantitative questions

The following problems are semi-quantitative questions about low temperature ideal systems.

In answering this type of questions recall some obvious facts:
(i) How the (one-particle) energy levels of a single particle confined in a box changes, if its volume is changed: If squished, the level spacings widen, and if expanded, they shrink (Fig. 22.6).

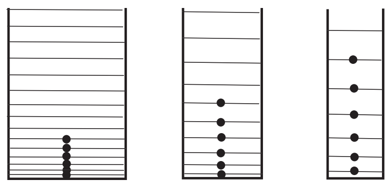

Figure 22.6: If the system is compressed, the spacings between energy levels widen; if expanded, they shrink.

(ii) If particles' energies shift with the energy levels (as if the particles just perch on the shifting energy levels), then the system changes adiabatically and reversibly; the system entropy stays constant.[358]
(iii) Try to use thermodynamics as much as possible. Recall $E = TS - PV + \mu N$[359] **20.4**.
(iv) $PV = 2E/3$ is universal[360] **21.15**.
(v) Recall how to 'guess' one-particle state density: D_t **21.14**; often dimensional analysis works.
(vi) Very low temperature features of average occupation numbers: fermions are with sharp cliffs (of width $\sim k_BT$; recall Figs. 21.2 and 22.2); bosons below T_c are with $\mu = 0$ (cf. Fig. 22.4).

D11.3 [Pressure changes under various conditions]
Assume that the particles do not interact, and answer the following questions for **both** ideal bosons and ideal fermions (both without any internal degree of freedom). You may assume that the initial temperature is sufficiently low (e.g., well below T_c for bosons). If your argument is sufficiently convincing in terms of elementary physics,

[358]This is the so-called quantum adiabatic change. Quantum adiabatic change is an example of thermodynamic adiabatic changes. However, it is an extremely special (unrealizably special, I should say) case. Such a process certainly preserves entropy, but it is far from necessary.
[359]As long as we keep the energy origin to be the one-particle ground state. Read, however, an important warning in **7**.
[360]As long as the system is 3-dimensional and the kinetic energy is given by $mv^2/2$.

you need not demonstrate your answers with the aid of formulas, but I strongly recommend you to check your intuitive answer using thermodynamics and/or statistical mechanics.

(1) The pressure P is increased under constant internal energy. Does the temperature of the gas increase? Assume that the initial temperature is sufficiently low (below T_c for bosons).
(2) The pressure P is increased under constant entropy. Does the temperature of the gas increase?
(3) The pressure P is increased under constant volume. Does the temperature of the gas increase?

Solution.
(1) Since E is constant, PV must be constant, so V must decrease. Decreasing V implies increase of the one particle level spacings.
(1F) For fermions, if T is low, to prevent E from increasing, you must cool the system further.

If you wish to proceed with minimum intuition, do the following.[361]

$$\left.\frac{\partial T}{\partial V}\right|_E = \frac{\partial(T,E)}{\partial(V,E)} = \frac{\partial(T,E)}{\partial(V,T)}\frac{\partial(V,T)}{\partial(V,E)} = -\frac{1}{C_V}\left.\frac{\partial E}{\partial V}\right|_T. \tag{22.69}$$

Although it is possible to calculate the partial derivative for an arbitrary T,[362] at $T = 0$ we can estimate it (as done in the lecture) easily from the $E(0)$-$\mu(0)$ relation:

$$\left.\frac{\partial E}{\partial V}\right|_T = -\frac{2}{3}\frac{E}{V} < 0. \tag{22.70}$$

Therefore, at $T = 0$

$$\left.\frac{\partial T}{\partial V}\right|_E = \frac{2}{3C_V}\frac{E}{V} > 0. \tag{22.71}$$

This is continuous, so for sufficiently low T this must also be true. Therefore, decreasing V under constant E requires decrease of T. Notice that (22.70) is for fermions, so the inequality is not sacred.

For a classical ideal gas E constant means T constant. That is, $(\partial T/\partial V)_E = 0$.

[361] If you wish to be more direct, start with

$$\left.\frac{\partial T}{\partial P}\right|_E = \left.\frac{\partial T}{\partial(2E/3V)}\right|_E = \frac{3}{2E}\left.\frac{\partial T}{\partial(1/V)}\right|_E = -\frac{3V^2}{2E}\left.\frac{\partial T}{\partial V}\right|_E.$$

[362] As we will see in (22.99):

$$\left.\frac{\partial E}{\partial V}\right|_T = \frac{2}{3V}(TC_V - E).$$

Since $E = E(0) + O[T^2]$ with a huge $E(0)$ for fermions, this is negative for lower temperatures. Thus, $(\partial T/\partial V)_E > 0$.

This 'strongly' suggests that for bosons $(\partial T/\partial V)_E < 0$, so for bosons we expect that T increases.
(1B) If you decrease V, then the amount of condensate increases (recall (i): condensate is less easy to evaporate), but this means the decrease of E, so you must raise the temperature to keep E.

How can you proceed less 'intuitively'? The most direct way is to use E, since $T < T_c$: $E \propto VT^{5/2} \propto (E/P)T^{5/2}$. Therefore, $P \propto T^{5/2}$. Thus, T increases. Another way is to evaluate (22.69) or $(\partial T/\partial V)_E$. We know $C_V \propto T^\alpha$ (actually $\alpha = 3/2$ as you can easily guess from counting the number of excitable degrees of freedom; recall Fig. 22.1 in the notes). $C_V = AT^\alpha$ with a positive constant A. Therefore. (I am cheating here to use footnote 8)

$$\left.\frac{\partial E}{\partial V}\right|_T \propto TC_V - E \propto A\left(T^{1+\alpha} - \frac{1}{1+\alpha}T^{1+\alpha}\right) = A\left(\frac{\alpha}{1+\alpha}T^{1+\alpha}\right) > 0. \quad (22.72)$$

Thus, the sign for bosons is opposite to that for fermions.

(2) If we increase V, the level spacings shrink. Under constant S (adiabatic), you may imagine that particles shift with the levels. This is possible only if you lower T. That is, for ideal quantum systems

$$\left.\frac{\partial T}{\partial V}\right|_S < 0. \quad (22.73)$$

That is, $(\partial T/\partial P)_S > 0$, because[363]

$$\left.\frac{\partial T}{\partial P}\right|_S = \left.\frac{\partial T}{\partial V}\right|_S \left.\frac{\partial V}{\partial P}\right|_S, \quad (22.74)$$

but the second partial derivative is negative (sacred) due to the convexity of E $(\partial^2 E/\partial V^2)_S > 0)$.

If you do not believe the logic leading to (22.73), calculate it:

$$\left.\frac{\partial T}{\partial V}\right|_S = \frac{\partial(V,T)}{\partial(V,S)}\frac{\partial(T,S)}{\partial(V,T)} = \frac{T}{C_V}\frac{\partial(T,S)}{\partial(V,P)}\frac{\partial(V,P)}{\partial(V,T)} \quad (22.75)$$

$$= -\frac{T}{C_V}\left.\frac{\partial P}{\partial T}\right|_V. \quad (22.76)$$

Now, we use $E = 3PV/2$:

$$\left.\frac{\partial T}{\partial V}\right|_S = -\frac{2T}{3VC_V}\left.\frac{\partial E}{\partial T}\right|_V = -\frac{2T}{3V} < 0. \quad (22.77)$$

[363]Improved by Jahan.

Here, the signs are statistics-independent, BUT not sacred, because we have used the equation of state.

We could directly compute what we want (our strategy is to get rid of S as much as possible):

$$\left.\frac{\partial T}{\partial P}\right|_S = \frac{\partial(T,S)}{\partial(P,T)}\frac{\partial(P,T)}{\partial(P,S)} = \frac{T}{C_P}\frac{\partial(T,S)}{\partial(P,V)}\frac{\partial(P,V)}{\partial(P,T)} = \frac{T}{C_P}\frac{\partial(P,V)}{\partial(T,V)}\frac{\partial(T,V)}{\partial(P,T)} \tag{22.78}$$

$$= -\frac{T}{C_P}\left.\frac{\partial V}{\partial P}\right|_T\left.\frac{\partial P}{\partial T}\right|_V = -\frac{T}{C_P}\left.\frac{\partial V}{\partial P}\right|_T\frac{2}{3V}\left.\frac{\partial E}{\partial T}\right|_V = -\frac{2TC_V}{3VC_P}\left.\frac{\partial V}{\partial P}\right|_T > 0. \tag{22.79}$$

(3) Let us compute (actually we just did this above)

$$\left.\frac{\partial T}{\partial P}\right|_V = \left.\frac{\partial T}{\partial(2E/3V)}\right|_V = \frac{3V}{2}\left.\frac{\partial T}{\partial E}\right|_V = \frac{3V}{2C_V} > 0. \tag{22.80}$$

Thus, for any ideal gas this is positive, so T must increase.

D11.4 [Quasistatic adiabatic expansion][364]

There is an ideal gas in a box with a piston. The whole system is thermally isolated. We double the volume in a quasiequilibrium fashion. Let the initial pressure be P_i and the initial temperature T_i.

Suppose the ideal gas consists of noninteracting fermions without any internal excitations.

(1F) Obtain the final pressure P_f in terms of the initial pressure P_i.

(2F) If $T_i = 0$, what is the final temperature T_f?

(3F) Suppose $T_i > 0$. What can you say about T_f?

Next, let us assume the ideal gas is a non-interacting bose gas.

(1B) Obtain the final pressure P_f in terms of the initial pressure P_i.

(2B) If $T_i = 0$, what is the final temperature T_f?

(3B) Find T_f in terms of T_i.

(4B) Let N_{0i} be the number of particles in the condensate initially. Is N_{0f}, the final number of particles in the condensate, larger or smaller than N_{0i} or unchanged?

Solution.

(1F) Use thermodynamics as much as you can. This problem is adiabatic and quasiequilibrium, so S does not change. Therefore,

$$dE = -PdV. \tag{22.81}$$

With the aid of $PV = (2/3)E$ or $P = 2E/3V$

$$dE = -\frac{2}{3}\frac{E}{V}dV. \tag{22.82}$$

[364] Discussed in a lecture, but let us record it here with more details.

This implies $EV^{2/3} =$ constant. That is, $PV^{5/3}$ is constant.

$$P_f(2V)^{5/3} = P_i V^{5/3}, \tag{22.83}$$

or

$$P_f = \frac{1}{2^{5/3}} P_i. \tag{22.84}$$

This is statistics-independent.

(2F) $T_f = 0$ is expected. Indeed, as we know at $T = 0$,

$$E = \int_0^{\mu(0)} d\varepsilon D_t(\varepsilon)\varepsilon = \frac{3}{4}\mu(0)N \propto N^{5/3}V^{-2/3}. \tag{22.85}$$

but we already know that $EV^{2/3}$ is constant. Thus, the $T = 0$ relation is maintained.

The isothermal and adiabatic processes can coincide only at $T = 0$. In our case the system is adiabatic, so if $T > 0$, then the temperature must change, but the system is loosing energy by doing work, so T cannot increase. Thus, T cannot help staying at $T = 0$. This argument, which is indifferent to statistics, also answers (3F), but we can do it more mechanically as follows.

(3F) We study $(\partial T/\partial E)_S$ or more directly $(\partial T/\partial V)_S$. Since $dE = -PdV$ under constant S,

$$\left.\frac{\partial T}{\partial E}\right|_S = -\frac{1}{P}\frac{\partial(T,S)}{\partial(V,S)} = -\frac{1}{P}\frac{\partial(T,S)}{\partial(P,V)}\frac{\partial(P,V)}{\partial(V,S)} = \frac{1}{P}\left.\frac{\partial P}{\partial S}\right|_V. \tag{22.86}$$

$$\left.\frac{\partial P}{\partial S}\right|_V = \frac{\partial(T,V)}{\partial(S,V)}\frac{\partial(P,V)}{\partial(T,V)} = \frac{T}{C_V}\left.\frac{\partial P}{\partial T}\right|_V. \tag{22.87}$$

For a gas (noninteracting system) the rightmost derivative is positive (due to mechanics; recall D Bernoulli or see the computations we already did in **4**). Therefore, $(\partial T/\partial E)_S > 0$ or $(\partial T/\partial V)_S < 0$. Since our system loses E (increases V), T must decrease as we argued at the end of (2F).

(1B) We already know the answer does not depend on statistics.

(2B) The argument in (3F) is purely thermodynamic, so $T_f = 0$ as well.

(3B) We know the system cools. In this case we can be quantitative. Since BCE occurs, $\mu = 0$, so

$$E = \int_0^\infty d\varepsilon\, D_t(\varepsilon)\frac{\varepsilon}{e^{\beta\varepsilon} - 1} \propto VT^{5/2}. \tag{22.88}$$

We already know $EV^{2/3}$ is constant independent of statistics (from the equation of state and thermodynamics; statistics-independent). Therefore, $V^{5/3}T^{5/2}$ is conserved. That is, $V^{2/3}T$ is constant. Therefore, $T_f = 2^{-2/3}T_i$.

(4B) We can expect that there should not be any change, because it is an adiabatic quasistatic process, so on the average the occupation number of the particles in the ground state should not change. If you realize this, no calculation is needed.

If you wish to check the conclusion with a concrete calculation, let us start with $N_{0i} = N - N_{1i}$, where $N_{1i} = cVT_i^{3/2}$, but we already know $V^{2/3}T$ is constant. Therefore, N_0 cannot change.

As you have seen, this problems is statistics indifferent, but you can exploit the indifference only if you use the universal equation of state and thermodynamics.

D11.5 [Isothermal compression]
There is a cylinder with a piston. It contains N identical particles and is maintained at a constant temperature T.
Fermion case
(F1) Suppose the system is maintained at $T = 0$. The volume is halved reversibly. The initial energy per particle is e_i. What is the final energy per particle e_f in terms of e_i?

(F2) What is the final and initial pressure ratio P_f/P_i at $T = 0$?

Boson case
(B1) Suppose the condensate density is positive under the initial temperature. Is the condensate density positive even after reversible isothermal compression $V \to V/2$?
(B2) What is the final and initial pressure ratio P_f/P_i?

Solution.
(F1) We know (writing $gD_t(\varepsilon) = \gamma V \varepsilon^{1/2}$, here g is the degeneracy of the translational kinetic energy level; for electrons $g = 2$ due to the spin, but in this problem, you may totally ignore it)

$$N = \frac{2}{3}gD_t(\mu(0))\mu(0) = \frac{2}{3}\gamma V \mu(0)^{3/2}, \tag{22.89}$$

$$E = \frac{2}{5}gD_t(\mu(0))\mu(0)^2 = \frac{2}{5}\gamma V \mu(0)^{5/2}. \tag{22.90}$$

Here, γ is a positive constant. Therefore, as we already know,

$$E/N = \frac{3}{5}\mu(0). \tag{22.91}$$

Notice that $\mu(0) \propto V^{-2/3}$ because N is constant, so

$$\frac{e_f}{e_i} = \frac{\mu_f(0)}{\mu_i(0)} = \frac{(V/2)^{-2/3}}{V^{-2/3}} = 2^{2/3}. \tag{22.92}$$

(F2) We use the universal law $P \propto E/V$:

$$P_f/P_i = 2(e_f/e_i) = 2^{5/3}, \tag{22.93}$$

where the prefactor 2 is the reciprocal of V_f/V_i.

(B1) If the volume is decreased, then the energy gaps widen, so more particles should fall into the ground state, or evaporation of the condensate becomes harder. That is, N_0 should increase.

To be more quantitative is also almost trivial, because $N_1 = AVT^{3/2}$ as already know and T is maintained, so N_1 is halved.

(B2) Since $E \propto VT^{5/2}$,[365] $P = (2/3)(E/V)$ does not depend on the volume. That is, there is no pressure change. The ratio is 1. You may think that the condensate becomes a pressure buffer.

D11.6 [Constant energetic compression]
A box of volume V with a piston is filled with N indistinguishable ideal gas atoms at temperature T_i. The final equilibrium state is obtained by halving the volume and removing the heat to maintain the total energy constant. That is, the final state is volume $V/2$ and internal energy E. Let T_f be the final temperature.

Suppose N particles are identical spinless bosons. Assume that the initial temperature is sufficiently low so there is a Bose-Einstein condensate.
(B1) Obtain (or write down/copy) the equation to find the number N_0 of atoms in the condensate.
(B2) Is $T_f < T_i$, $T_f = T_i$ or $T_f > T_i$?
(B3) Does the number of particles in the condensate increase or decrease?
Suppose N particles are identical spin 1/2 fermions.
(F1) Find the final pressure P_f.
(F2) Is there any positive lower bound for the initial temperature for this process to be feasible?
(F3) Is $T_f < T_i$, $T_f = T_i$ or $T_f > T_i$?

Solution.
(B1)
$$N_0 = N(1 - (T/T_c)^{3/2}), \tag{22.94}$$
where $T_c \propto n^{2/3}$.
(B2) An intuitive guess may be: since the energy level spacings widen, if we keep T, too many particles tumble down to be absorbed by the condensate. So you must warm up the system to keep the total energy.

We know below T_c $E \propto VT^{5/2}$. Therefore,
$$VT_i^{5/2} = (V/2)T_f^{5/2}. \tag{22.95}$$

[365] Repeated comment: 5/2 comes from the total ε power in the formula for E: $d\varepsilon \times \varepsilon^{1/2} \times \varepsilon$.

That is, $T_f = 2^{2/5}T_i$ or $T_f > T_i$.
(B3) As discussed in (B2) the system must be warmed up to maintain E. However, since the excited levels are pushed up by volume shrinking, if they have the same number of particles, E should go up. Therefore, the number of particles in the condensate should increase.

We know $T_c \propto n^{2/3}$, so $T_{cf} = T_{ci}2^{2/3}$ and $T_f = 2^{2/5}T_i$, so

$$T_f/T_{cf} = 2^{2/5-2/3}T_i/T_{ci} = 2^{-4/15}T_i/T_{ci} < T_i/T_{ci}. \tag{22.96}$$

Therefore, the ratio in (22.94) decreases, so N_0 increases.

(F1)

$$P_iV = 2E/3 = P_f(V/2), \tag{22.97}$$

so $P_f = 2P_i = 4E/3V$.
(F2) At $T = 0$ $E \propto n^{2/3}$, so E_f increases with compression. There is no way to cool the system, so isoenergetic compression is impossible at $T = 0$ (This should be obvious from the spread of the energy level spacings by compression.) Thus, sufficiently high temperature is needed.
(F3) We can derive from the Gibbs relation and a Maxwell's relation $\partial(S,T)/\partial(V,P) = 1$

$$\left.\frac{\partial E}{\partial V}\right|_T = T\left.\frac{\partial S}{\partial V}\right|_T - P = T\left.\frac{\partial P}{\partial T}\right|_V - P. \tag{22.98}$$

Introducing the equation of state into this, we have

$$\left.\frac{\partial E}{\partial V}\right|_T = \frac{2}{3V}\left[T\left.\frac{\partial E}{\partial T}\right|_V - E\right] = \frac{2}{3V}\left[TC_V - E\right]. \tag{22.99}$$

For an ideal Fermi gas for low temperatures $TC_V \ll E$, so this is negative as already discussed in footnote 8. Therefore, if T is constant, and if V is reduced, then E increases. To maintain E we must export heat. That is, the final temperature must be cooler. $T_i > T_f$.

Important Warning: I emphasized the use of thermodynamics, and illustrated how to use $E = TS - PV + \mu N$ in the notes. However, I never used this equation when I change V. If you do so the ground state energy changes! Therefore, you must not use this equation. If you ignore this warning, what happens? **The following small lettered calculation is nonsense.**

[NONSENSE CALCULATION] Since $E = ST - PV$ and $E = (3/2)PV$, we have $ST = (5/3)E$. Therefore,

$$\left.\frac{\partial T}{\partial V}\right|_E = -\frac{1}{C_V}\left.\frac{\partial E}{\partial V}\right|_T = -\frac{3T}{5C_V}\left.\frac{\partial S}{\partial V}\right|_T = -\frac{3T}{5C_V}\frac{(S,T)}{(V,T)} \tag{22.100}$$

$$= -\frac{3T}{5C_V}\frac{(S,T)}{(V,P)}\frac{(V,P)}{(V,T)} = -\frac{3T}{5C_V}\left.\frac{\partial P}{\partial T}\right|_V \tag{22.101}$$

Now, we use $P = 2E/3V$:

$$\left.\frac{\partial T}{\partial V}\right|_E = -\frac{2T}{5VC_V}\left.\frac{\partial E}{\partial T}\right|_V = -\frac{2T}{5V} < 0. \tag{22.102}$$

Thus, the result is opposite to the correct one.

D11.7 [Adiabatic sudden expansion]
There is an ideal gas in a thermally isolated box with a piston. We double the volume suddenly by pulling the piston out very rapidly. Let the initial pressure be P_i and the initial temperature be T_i.

Suppose the ideal gas consists of noninteracting fermions without any internal excitations.
(F1) Obtain the final pressure P_f in terms of the initial pressure P_i.
(F2) $T_i < T_f$, $T_i = T_f$ or $T_i > T_f$?

Next, let us assume the ideal gas is a non-interacting bose gas.
(B1) Obtain the final pressure P_f in terms of the initial pressure P_i.
(B2) Let us assume that the system is below the BEC temperature even after expansion. What is the final temperature T_f?
(B3) The initial temperature T_i is below T_c. After expansion, the temperature T_f was exactly at the critical temperature (after expansion T_{cf}). What is the initial temperature T_i in terms of the T_c (before expansion T_{ci}).

Solution.
(F1) There is no exchange of heat nor work, so E is constant. An important relation we use is

$$PV = \frac{2}{3}E. \tag{22.103}$$

Therefore, PV is constant:

$$P_i V = P_f(2V). \tag{22.104}$$

That is, $P_f = P_i/2$. Notice that this is statistics-indifferent.
(F2) Expansion makes the energy levels denser than the initial case. Therefore, below a given energy more particles can be accommodated after expansion. Therefore, temperature increases: $T_i < T_f$. This is especially easy to see if $T_i = 0$; you can immediately say $T_f = 0$ is impossible.

The conclusion cannot be obtained purely thermodynamically. Let us study

$$\left.\frac{\partial T}{\partial V}\right|_E = \frac{\partial(T,E)}{\partial(V,T)}\frac{\partial(V,T)}{\partial(V,E)} = -\frac{1}{C_V}\left.\frac{\partial E}{\partial V}\right|_T. \tag{22.105}$$

We have, using $E = 3PV/2$,

$$\left.\frac{\partial E}{\partial V}\right|_T = \frac{3}{2}\left[\left.\frac{\partial P}{\partial V}\right|_T V + P\right]. \tag{22.106}$$

We saw this many times now. Here let us proceed in a slightly different fashion. For the classical ideal gas, as we know well, this is zero:

$$V \left.\frac{\partial P}{\partial V}\right|_T = -\frac{Nk_BT}{V} = -P. \tag{22.107}$$

Compared with the classical gas, Fermi gas must be harder to compress. That is, the derivative must be more negative. That is, $(\partial E/\partial V)_T < 0$, so $(\partial T/\partial V)_E > 0$. Therefore if we expand the fermi gas under constant energy, the temperature must increase.

(B1) This is the same as the Fermion case.

(B2) Below T_c, since $\mu = 0$, we can compute E as (recall that $D_t(\varepsilon) \propto V\varepsilon^{1/2}$; power counting suffices)

$$E = \int_0^\infty d\varepsilon\, D_t(\varepsilon)\frac{\varepsilon}{e^{\beta\varepsilon}-1} \propto V\beta^{-1/2-2} \propto VT^{5/2}. \tag{22.108}$$

Therefore, conservation of E means

$$VT_i^{5/2} = (2V)T_f^{5/2} \tag{22.109}$$

or $T_f = 2^{-0.4}T_i \simeq 0.758T_i$. That is, in the Boson case, the temperature decreases.

This could be guessed, since for classical ideal gases the temperature does not change, fermions and bosons should be opposite.

(B3) (22.18) tells us that T_c before expansion is

$$T_c = Cn^{2/3}. \tag{22.110}$$

Following (22.109) $2(T_{cf})^{5/2} = T_i^{5/2}$, where T_{cf} is the critical temperature after expansion. Therefore, if n is the initial density

$$2^{-2/5}T_i = T_{cf} = C(n/2)^{2/3} = T_{ci}2^{-2/3}. \tag{22.111}$$

Therefore,

$$2^{-2/5+2/3}T_i = T_{ci} \ \Rightarrow T_i = 2^{-4/15}T_{ci}. \tag{22.112}$$

Exercise11

E11.1 [Finite T correction for fermion chemical potential in D-space].
(1) Assuming that the dispersion relation (the momentum-energy relation) is $\varepsilon = |\boldsymbol{p}|^2/2m$, find the relation among E, P and V in D-dimensional space of an ideal gas system. [Mimic the derivation of $PV = (2/3)E$.]
(2) What is the ratio $E/\mu(0)N$ at $T = 0$, if all the particles are identical fermions?
(3) For fermions we can conclude (under constant V and N) that

$$E = E_0 + \frac{1}{2}\alpha_D NT^2 + o[T^2], \tag{22.113}$$

where $\alpha_D > 0$ is a (D-dependent) constant. Using this fact, compute the correction to the Fermi energy $\mu(T)$ to oder T^2. [Fully use thermodynamics.]
(4) For bosons below T_c ($D \geq 3$), find the temperature dependence of the non-condensate N_1.

Solution.
(1) We need the one-particle state density $\mathcal{D}$:

$$\int_0^\varepsilon d\varepsilon\, \mathcal{D}(\varepsilon) = \frac{V}{h^D}\int_{|\boldsymbol{p}|\leq\sqrt{2m\varepsilon}} d^D\boldsymbol{p} \propto V\varepsilon^{D/2} \tag{22.114}$$

Therefore, we have $\mathcal{D}(\varepsilon) \propto V\varepsilon^{D/2-1}$. From this, we see (I may write a full detail in the final version)

$$\int_0^\varepsilon d\varepsilon\, \mathcal{D}(\varepsilon) = \frac{2}{D}\varepsilon\mathcal{D}(\varepsilon). \tag{22.115}$$

Therefore, the same logic as in 3D gives

$$PV = \frac{2}{D}E. \tag{22.116}$$

(2) We know at $T = 0$

$$E = -PV + \mu(0)N \;\Rightarrow\; \frac{D+2}{D}E = \mu(0)N. \tag{22.117}$$

Thus, the ratio is $D/(D+2)$.

If you do not like thermodynamics, you can proceed as follows: since $\mathcal{D}(\varepsilon) = A\varepsilon^{D/2-1}$ for some positive constant A,

$$N = \int_0^{\mu(0)} d\varepsilon\, \mathcal{D}(\varepsilon) = \frac{2}{D}A\mu(0)^{D/2}, \tag{22.118}$$

and

$$E = \int_0^{\mu(0)} d\varepsilon\, \varepsilon\mathcal{D}(\varepsilon) = \frac{2}{D+2}A\mu(0)^{D/2+1}. \tag{22.119}$$

Taking the ratio, we get the desired result.

(3) We get $C_V = \alpha NT$ from E. On the other hand, under constant V and N

$$\left.\frac{\partial S}{\partial T}\right|_{V,N} = \frac{C_V}{T} = \alpha N, \tag{22.120}$$

so the temperature dependence of S under constant V and N is given by $S = \alpha NT$ ($S(0) = 0$, following Planck). Therefore, a thermodynamic relation

$$E = TS - PV + \mu N \ \Rightarrow\ E + PV = \frac{D+2}{D}E = TS + \mu(T)N \tag{22.121}$$

tells us

$$E(T) = E(0) + \frac{1}{2}\alpha NT^2 + o[T^2] = \frac{D}{D+2}N\mu(0) + \frac{1}{2}\alpha NT^2 + o[T^2] \tag{22.122}$$

and

$$E(T) = \frac{D}{D+2}(\alpha NT^2 + o[T^2] + \mu(T)N), \tag{22.123}$$

or

$$\mu(T) = \mu(0) + \frac{D+2}{2D}\alpha T^2 - \alpha T^2 + o[T^2] = \mu(0) + \frac{2-D}{2D}\alpha T^2 + o[T^2]. \tag{22.124}$$

Notice that the sign of the prefactor switches at $D = 2$.

(4) N_1 is determined by

$$N_1 = \int_0^\infty d\varepsilon\, \mathcal{D}(\varepsilon)\frac{1}{e^{\beta\varepsilon} - 1} = AVT^{D/2}, \tag{22.125}$$

where A is a positive constant (that depends on D). We also know

$$N = \int_0^\infty d\varepsilon\, \mathcal{D}(\varepsilon)\frac{1}{e^{\beta\varepsilon} - 1} = AVT_c^{D/2}. \tag{22.126}$$

Therefore,

$$N_1 = N\left(\frac{T}{T_c}\right)^{D/2}. \tag{22.127}$$

E11.2 [Adiabatic free expansion]
There is a cylinder with a piston. It contains N identical particles and is thermally isolated. The volume of the cylinder is suddenly expanded (by pulling the piston out

a bit) by 10%.

We wish to know what happens after the system equilibrates. Let P_i (P_f) be the initial (final) pressure and T_i (T_f) be the initial (final) temperature.
Fermion case
(F1) Find P_f/P_i.
(F2) Which is larger, T_i or T_f? Explain your answer qualitatively in plain terms.
Boson case
(B1) Find P_f/P_i.
(B2) What happens, qualitatively, to the BEC (= Bose-Einstein condensation) temperature T_c? Explain your answer in plain terms intuitively.
(B3) Suppose $T_i = T_c$ for the initial system. Does the system maintain BEC after expansion?

Solution.
(F1) We know $PV \propto E$ and E is maintained (no work done by the system), so $P_f/P_i = V_i/V_f = 1/1.1 = 0.91$.
(F2) Since the volume expands, the level spacings generally diminish, so the Fermi level decreases. Therefore, more excited states must be occupied to maintain the energy. Therefore, $T_f > T_i$.
(B1) No change from the fermion case.
(B2) Again, the level spacings diminish, so it is easier for the condensate to evaporate. Therefore, T_c should go down.
(B3) Let us assume that BEC is maintained. Then, $T_c \propto V^{-2/3}$ and $T_f \propto V^{-2/5}$ since $E \propto VT^{5/2}$, so T_c decreases more than T_f, a contradiction. Therefore, BEC disappears.

Intuitively, expansion means the decrease of level spacings. This means that the condensate is easier to evaporate, so you need a lower temperature to maintain the condensate. This is also clear from (22.126).

E11.3 [Thermodynamic questions for ideal quantum gases]
Consider a quantum ideal gas (fermion and boson cases separately, if different). No hand-waving argument will be accepted. [Hint: Use $PV = 2E/3$ in this problem.]
(1) The volume is increased under constant temperature. Does the entropy increase? You must demonstrate your result without any hand-waving argument. Notice that thermodynamics alone cannot answer this question.
(2) You wish to decrease the temperature while keeping the pressure. How do you have to change the system volume?

Solution.
(1)

$$\left.\frac{\partial S}{\partial V}\right|_T = \frac{\partial(S,T)}{\partial(V,T)} = \frac{\partial(S,T)}{\partial(V,P)}\frac{\partial(V,P)}{\partial(V,T)} = \left.\frac{\partial P}{\partial T}\right|_V = \frac{2}{3V}\left.\frac{\partial E}{\partial T}\right|_V > 0. \tag{22.128}$$

In this case there is no difference due to statistics.
(2)

$$\left.\frac{\partial V}{\partial T}\right|_P = \frac{\partial(V,P)}{\partial(T,P)} = \frac{\partial(V,S)}{\partial(T,P)}\frac{\partial(V,T)}{\partial(V,S)}\frac{\partial(V,P)}{\partial(V,T)} = \frac{\partial(V,S)}{\partial(-P,T)}\frac{T}{C_V}\left.\frac{\partial P}{\partial T}\right|_V \tag{22.129}$$

The first Jacobian is positive definite due to stability. Since $P = 2E/3V$,

$$\left.\frac{\partial P}{\partial T}\right|_V = \frac{2}{3V}\left.\frac{\partial E}{\partial T}\right|_V = \frac{2C_V}{3V} > 0. \tag{22.130}$$

Therefore, V must be reduced. Again, there is no difference due to statistics.

23 Photons, Phonons and Internal Motions

Summary
∗ The photon gas statistical thermodynamics is explained.
∗ We will guess low temperature behaviors of E, S, μ for free fermions.
∗ Analogy to $\mu = 0$ grand canonical ensemble may be useful, but do no read it too literally.

Key words
photon gas, Planck's radiation formula, ultraviolet catastrophe, Stefan-Boltzmann law, internal degrees of freedom, vibrational and rotational partition functions

What you should be able to do
∗ You must be able to derive Planck's formula.
∗ You must clearly recognize the main features of Planck's formula.
∗ You must be able to itemize internal degrees of freedom of a molecule and tell their energy scales (in K).

23.1 Quantization of harmonic degrees of freedom

Photons and phonons are obtained through quantization of the systems that can be described as a collection of harmonic oscillators.[366] Possible energy levels for the i-th mode whose angular frequency is ω_i[367] are $(n + 1/2)\hbar\omega_i$, where $n = 0, 1, 2, \cdots$. The canonical partition function of a system with modes $\{\omega_i\}$ is given by

$$Z(\beta) = \prod_i \left(\sum_{n_i=0}^{\infty} e^{-\beta(n_i+1/2)\hbar\omega_i} \right), \tag{23.1}$$

since no modes interact with each other. Here, the product is over all the modes. The sum in the parentheses gives the canonical partition function for a single harmonic oscillator, which we have already computed. The canonical partition function may

[366] That is, the system whose Hamiltonian is quadratic in canonical coordinates (quantum mechanically in the corresponding operators).

[367] A system with a quadratic Hamiltonian may be described in terms of canonical coordinates (or corresponding operators) that makes the Hamiltonian diagonal. In other words, the system may be described as a collection of independent harmonic oscillators. The motion corresponding to each such harmonic oscillator is called a *mode*. If more than one modes have identical angular frequencies, modes cannot be uniquely chosen, but this does not cause any problem to us because partition functions need the system energies and their degeneracies only.

be rewritten as:

$$Z(\beta) = \left[\prod_i \left(e^{-\beta\hbar\omega_i/2}\right)\right] \prod_i \left(\sum_{n_i=0}^{\infty} e^{-\beta n_i \hbar\omega_i}\right) = \left[\prod_i \left(e^{-\beta\hbar\omega_i/2}\right)\right] \Xi(\beta, 0). \quad (23.2)$$

Here, we have used the formula

$$\Xi(\beta, 0) = \prod_i \left(\sum_{n=0}^{\infty} e^{-\beta n\hbar\omega_i}\right), \quad (23.3)$$

which may be obtained from the definition of the grand partition function by setting $\varepsilon_i = \hbar\omega_i$, and $\mu = 0$. As long as we consider a single system, the total zero-point energy of the system $\sum_i \hbar\omega_i/2$ is constant and may be ignored by shifting the energy origin.[368]

Therefore, the canonical partition function of the system consisting of harmonic modes (or equivalently, consisting of photons or phonons) may be written as $\Xi_{BE}(\beta, 0)$, regarding each mode $\hbar\omega_i$ as a single particle state energy. That is, it is written as the bosonic grand partition function with a zero chemical potential. From this observation, you should immediately recognize that T dependence of various thermodynamic quantities can be computed easily (or dimensional analytic approaches allow us to guess many T-dependent behaviors).

23.2 Warning: grand partition function with $\mu = 0$ is only a gimmick

See Important Remark in **D12.6**.

The thermodynamic potential for the system consisting of photons or phonons is the Helmholtz free energy A whose independent variables are T and V, because the expected number $\langle n_i \rangle$ of phonons (photons) of mode i is determined, if the temperature T and the volume V are given. Notice that we do not have any more 'handle' like μ to modify the expectation value. Since $dA = -SdT - PdV$, we have $A = -PV$. That is, our observation $\log Z(\beta) = \log \Xi(\beta, 0)$ holds as a thermodynamic relation for a system that can be described by a collection of harmonic oscillators (as long as we ignore the zero-point energy). Thus, we may conclude that systems consisting of phonons or photons can be described consistently by the grand partition function with a zero chemical potential. For example, the pressure of the photon or phonon system can be computed immediately as we see below.

However, do not understand this relation to indicate that the chemical potentials

[368]**Warning**: However, if the system is deformed or chemical reactions occur, the system zero-point energy can change, so we must go back to the original formula with the total zero-point energy and take into account its contribution. For electromagnetic field, the change of the total zero-point energy may be observed as force. This is the *Casimir effect*.

of photons and phonons are indeed zero; actually they cannot be defined. The relation is only a mathematical formal relation that can be sometimes useful.[369]

23.3 Expectation number of photons

The $\mu = 0$ boson analogy tells us that the average number of phonons of a harmonic mode is given by

$$\langle n \rangle = \frac{1}{e^{+\beta\hbar\omega} - 1}. \tag{23.4}$$

23.4 Internal energy of photon systems

The phonon contribution to the internal energy of a system may be computed just as we did for the Debye model. We need the density of states (i.e, phonon spectrum, i.e., the distribution of the frequencies of the modes) $D_{\rm ph}(\omega)$. The internal energy of all the phonons is given by

$$E = \sum_{\rm modes} \langle n(\omega) \rangle \hbar\omega = \int d\omega D_{\rm ph}(\omega) \frac{\hbar\omega}{e^{+\beta\hbar\omega} - 1}. \tag{23.5}$$

This is the internal energy without the contribution of zero-point energy.

A standard way to obtain the density of states $D_{\rm ph}(\omega)$ is to study the wave equation governing the electromagnetic waves, but here we use our usual shortcut. The dispersion relation for photons is $\varepsilon = c|\boldsymbol{p}| = \hbar\omega$, so

$$\int_0^\omega D_{\rm ph}(\omega')d\omega' = \frac{V}{h^3} \int_{|\boldsymbol{p}| \le \hbar\omega/c} d^3\boldsymbol{p}. \tag{23.6}$$

Here, we do not include the factor 2 due to polarization states. Differentiating the above equality, we obtain

$$D_{\rm ph}(\omega) = \frac{4\pi V}{h^3} \left(\frac{\hbar\omega}{c}\right)^2 \frac{\hbar}{c} = \frac{V\omega^2}{2\pi^2 c^3}. \tag{23.7}$$

Photons have two polarization directions,[370] so the actual density of the modes is this formula $\times$ 2.

---

[369] Intuitively speaking, chemical potential may be defined only for particles you can 'pick up.' More precisely speaking, if no (conserved) charge of some kind (say, electric charge, baryon number) is associated with the particle, its chemical potential is a dubious concept.

[370] Photons are spin =1 particles, but are running always at a speed of light, so only the transversal spin components can change. Thus, the number of the spin degrees of freedom is 2 instead of 3.

23.5 Planck's distribution, or radiation formula

The internal energy dE_ω and the number dN_ω of photons in $[\omega, \omega + d\omega)$ in a box of volume V are given by

$$dE_\omega = 2D_{\rm ph}(\omega)\frac{\hbar\omega}{{\rm e}^{+\beta\hbar\omega} - 1}d\omega, \tag{23.8}$$

$$dN_\omega = 2D_{\rm ph}(\omega)\frac{1}{{\rm e}^{\beta\hbar\omega} - 1}d\omega. \tag{23.9}$$

The factor 2 comes from the polarization states (i.e., $D_{\rm ph}$ here is given by (23.7)).

Therefore, the energy density $u(T, \omega)$ at temperature T due to the photons with the angular frequencies around ω reads

$$u(T, \omega) = \frac{\omega^2}{\pi^2 c^3}\frac{\hbar\omega}{e^{\beta\hbar\omega} - 1}. \tag{23.10}$$

This is *Planck's radiation formula*.

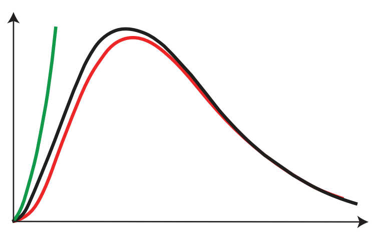

Figure 23.1: Classical electrodynamics gives the Rayleigh-Jeans formula (23.12) (green); this is the result of equipartition of energy and due to many UV modes, the density is not integrable (the total energy diverges). Wien reached (23.13) empirically (red). Planck arrived at his formula (black) originally by interpolation of these two results. Notice that the peak position is proportional to the temperature.

It is important to know some qualitative features of this law (Fig. 23.1):
(i) Planck's law can explain why the spectrum blue-shifts as temperature increases; this was not possible within the classical theory.
(ii) The total energy density $u(T) = E/V$ of a radiation field at temperature T is finite. $u(T)$ is obtained by integration:

$$u(T) = \int_0^\infty d\omega\, u(T, \omega). \tag{23.11}$$

With Planck's law (23.10) this is always finite (we will study this later).
(iii) In the classical limit $\hbar \to 0$, we get

$$u(T, \omega) = \frac{k_B T\omega^2}{\pi^2 c^3} \quad \big(= 2D_{\rm ph}(\omega)k_B T\big), \tag{23.12}$$

which is the formula obtained by classical physics (i.e., the equipartition of energy). Upon integration, the classical limit gives an infinite $u(T)$. This divergence is obviously due to the contribution from the high frequency modes. Thus this difficulty is called the *ultraviolet catastrophe*, which destroyed classical physics.
(iv) In the high frequency limit $\hbar\omega \gg k_B T$ Planck's law (23.10) goes to

$$u(T,\omega) \simeq \frac{k_B T}{\pi^2 c^3}\omega^2 \mathrm{e}^{-\beta\hbar\omega}, \tag{23.13}$$

which was empirically proposed by Wien.

23.6 Statistical thermodynamics of black-body radiation

Let us finish the statistical mechanics of back-body radiation.

$$u(T) = \int_0^\infty \frac{\omega^2}{\pi^2 c^3}\frac{\hbar\omega}{e^{\beta\hbar\omega}-1}d\omega = \beta^{-4}\int_0^\infty \frac{(\beta\omega)^2}{\pi^2 c^3}\frac{\hbar\beta\omega}{e^{\beta\hbar\omega}-1}d(\beta\omega). \tag{23.14}$$

This immediately implies (as seen above)

$$u(T) \propto T^4. \tag{23.15}$$

which is called the *Stefan-Boltzmann law*.[371]

Since we know the T^3-law of the phonon low temperature specific heat (the Debye theory), this should be expected. This is understandable by counting the number of degrees of freedom (Fig. 22.1) explained before. Although we did not calculate the proportionality constant, if you follow the above calculation you can get it. This proportionality was obtained purely thermodynamically by Boltzmann before the advent of quantum mechanics. The proportionality constant contains $\hbar$, so it was impossible to theoretically obtain the proportionality constant before Planck (Stefan experimentally obtained it).

23.7 Black-body equation of state

Photons may be treated as ideal bosons with $\mu = 0$,[372] so the equation of state is immediately obtained as

$$\frac{PV}{k_B T} = \log \Xi = -\int d\varepsilon\, D(\varepsilon)\log(1-\mathrm{e}^{-\beta\varepsilon}). \tag{23.16}$$

For 3D superrelativistic particles, $D(\varepsilon) \propto \varepsilon^2$, so

$$\int_0^\varepsilon d\varepsilon\, D(\varepsilon) = \frac{1}{3}\varepsilon D(\varepsilon). \tag{23.17}$$

[371]The proportionality constant can be computed as $k_B^4\pi^2/15\hbar^3c^3$.
[372]If $\mu = 0$, then $A = -PV = -k_B T \log Z$.

This gives us (review what we did to derive $PV = 2E/3$ for ordinary particles in **21.15**)

$$PV = \frac{1}{3}E. \tag{23.18}$$

23.8 Thermodynamic derivation of black-body equation of state

Just as $PV = 2E/3$ is a result of pure mechanics, (23.18) is a result of pure electrodynamics, so this was known before quantum mechanics. Boltzmann started with (23.18) to obtain the Stefan-Boltzmann law as follows.

Since we know generally

$$E = TS - PV = TS - \frac{1}{3}E, \tag{23.19}$$

$$ST = \frac{4}{3}E \quad \text{or} \quad S = \frac{4}{3}\frac{E}{T}. \tag{23.20}$$

Differentiating S wrt E under constant V, noting $(\partial S/\partial E)_V = 1/T$, we obtain

$$\frac{1}{T} = -\frac{4}{3T^2}\left.\frac{\partial T}{\partial E}\right|_V E + \frac{4}{3T} \tag{23.21}$$

or

$$\frac{1}{3T} = \frac{4}{3T^2}\left.\frac{\partial T}{\partial E}\right|_V E, \tag{23.22}$$

that is, under constant V

$$\frac{dE}{E} = 4\frac{dT}{T}. \tag{23.23}$$

This implies the Stefan-Boltzmann law $E \propto T^4$. The proportionality coefficient contains $\hbar$, so Boltzmann could not get it; Stefan experimentally determined the value.

23.9 Blackbody - low temperature phonon system analogy

For a phonon system of a lattice **16.10**, we have a high-frequency cutoff in the energy spectrum, but its effect is almost negligible in the low temperature limit. Except for the number of modes, you must clearly recognize a direct relation between the photons in the vacuum and phonons in the crystal. Debye's T^3 law **16.12** is 'almost the same' as the Stefan-Boltzmann law.

23.10 Internal degrees of freedom of classical ideal gas

If noninteracting particles are sufficiently dilute ($\mu \ll 0$), we know classical ideal gas approximation is OK. However, the internal degrees of freedom may not be handled classically, because energy gaps may be huge. We have already glimpsed this when we discussed the gas specific heat.

Let us itemize internal degrees of freedom of a molecule:
i) Each atom has a nucleus, and its ground state could have nonzero nuclear spin. This interacts with electronic angular momentum to produce the *ultrafine structure*. The splitting due to this effect is very small, so for the temperature range relevant to the gas phase we may assume all the levels are energetically equal. Thus, (usually) we can simply assume that the partition function is multiplied by a constant $g =$ degeneracy of the nuclear ground state.[373]
ii) Electronic degrees of freedom has a large excitation energy (of order of ionization potential $\sim$a few eV, so unless the ground state of the orbital electrons is degenerate), we may ignore it.[374]
iii) If a molecule contains more than one atom, it can exhibit rotational motion. The quantum of rotational energy (Θ_R below) is usually of order 10 K.[375]
iv) Also such a molecule can vibrate. The vibrational quantum (Θ_V below) is of order 1000 K.[376]

23.11 Rotation and vibration

Notice that there is a wide temperature range, including the room temperature, where we can ignore vibrational excitations and can treat rotation classically (Fig. 23.2). Thus, equipartition of energy applied to translational and rotational degrees of freedom can explain the specific heat of many gases.

The Hamiltonian for the internal degrees of freedom for a diatomic molecule reads

$$H = \frac{1}{2I} J^2 + \hbar\omega \left(\hat{n} + \frac{1}{2} \right), \tag{23.24}$$

where I is the moment of inertia, J the total angular momentum and $\hat{n}$ is the phonon number operator. Therefore, the partition function for the internal degrees

[373]In the case of homonuclear diatomic molecules, nuclear spins could interfere with rotational degrees of freedom through quantum statistics, but otherwise we can simply assume as is stated in the text.

[374]If the ground state is degenerate, then it could have a fine structure with an energy splitting of order a few hundred K. For ground state oxygen ($^3P_2$) the splitting energy is about 200 K, so we cannot simply assume that all the states are equally probable nor that only the ground slate is relevant.

[375]However, for H_2 it is 85.4 K. For other molecules, the rotational quantum is rather small: N_2: 2.9 K; HCl: 15.1 K.

[376]N_2 3340 K; O_2: 2260 K; H_2: 6100 K.

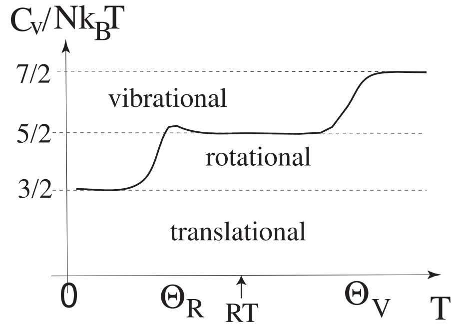

Figure 23.2: The constant volume specific heat.

of freedom reads $z_i = z_r z_v$:

$$z_r = \sum_{J=0}^{\infty}(2J+1)e^{-(\Theta_R/T)J(J+1)}, \tag{23.25}$$

with $\Theta_R = \hbar^2/2k_BI$ and

$$z_v = \sum_{n=0}^{\infty} e^{-(\Theta_V/T)(n+1/2)}. \tag{23.26}$$

with $\Theta_V = \hbar\omega/k_B$.

23.12 Low and hight temperature limit of rotational contribution

If the temperature is sufficiently low, then

$$z_r \simeq 1 + 3e^{-2\Theta_R/T}. \tag{23.27}$$

The contribution of rotation to specific heat is

$$C_{\rm rot} \simeq 3Nk_B\left(\frac{\Theta_R}{T}\right)^2 e^{-2\Theta_R/T}. \tag{23.28}$$

For $T \gg \Theta_R$, we may approximate the summation by integration (Large Js contribute, so we may approximate $J \simeq J+1$):

$$z_r \simeq 2\int_0^{\infty} dJJe^{-J^2(\Theta_R/T)} = \frac{T}{\Theta_R}. \tag{23.29}$$

This gives the rotational specific heat, but it is more easily obtained by the equipartition of energy, because the rotational energy is with a quadratic form. Thus, $C_{rot} = k_B$ in the high temperature limit.

23.13 Low and high temperature limit of vibrational contribution

The vibrational partition function can be summed as

$$z_v = 1/2\sinh(\beta\hbar\omega/2). \tag{23.30}$$

For small T

$$z_v \simeq (1 + e^{-\beta\hbar\omega})e^{\beta\hbar\omega/2} \tag{23.31}$$

is enough. Consequently,

$$C_{\mathrm{vib}} \sim k_B N \left(\frac{\Theta_V}{T}\right)^2 e^{-\Theta_R/T}. \tag{23.32}$$

Since $\Theta_R \ll \Theta_V$, as already noted, there is a wide range of temperature where only rotation contributes to the specific heat.

Discussion 12

Various quantum effect will be discussed, but mainly about internal degrees of freedom.

D12.1 [Internal degrees of freedom of heavy hydrogen]
The potential energy function describing the chemical bond in a heavy hydrogen D_2 may be approximately described by

$$\phi(r) = \varepsilon \left[e^{-2(r-d)/a} - 2e^{-(r-d)/a} \right], \tag{23.33}$$

where $\varepsilon = 7 \times 10^{-19}$ J, $d = 8 \times 10^{-11}$ m and $a = 5 \times 10^{-11}$ m. Deuterium mass M is 1.66×10^{-27} kg.
(1) Evaluate the smallest energy required to excite the rotational motion, and estimate the temperature T_r for which the rotation contribution becomes significant.
(2) Evaluate the smallest energy required to excite the vibrational motion, and estimate the temperature T_v for which the vibration contribution becomes significant.
Solution.
(1) The moment of inertia is

$$I = \frac{1}{2} M d^2 = (1/2) \times (1.66 \times 10^{-27}) \times (8 \times 10^{-11})^2 = 5.31 \times 10^{-48} \text{ kg}\cdot\text{m}^2, \tag{23.34}$$

so the rotational energy levels are given by

$$\varepsilon_J = \frac{\hbar^2}{2I} J(J+1). \tag{23.35}$$

Thus, the representative temperature for rotational excitation is

$$\Theta_r = \frac{\hbar^2}{2k_B I} = \frac{(1.055 \times 10^{-34})^2}{2 \times (1.38 \times 10^{-23}) \times (5.31 \times 10^{-48})} \tag{23.36}$$

$$= \frac{1.113 \times 10^{-68}}{1.466 \times 10^{-70}} \simeq 76 \text{ K}. \tag{23.37}$$

(2) The minimum point of the potential $\phi(r)$ is $r = d$ with $\phi(d) = -\varepsilon$. Since

$$e^{-2x} - 2e^{-x} = 1 - 2x + 2x^2 + \cdots - 2(1 - x + x^2/2 + \cdots) = -1 + x^2 + \cdots, \tag{23.38}$$

$$\phi(r) = -\varepsilon + \frac{\varepsilon}{a^2}(r-d)^2 + \cdots. \tag{23.39}$$

The vibrational equation of motion is (here $M/2$ is the reduced mass)

$$\frac{M}{2}\ddot{x} = -2\frac{\varepsilon}{a^2}x + \cdots. \tag{23.40}$$

Therefore,

$$\omega = \sqrt{\frac{4\varepsilon}{Ma^2}} = \frac{2}{a}\sqrt{\frac{\varepsilon}{M}} = \frac{2}{5\times 10^{-11}}\sqrt{\frac{7\times 10^{-19}}{1.66\times 10^{-27}}} = 8.21\times 10^{14}\ \text{rad/s}. \tag{23.41}$$

The vibrational quantum is

$$\Theta_v = \frac{\hbar\omega}{k_B} = \frac{1.055\times 10^{-34}\times 8.21\times 10^{14}}{1.38\times 10^{-23}} = 6276\ \text{K}. \tag{23.42}$$

Therefore, around 6000 K the vibration becomes significant.

D12.2 [**Specific heat of various hydrogen gases**]
Consider a 1 mole of ideal gas at 10 K consisting of pure HD, pure HT or pure DT (H: hydrogen, D: deuterium, T: tritium; you should know their masses). Whose specific heat C_V is the largest? Give your answer without detailed computation. You may assume that the length of the chemical bonds are all the same. You may take the fact into account that the rotational contribution reaches its peak beyond 40 K.

Solution.
We may totally ignore the contribution of oscillations. There is no difference in the contribution of translational motions. These are all heteronuclear molecules, so we need not worry about spin-rotation coupling.[377] Therefore, we have only to pay attention to the rotational contributions. The molecules with the largest moment of inertia is the easiest to excite, so their rotational specific heat is the largest (notice that the 10K is still away from the peak of the rotational specific heat). Therefore, around 10 K the specific heat of DT must be the largest among the three. This is indeed the case.

D12.3 [**Black body box expansion**]
A cavity of volume V is filled with electromagnetic wave in equilibrium with temperature T_i initially. If the volume is doubled adiabatically and quasistatically, what is the final temperature T_f?

Solution.
(1) Since S is constant and since $PV = E/3$, we get

$$dE = -PdV = -\frac{E}{3V}dV. \tag{23.43}$$

Therefore, $EV^{1/3}$ is constant, or $PV^{4/3}$ is constant.

On the other hand, Planck's law tells us $E \propto VT^4$; if you wish to proceed from

[377] which we do not discuss in this course.

scratch, we get the one particle density $D \propto Vp^2dp/d\omega \propto p^2 \propto \omega^2$ (cf. $p = \hbar\omega/c$), so 'power counting' is enough to conclude

$$E = \int d\omega\, D(w)\frac{\omega}{e^{\beta\hbar\omega} - 1} \propto VT^4. \tag{23.44}$$

Thus, $P \propto T^4$. This with $PV^{4/3}$ implies that $T^4V^{4/3}$ or VT^3 is constant. Therefore, $T_f = T_i/2^{1/3}$.

D12.4 [Quantum gas with internal degrees of freedom]
Let us consider a quantum gas consisting of N particles. Individual particles have internal states consisting of two levels: the ground state and the non-degenerate excited state with energy ε (> 0).
(1) Suppose the particles are fermions. How does the Fermi energy μ_F (i.e., the chemical potential at $T = 0$) change as ε is increased?
(2) Suppose the particles are bosons. How does the Bose-Einstein critical temperature T_c depends on ε qualitatively?

For both cases, you must state your supporting logic clearly.
Solution.
(1) The Fermi energy μ_F is determined by

$$N = \int_0^{\mu_F} dE\, \mathcal{D}(E). \tag{23.45}$$

Here, D is the one-particle energy level density <u>including</u> the internal energy. If ε is increased, then the total occupation number of the one-particle states with internal excitation decreases. The 'spilt particles' from the states with the internal excitation must be accommodate by the states without internal excitations. Therefore, μ_F is an increasing function of ε.

(2) Consider the total number of the particles in the non-condensate (note that $\mu = 0$):

$$N_1 = \int_0^{\infty} dE\, \mathcal{D}(E)\frac{1}{e^{\beta E} - 1}. \tag{23.46}$$

If ε is increased, N_1 decreases, so this favors the formation of condensate. That is, T_c increases with ε. Or, you can say that increasing ε makes particles to evaporate from the condensate into internally excited non-condensate becomes harder, so T_c goes up.

D12.5 [The classical-quantum specific heat difference of insulating solid]

Let $C_V(T)$ be the true quantum-mechanical specific heat of a non-conducting solid that obeys asymptotically the T^3-law at low temperatures. We know $C_V(\infty)$ is obtained by the equipartition of energy for harmonic oscillators (i.e., the Dulong-Petit law).

Let $\Delta C_V = C_V(\infty) - C_V(T)$. Then, we happen to obtain

$$\int_0^\infty dT\, \Delta C_V(T) = \text{the zero-point energy of the solid.} \tag{23.47}$$

This is just the area of A in Fig. 23.3.

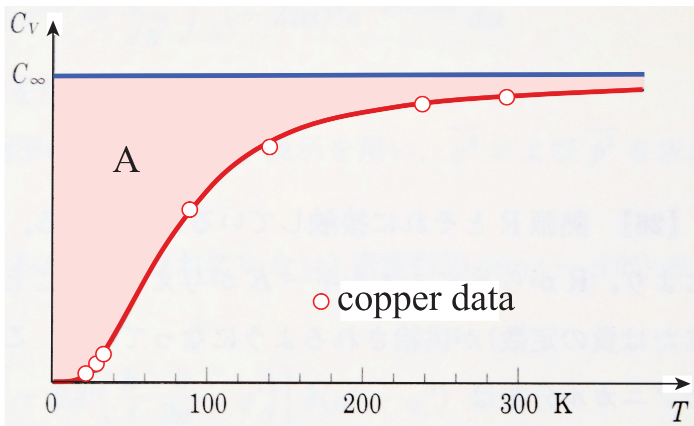

Figure 23.3: The area of the pale red region A agrees with the total zero-point energy of copper. [Figure from Kubo's workbook; however, the demonstration in the book is physically and mathematically wrong.]

Let us demonstrate this result.

Let $D(\omega)$ be the true (not the Debye approximate version) mode density (i.e., the actual single phonon energy level density or the phonon spectrum).

(1) Find the total phonon (i.e., oscillation) internal energy of the solid $E(T)$ in terms of $D(\omega)$.

(2) Find its classical approximation $E_C(T)$.

(3) By differentiating $E_C(T) - E(T)$ with respect to T, we can get ΔC. Then calculate the integral in (23.47) to demonstrate the desired equality.

Solution.

(1) This is just we did for the Debye model (but without his approximation):

$$E(T) = \int d\omega D(\omega) \left[\frac{\hbar\omega}{2} + \frac{\hbar\omega}{e^{\beta\hbar\omega} - 1}\right]. \tag{23.48}$$

(2) This is the classical limit: for sufficiently large T

$$E_C(T) = \int d\omega D(\omega) k_B T. \tag{23.49}$$

(3)

$$\Delta C = \frac{d}{dT}\int d\omega D(\omega)\left[k_BT - \frac{\hbar\omega}{2} - \frac{\hbar\omega}{e^{\beta\hbar\omega}-1}\right] \tag{23.50}$$
$$= \int d\omega D(\omega)\frac{d}{dT}\left[k_BT - \frac{\hbar\omega}{2} - \frac{\hbar\omega}{e^{\beta\hbar\omega}-1}\right] \tag{23.51}$$
$$= \int d\omega D(\omega)\frac{d}{dT}\left[k_BT - \frac{\hbar\omega}{e^{\beta\hbar\omega}-1}\right]. \tag{23.52}$$

The exchange of differentiation and integration is legitimate.[378] Now,

$$\int_0^\infty dT\,\Delta C(T) = \int d\omega D(\omega)\int_0^\infty dT\,\frac{d}{dT}\left[k_BT - \frac{\hbar\omega}{e^{\beta\hbar\omega}-1}\right] \tag{23.53}$$
$$= \int d\omega D(\omega)\left[k_BT - \frac{\hbar\omega}{e^{\beta\hbar\omega}-1}\right]_{T=0}^{\infty}. \tag{23.54}$$

There is no contribution from the $T=0$ end. Setting $x = \hbar\omega/k_BT$, we have

$$\lim_{T\to\infty}\left[k_BT - \frac{\hbar\omega}{e^{\beta\hbar\omega}-1}\right] = \hbar\omega\lim_{x\to 0}\left[\frac{1}{x} - \frac{1}{e^x-1}\right] = \hbar\omega\lim_{x\to 0}\frac{e^x-1-x}{x(e^x-1)} \tag{23.55}$$
$$= \hbar\omega\lim_{x\to 0}\frac{x^2/2+x^3/6+\cdots}{x^2+x^3/2+\cdots} = \frac{\hbar\omega}{2}, \tag{23.56}$$

which happens to be the zero-point energy of the mode with ω. Thus, we have arrived at the desired result:

$$\int_0^\infty dT\,[C_{\text{classical}} - C(T)] = \int d\omega D(\omega)\frac{\hbar\omega}{2}. \tag{23.57}$$

Does this have a deep meaning? I am very sceptical.

D12.6 [Electron-positron-photon equilibrium]
Assume the whole system is charge neutral. Electrons 'e' and positrons 'p' are in equilibrium with the photon field (electromagnetic field) through the pair creation/annihilation:

$$e + p \leftrightarrow \gamma. \tag{23.58}$$

Let us assume the temperature T is much higher than the rest mass of the electron (i.e., $k_BT \gg mc^2$), so there is an equilibrium between the electromagnetic field (i.e.,

[378]The exchange of integrals in the following line is also legitimate. Every physicist must learn Lebesgue integration theory to be reasonable.

black-body radiation) and the positron/electron plasma.
(1) Show that the chemical potential μ_e of electrons and that μ_p of positrons are identical and zero $\mu_e = \mu_p = 0$. Do not forget that the chemical potential of photons is not definable. You may ignore the interactions among particles except for pair creation/annihilation.
(2) Let us consider a finite domain of volume V in the system filled with the high temperature radiation field. Assuming particles are super relativistic, find the numbers of electrons (N_e) and positrons (N_p) [You need not perform the integrals, but pay attention to the degeneracy due to spins].

Solution.
(1) Let us minimize the Helmholtz free energy of the whole system under the condition that $N_e = N_p$, since T is uniform.[379] We use the Helmholtz free energy for photons $A_{h\nu}$, that for electrons A_e and that for positrons A_p:

$$A = A_{h\nu}(T) + A_e(T, N_e) + A_p(T, N_p). \tag{23.59}$$

Let us minimize $A + \lambda(N_e - N_p)$, where λ is Lagrange's multiplier to impose the charge neutrality. We get

$$\left.\frac{\partial A_e}{\partial N_e}\right|_T + \lambda = \mu_e + \lambda = 0, \tag{23.60}$$
$$\left.\frac{\partial A_p}{\partial N_p}\right|_T - \lambda = \mu_p - \lambda = 0. \tag{23.61}$$

Therefore, we have

$$\mu_e + \mu_p = 0. \tag{23.62}$$

This is due to the electrical charge conservation.
Since $N_e = N_p$, $\mu_e = \mu_p$. Therefore, $\mu_e = \mu_p = 0$.

Important Remark.
The 'standard' textbooks including Landau-Lifshitz claim that photons indeed have zero chemical potential, because the number N of phonons is determined when T is fixed by an equilibrium condition:

$$\left.\frac{\partial A}{\partial N}\right|_T = 0. \tag{23.63}$$

Therefore, the chemical equilibrium means $\mu_e + \mu_p = 0$, because the sum of chemical potentials of the reactants and products are identical. As you see below this argument is totally wrong.

[379] Following Akira Shimizu (U Tokyo), who emphasizes (as quoted in the lecture notes and in my lectures) that chemical potential is coupled (basically) to conserved quantities.

You might think the situation is just like the following logic introducing T to a microcanonical calculation:

$$\left.\frac{\partial S}{\partial E}\right|_V = \frac{1}{T}. \tag{23.64}$$

(23.63) just looks like this argument to introduce a new thermodynamic variable μ. However, there is a fundamental difference: E in (23.64) is one of the thermodynamic coordinates, and you can change it independently with V.

In contrast, for photons E and N are not independent variables, so the following derivative is meaningless:

$$\left.\frac{\partial S}{\partial N}\right|_E = -\frac{\mu}{T}. \tag{23.65}$$

Just as illegitimate as this, in (23.63), you cannot change N while keeping T, since they are not independent variables.

Therefore, μ is not defined for photons in the 'standard way' (under true equilibrium conditions). □

(2) Since the particles are superrelativistic, the dispersion relation is $\varepsilon = c|\boldsymbol{p}|$. Therefore, the density D of one-particle (translational) states may be obtained as

$$\int_0^{\varepsilon} d\varepsilon\, D(\varepsilon) = \frac{4\pi V}{h^3}\int_0^{\varepsilon/c} p^2 dp = \frac{4\pi V}{3h^3c^3}\varepsilon^3, \tag{23.66}$$

or

$$D(\varepsilon) = \frac{4\pi V}{h^3c^3}\varepsilon^2. \tag{23.67}$$

Therefore, taking the spin degrees of freedom into account by multiplying the degeneracy factor 2, we get

$$N_e = 2 \times \frac{4\pi V}{h^3c^3}\int_0^{\infty} d\varepsilon\, \frac{\varepsilon^2}{e^{\beta\varepsilon}+1} = N_p. \tag{23.68}$$

Its temperature dependence is $\propto T^3$ (use power counting).

D12.7 [Effective interaction due to statistics][380]

Fig. 21.6 illustrates how we can intuitively understand the effective interactions between particles: compared with classical particles, between bosons there is an effective attraction, and between fermions there is an effective repulsion. Let us make this understanding slightly quantitative. Here, we proceed step by small step, reviewing elementary quantum mechanics.

[380]Without elementary QM, this may be a bit too hard to understand, but the result Fig. 23.4 is intuitively appealing.

We wish to consider a two-particle system in terms of canonical ensemble theory. The system Hamiltonian reads

$$H = \frac{\boldsymbol{p}_1^2}{2m} + \frac{\boldsymbol{p}_2^2}{2m}, \tag{23.69}$$

and the canonical partition function is

$$Z = \mathrm{Tr}\, e^{-\beta H}, \tag{23.70}$$

where the trace is with respect to the microstates specified by two momenta $|\boldsymbol{p}, \boldsymbol{p}'\rangle$. To compute this trace semi-classically, we introduce a single-particle momentum state $|\boldsymbol{p}\rangle$.
(1) Express $|\boldsymbol{p}, \boldsymbol{p}'\rangle$ both for the boson and fermion cases in terms of single particle kets $|\boldsymbol{p}\rangle$. You may regard two momenta are distinct, but the obtained states must be properly normalized. Recall that boson wave functions are totally symmetric with respect to the permutation of particle numberings; fermion wave functions are totally antisymmetric
(2) Assuming that the space is unbounded (for simplicity), find the position representation $\langle \boldsymbol{r}|\boldsymbol{p}\rangle$ (i.e., the wave function) of the momentum ket $|\boldsymbol{p}\rangle$ (use the δ-function normalization).
(3) Let $\boldsymbol{r}_i$ be the position vector of the i-th particle. Find the position representation of $|\boldsymbol{p}, \boldsymbol{p}'\rangle$. [This is of course virtually the same question as (1).]

For an N-particle system in the semi-classical limit, the calculation of trace in Z may be performed as follows:

$$\begin{aligned}
\mathrm{Tr} \quad &\to \quad \frac{1}{N!}\int_{\mathbb{R}^{3N}} d\{\boldsymbol{r}_k\} \prod_{k=1}^{N} \langle \boldsymbol{r}_k| \cdots \prod_{k=1}^{N} |\boldsymbol{r}_k\rangle &(23.71)\\
&= \quad \frac{1}{N!}\int_{\mathbb{R}^{3N}} d\{\boldsymbol{r}_k\} \prod_{k=1}^{N} \langle \boldsymbol{r}_k| \left[\left(\int_{\mathbb{R}^{3N}} d\{\boldsymbol{p}_k\} |\{\boldsymbol{p}_i\}\rangle\langle\{\boldsymbol{p}_i\}| \right) \cdots \left(\int_{\mathbb{R}^{3N}} d\{\boldsymbol{p}_k\} |\{\boldsymbol{p}_i\}\rangle\langle\{\boldsymbol{p}_i\}| \right) \right] \prod_{k=1}^{N} |\boldsymbol{r}_k\rangle. &(23.72)
\end{aligned}$$

(4) Write Z down using $h^{-3/2} e^{i\boldsymbol{r}\cdot\boldsymbol{p}/\hbar} = \langle \boldsymbol{r}_i|\boldsymbol{p}\rangle$.
(5) The outcome of (4) must have the following form:

$$\frac{1}{2h^6}\int d\boldsymbol{r}_1 d\boldsymbol{r}_2 d\boldsymbol{p} d\boldsymbol{p}' e^{-\beta(\boldsymbol{p}^2+\boldsymbol{p}'^2)/2m}[\cdots]. \tag{23.73}$$

Perform the integrations with respect to $\boldsymbol{p}$ and $\boldsymbol{p}'$ in this expression and find $F(\boldsymbol{r}_1, \boldsymbol{r}_2)$ in the following formula:

$$Z = \frac{1}{2h^6}\int d\boldsymbol{r}_1 d\boldsymbol{r}_2 d\boldsymbol{p} d\boldsymbol{p}'\, e^{-\beta(\boldsymbol{p}^2+\boldsymbol{p}'^2)/2m} F(\boldsymbol{r}_1, \boldsymbol{r}_2). \tag{23.74}$$

(6) F may be interpreted as the Boltzmann factor coming from the effective interaction originating from particle statistics. Sketch the potential ($\times\beta$) of this effective interaction for bosons and fermions.

Solution

(1) The ket $|\boldsymbol{p}\rangle|\boldsymbol{p}'\rangle$ must be correctly symmetrized; $+$ is for bosons and $-$ for fermions:

$$|\boldsymbol{p}, \boldsymbol{p}'\rangle = \frac{1}{\sqrt{2}}(|\boldsymbol{p}\rangle|\boldsymbol{p}'\rangle \pm |\boldsymbol{p}'\rangle|\boldsymbol{p}\rangle). \tag{23.75}$$

(2) $|\boldsymbol{p}\rangle$ describes a plane wave of wave vector $\boldsymbol{k} = \boldsymbol{p}/\hbar$:

$$\langle \boldsymbol{r}|\boldsymbol{p}\rangle \propto e^{i\boldsymbol{p}\cdot\boldsymbol{r}/\hbar}. \tag{23.76}$$

The normalization condition is

$$\delta(\boldsymbol{p} - \boldsymbol{p}') = \frac{1}{h^3}\int_{\mathbb{R}^3} d^3\boldsymbol{r}\,\langle \boldsymbol{p}'|\boldsymbol{r}\rangle\langle \boldsymbol{r}|\boldsymbol{p}\rangle. \tag{23.77}$$

Therefore,

$$\langle \boldsymbol{r}|\boldsymbol{p}\rangle = \frac{1}{h^{3/2}}e^{i\boldsymbol{p}\cdot\boldsymbol{r}/\hbar}. \tag{23.78}$$

(3)

$$(\langle \boldsymbol{r}_1|\langle \boldsymbol{r}_2|)|\boldsymbol{p}, \boldsymbol{p}'\rangle = \frac{1}{\sqrt{2}}(\langle \boldsymbol{r}_1|\boldsymbol{p}\rangle\langle \boldsymbol{r}_2|\boldsymbol{p}'\rangle \pm \langle \boldsymbol{r}_1|\boldsymbol{p}'\rangle\langle \boldsymbol{r}_2|\boldsymbol{p}\rangle). \tag{23.79}$$

(4) Using the results of (2) and (3), we get (the overall factor $1/2$ comes from $1/N!$ in the definition of trace (23.71))

$$\begin{aligned}
Z &= Tr\, e^{-\beta H} = \frac{1}{2}\int d\boldsymbol{r}_1 d\boldsymbol{r}_2 \langle \boldsymbol{r}_1|\langle \boldsymbol{r}_2|e^{-\beta H}|\boldsymbol{r}_1\rangle|\boldsymbol{r}_2\rangle & (23.80)\\
&= \frac{1}{2}\int d\boldsymbol{r}_1 d\boldsymbol{r}_2 \int d\boldsymbol{p}d\boldsymbol{p}'\, e^{-\beta(\boldsymbol{p}^2+\boldsymbol{p}'^2)/2m}|(\langle \boldsymbol{r}_1|\langle \boldsymbol{r}_2|)|\boldsymbol{p}, \boldsymbol{p}'\rangle|^2 & (23.81)\\
&= \frac{1}{2}\int d\boldsymbol{r}_1 d\boldsymbol{r}_2 \int d\boldsymbol{p}d\boldsymbol{p}'\, e^{-\beta(\boldsymbol{p}^2+\boldsymbol{p}'^2)/2m}\frac{1}{2}|\langle \boldsymbol{r}_1|\boldsymbol{p}\rangle\langle \boldsymbol{r}_2|\boldsymbol{p}'\rangle \pm \langle \boldsymbol{r}_1|\boldsymbol{p}'\rangle\langle \boldsymbol{r}_2|\boldsymbol{p}\rangle|^2. & (23.82)
\end{aligned}$$

If we write the matrix elements explicitly,

$$Z = \frac{1}{2h^6}\int d\boldsymbol{r}_1 d\boldsymbol{r}_2 \int d\boldsymbol{p}d\boldsymbol{p}' e^{-\beta(\boldsymbol{p}^2+\boldsymbol{p}'^2)/2m}[1 \pm Re\exp(i(\boldsymbol{p}-\boldsymbol{p}')\cdot(\boldsymbol{r}_1-\boldsymbol{r}_2)/\hbar)]. \tag{23.83}$$

(5) To obtain F we compute

$$\frac{\int d\boldsymbol{p}\, e^{-\beta(p^2/2m)+i\boldsymbol{p}\cdot\boldsymbol{r}/\hbar}}{\int d\boldsymbol{p}\, e^{-\beta(p^2/2m)}} = e^{-mk_BTr^2/2\hbar^2}. \tag{23.84}$$

Hence,

$$F = 1 \pm e^{-mk_BT(\boldsymbol{r}_1 - \boldsymbol{r}_2)^2/\hbar^2}. \tag{23.85}$$

(6) If we introduce the effective potential ϕ by $F = e^{-\beta\phi}$, we get

$$\beta\phi(\boldsymbol{r}) = -\log[1 \pm e^{-mk_BT(\boldsymbol{r}_1 - \boldsymbol{r}_2)^2/\hbar^2}]. \tag{23.86}$$

The sketches of the potential are given in Fig. 23.4.

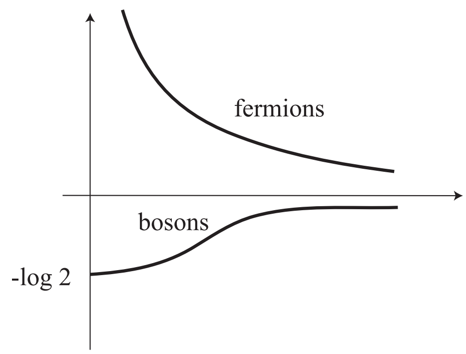

Figure 23.4: Effective potential for bosons and fermions

As expected, the effective interaction is attractive for bosons, and repulsive for fermions.

Exercise 12

E12.1 [Cosmic background temperature]
At present, the cosmic background radiation is at 3 K. Suppose the universe expands adiabatically (but not necessarily quasistatically). What can you say about the temperature of the cosmic background radiation when the total volume of the universe was one half of the present volume?

Solution.
If you can assume that the process is quasistatic, this is just Discussion 11.3, but compression to halve the volume. Therefore, the temperature in the past is estimated to be $3 \times 2^{1/3} = 3.8$ K. If the expansion is not quasistatic, then what could happen? This means 'heat' is generated. Thus, the temperature in the past should be lower than the quasistatic case. That is, 3.8 K is the upper bound.

E12.2 [Electron-positron-photon equilibrium]
In **D12.6** we discussed the electrons 'e' and the positrons 'p' in equilibrium with the photon field (electromagnetic field) and determined their chemical potentials: $\mu_e = \mu_p = 0$.
(1) Calculate the total energy E_e of electrons [You need not perform the integrals.].
(2) Find their T dependence.
(3) Let $E_{h\nu}$ be the total electromagnetic wave in this same volume. Which is larger, E_e or $E_{h\nu}$?

Solution.
(1) The total energy of electrons is given by

$$E_e = 2 \times \frac{4\pi V}{h^3c^3} \int_0^\infty d\varepsilon \, \frac{\varepsilon^3}{e^{\beta\varepsilon} + 1} = E_p. \tag{23.87}$$

(2) T-dependence can be read off by power counting as $[E_p] = [\varepsilon]^4$ or $E_p \propto T^4$.
(3) The total energy of photons is, by taking the polarizations into account,

$$E_{h\nu} = \frac{8\pi V}{h^3c^3} \int_0^\infty d\varepsilon \, \frac{\varepsilon^3}{e^{\beta\varepsilon} - 1}. \tag{23.88}$$

Comparing the integrands, we see $E_{h\nu} > E_e = E_p$.[381]

E12.3 [Molecular vibration]
The vibrational spectrum of I_2 is at (reciprocal wavelength) 213 cm^{-1}.
(1) What is the occupation number ratio of the ground and the first excited states at room temperature 300 K?

[381] Exact evaluations are possible and the ratio is 8/7.

(2) What is the contribution in % of vibration to the total C_V?

Solution.
(1) This is just the Boltzmann factor question. Let λ be the wavelength. Then, $\nu = c/\lambda$, so (notice that $1/213$ cm $= 1/(213 \times 100)$ m , so the reciprocal wavelength is 21300 m^{-1})

$$\nu = 3 \times 10^8 \times 213 \times 100 = 6.30 \times 10^{12} \text{ Hz}. \tag{23.89}$$

Thus,

$$\Theta_v = h\nu/k_B = (6.62 \times 10^{-34}) \times (6.30 \times 10^{12})/1.38 \times 10^{-23} = 302 \text{ K}. \tag{23.90}$$

Therefore, for $T = 300$ K

$$e^{-302/300} = 0.365. \tag{23.91}$$

(2) Since

$$C_v = R(\beta h\nu)^2 \frac{e^{\beta h\nu}}{(e^{\beta h\nu} - 1)^2} \tag{23.92}$$

with $\beta h\nu \simeq 1$, we have

$$C_v = R\frac{e}{(e-1)^2} = 0.92R. \tag{23.93}$$

This is 92% of the full contribution of the vibrational degree of freedom (i.e., the classical contribution). If we ignore the contribution of vibration, the total constant volume specific heat is $5R/2$. Therefor $0.92/(0.92 + 2.5) = 0.269$. That is about 27%.

24 Phases and phase transitions

Summary
∗ Statistical thermodynamics is briefly reviewed with illustrations relevant to the phase transition.
∗ Qualitative change of phases is the phase transition, which corresponds to some mathematical singularities of thermodynamic potentials.
∗ Phase coexistence conditions (under given T and P) are a set of equalities among chemical potentials. Gibbs' phase rule follows from the condition.
∗ Thermodynamic limit is absolutely needed to rationalize phase transitions statistical-mechanically.

Key words
phase, phase transition, phase diagram, coexistence curve, triple point, kelvin scale, Gibbs' phase rule, first order phase transition, second order phase transition, Ising model, thermodynamic limit.

What you should be able to do
∗ Draw the phase diagram of a ordinary one-component fluid on the PT plane.
∗ Sketch $G(T, P)$ for an ordinary fluid.
∗ Understand why thermodynamic limit is required.

So far we have not discussed systems with interactions. If there are interactions, there are various phases as is exemplified by ice, liquid and vapor of water. First, let us discuss how to describe thermodynamically what we experience. Then, let us discuss whether statistical mechanics can discuss phase transitions.

24.1 What is a phase?

Intuitively, under different conditions (say, at various (T, P)) a system can exhibit qualitatively different properties. When this happens, we say the system (or the material) is in different phases.[382] To understand a substance is to understand its various phases and their characteristic features. Therefore, we wish to map out what happens at various points in the thermodynamic space or at least in terms of thermodynamic parameters (e.g., T, P, etc.), i.e., we wish to construct the *phase diagram* (see, e.g., Fig. 24.1). To understand the world we must understand where the state boundaries are and what the features of the territories are. To understand

[382] We may say an equilibrium state is in a single phase, if it is macroscopically homogeneous.

the boundaries corresponds to the understanding of phase transitions, and to understand the features of the territories corresponds to characterizing individual phases.

In the above, 'qualitative differences' do not imply quantitative difference such as soft-hard, hot-cold, hue changes, etc., but existence-non existence of some properties such as symmetry, long-range correlation, etc. For example, solid, liquid, and gas phases may be characterized by the following table:

	long-range order	coherence
solid	Y	Y
liquid	N	Y
gas	N	N

Here, 'long-range' correlation implies that if you know a position of a particle, you can tell the position of another particle far away from the first one. Crystalline spatial regularity implies long-range spatial ordering of the particles. For fluid phases we cannot have this property. This property can either exist or not exist. This is the qualitative difference between solid and fluid phases. To distinguish fluid phases is not easy. One possibility is stated in the above table. We know gases can be compressed easily but liquids cannot; they are as incompressible as solids. This must be due to the interactions ('touching') among molecular hard cores. 'coherence' implies that each particle has at least four repulsive interactions with its surrounding particles simultaneously.[383]

Since some qualitative properties appear or disappear upon crossing a phase boundary, something 'singular' can happen thermodynamically (e.g., loss of differentiability or continuity of some thermodynamic quantities), and this change is called a *phase transition*.

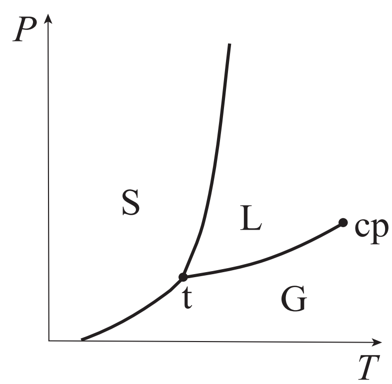

Figure 24.1: A representative phase diagram of an ordinary fluid. S: solid; L: liquid; G: gas; t: triple point; cp: critical point. The curves denote the phase boundaries where phase transitions occur.

[383]But the characterizations mentioned here is rather microscopic. Try thermodynamic characterizations; I think it is not so easy.

24.2 Phase may not sometimes be well-defined globally

However, a precise definition of 'phase' is actually rather difficult. Near the phase boundaries we may clearly distinguish the phases, but the 'territory where a phase occupies' may not be well-defined as in the case of gases and liquids. Therefore, here, the concept of 'phase' is used 'locally' when precise statements are needed. We say the states (near the phase transition point) that cannot be changed into each other without a phase transition (= thermodynamic singularity) are distinct phases (near the phase transition).

Since we have come a long way from Maxwell, Clausius, Boltzmann and other founding fathers of our subject, let us review salient points of statistical thermodynamics that we need to understand phase transitions with relevant illustrations.

24.3 Phase diagram in thermodynamic space

For a given system its any equilibrium state is described (uniquely) as a point in its thermodynamic space spanned by its thermodynamic coordinates (= its internal energy E and work coordinates X, say, V) **9.6** and **9.7**. Thermodynamic coordinates are crucial when we build thermodynamics, since they do not require thermodynamics to describe (purely mechanical description is possible). The unique relation of a point in the thermodynamic space to an equilibrium state of the system allows us to describe phase coexistence unambiguously.

To illustrate this point look at the ordinary solid-liquid-gas phase diagram (Fig. 24.2).

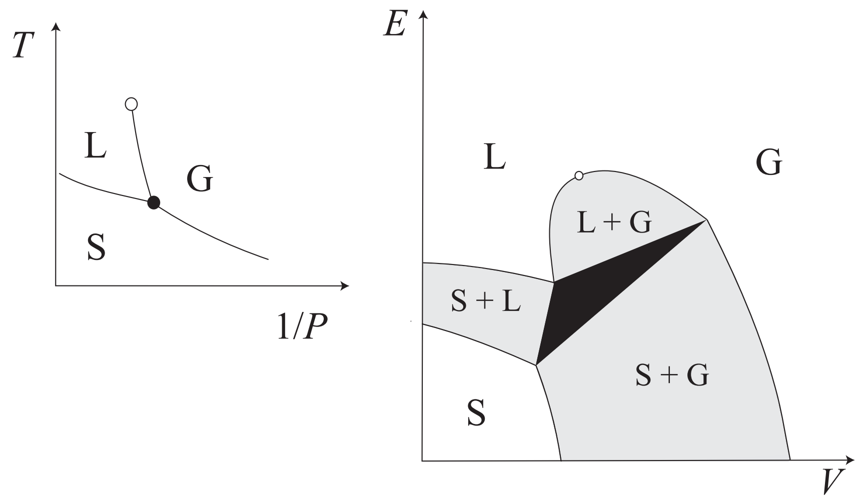

Figure 24.2: The phase diagram superposed on the thermodynamics space. The open circle indicates the critical point, and the black disk and triangle denote the triple point. The gray potions are two-phase coexisting states. The diagram may not be very accurate, but its aim is to exhibit that the transition lines and the triple point in the ordinary phase diagram (inset) are resolved and that you can even tell the relative amount of coexisting phases at a given point in the thermodynamic space.

24.4 Thermodynamic potentials and partition functions

You must be able to write the Gibbs relation **20.3**

$$dS = \frac{1}{T}dE + \frac{P}{T}dV - \frac{B}{T}dM - \frac{\mu}{T}dN + \cdots, \tag{24.1}$$

and the corresponding Gibbs-Duhem relation **20.4**

$$Ed\frac{1}{T} + Vd\frac{P}{T} - Md\frac{B}{T} - Nd\frac{\mu}{T} + \cdots = 0. \tag{24.2}$$

The fundamental principle of statistical thermodynamics is the following translation of entropy into phase volume compatible with a point in the thermodynamic space by Boltzmann **12.4**, **12.11**:

$$S = k_B \log w(E, X). \tag{24.3}$$

However, we often wish to describe the phase transition under constant T, P, etc., so we must Legendre transform S to a generalized Gibbs free energy $\tilde{G}$.[384]

$$S \to S - \frac{1}{T}E - \frac{P}{T}V + \frac{B}{T}M = -\frac{\tilde{G}}{T} \tag{24.4}$$

The generalized canonical formalism reads (cf. **13.7**, **18.10**)

$$\tilde{G} = -k_B T \log \tilde{Z} \;\text{ with }\; \tilde{Z} = \sum_{E,V,M} w(E, V, M) e^{-\beta(E+PV-BM)}. \tag{24.5}$$

[384]Generally, the Legendre transformation of entropy is called *Massieu functions*. $-\tilde{G}/T$ is a typical example.

24.5 Stability, fluctuation and response

The equilibrium condition under $T, P, \cdots$ constant is the minimization of $\tilde{G}$ **11.5**, **11.7**. However, the equilibrium stability condition can always be written as $\delta^2 E \geq 0$ **18.4** (or $\delta^2 S \leq 0$ **18.3**) . The positivity of the diagonal terms of this Hessian is le Chatelier's principle **18.5**

$$\left.\frac{\partial X}{\partial x}\right|_y > 0, \tag{24.6}$$

where y denotes other intensive quantities.

Here, we have assumed that E is twice differentiable, but this does not always hold. For example, if a phase transition occurs, this is highly questionable. Recall that the really important point is that E is a convex function **10.5**. It is also guaranteed that E is continuously once differentiable (i.e., a C^1 function),[385] but the second derivatives may not exist. The true implication of (24.6) is that if x increases, then so does X.

Suppose a phase transition between phase I and II occurs. If the transition to II occurs from I by increasing temperature (i.e., II is a higher temperature phase than I), then $S_{\mathrm{I}} < S_{\mathrm{II}}$, because increasing T implies increasing its conjugate variable: entropy. Or, if II is a higher pressure phase than I, then $-V_{\mathrm{II}} > -V_{\mathrm{I}}$, i.e., $V_{\mathrm{I}} > V_{\mathrm{II}}$ (the conjugate variable of P is not V but $-V$).

We discussed the fluctuation-response relation **18.11**

$$\chi = \left.\frac{\partial X}{\partial x}\right|_y = \beta\langle\delta X^2\rangle. \tag{24.7}$$

If the ordered phase is stable, to destroy its order very large fluctuation is needed. This actually happens near the critical point, and for example magnetic susceptibility or compressibility diverges (see around **26.5**).

24.6 Can phases coexist?

If there is a phase transition from one phase to another, there may or may not be a coexistence of these phases.[386] Thus, 'condition' in the following means, at best, a necessary condition.

[385] This is due to the relation between the work coordinates and the work (in **9.20**) and the definition of entropy **9.25**.

[386] It is impossible to know whether the given two phases coexist or not purely thermodynamically, although, usually, we may say the phases satisfying the thermodynamic coexistence conditions do coexist.

24.7 Coexistence condition for two phases

Suppose a system is described by its thermodynamic coordinates (E, X) and two phases I and II coexist in equilibrium when E and X exchange is allowed between the phases (in an isolated box). When two phases coexist, the substance may be exchanged freely across the phase boundary between the two phases. Therefore, we must also take the exchange of the material into account. We know $S = S_{\mathrm{I}} + S_{\mathrm{II}}$ must be maximized, so the equilibrium condition is the identity of T, x/T and μ/T as we discussed long ago (**10.8**, **10.9**, **20.6**). Let us review it.

The Gibbs relation implies

$$\delta S = \frac{1}{T}\delta E - \frac{x}{T}\delta X - \frac{\mu}{T}\delta N. \tag{24.8}$$

Here, δ implies variation or virtual change, BUT in reality fluctuations actually realize these needed changes spontaneously. $\delta E_{\mathrm{I}} + \delta E_{\mathrm{II}} = 0$, $\delta X_{\mathrm{I}} + \delta X_{\mathrm{II}} = 0$ and $\delta N_{\mathrm{I}} + \delta N_{\mathrm{II}} = 0$ imply the following equilibrium condition:

$$\begin{aligned}
\delta S &= \frac{1}{T_{\mathrm{I}}}\delta E_{\mathrm{I}} - \frac{x_{\mathrm{I}}}{T_{\mathrm{I}}}\delta X_{\mathrm{I}} - \frac{\mu_{\mathrm{I}}}{T_{\mathrm{I}}}\delta N_{\mathrm{I}} + \frac{1}{T_{\mathrm{II}}}\delta E_{\mathrm{II}} - \frac{x_{\mathrm{II}}}{T_{\mathrm{II}}}\delta X_{\mathrm{II}} - \frac{\mu_{\mathrm{II}}}{T_{\mathrm{II}}}\delta N_{\mathrm{II}} && (24.9)\\
&= \left(\frac{1}{T_{\mathrm{I}}} - \frac{1}{T_{\mathrm{II}}}\right)\delta E_{\mathrm{I}} - \left(\frac{x_{\mathrm{I}}}{T_{\mathrm{I}}} - \frac{x_{\mathrm{II}}}{T_{\mathrm{II}}}\right)\delta X_{\mathrm{I}} - \left(\frac{\mu_{\mathrm{I}}}{T_{\mathrm{I}}} - \frac{\mu_{\mathrm{II}}}{T_{\mathrm{II}}}\right)\delta N_{\mathrm{I}} = 0. && (24.10)
\end{aligned}$$

Therefore, $T_{\mathrm{I}} = T_{\mathrm{II}}$ and $x_{\mathrm{I}} = x_{\mathrm{II}}$ are required in general. Usually, $X = V$ and N, so T, P and μ must be identical between two phases:

$$T_{\mathrm{I}} = T_{\mathrm{II}}, \quad P_{\mathrm{I}} = P_{\mathrm{II}}, \quad \mu_{\mathrm{I}} = \mu_{\mathrm{II}}. \tag{24.11}$$

The last equality in (24.11) is

$$\mu_{\mathrm{I}}(T, P) = \mu_{\mathrm{II}}(T, P). \tag{24.12}$$

This functional relation determines a curve called the *coexistence curve* in the T-P diagram (see Fig. 24.1).[387]

Along this line the Gibbs free energy G of the whole system may be written as

$$G = N_{\mathrm{I}}\mu_{\mathrm{I}} + N_{\mathrm{II}}\mu_{\mathrm{II}}. \tag{24.13}$$

Thus, without changing the value of G, any mass ratio of the two phases is admissible, if they can coexist. This implies that in the phase diagram in the thermodynamic space the phase coexistence relation is described as a boundary 'mine field' (see Fig. 24.2 Right) instead of a line.

[387](24.12) may be obtained by minimizing the Gibbs free energy under the constant T and P, because in the thermodynamic limit (i.e., if the system is large enough) what we can obtain from an isolated system and the same system under T, P constant condition with the consistent T and P are indistinguishable (statistical-mechanically, it is the ensemble equivalence).

24.8 Phase coexistence condition: pure substance case

How many phases can coexist at a given T and P? Suppose we have X coexisting phases. The following conditions must be satisfied:

$$\mu_{\rm I}(T,P) = \mu_{\rm II}(T,P) = \cdots = \mu_{\rm X}(T,P). \tag{24.14}$$

We believe that for the generic case, μ's are sufficiently functionally independent. To be able to solve for T and P, we can allow at most two independent relations. That is, at most three phases can coexist at a given T and P for a pure substance.

24.9 Triple point

For a pure substance, if three phases coexist, T and P are uniquely fixed. This point on the T-P diagram is called the *triple point*. The kelvin scale of temperature is *defined* so that triple point of water is at $T = 273.16$K (since 1954). $t = T - 273.15$ is the temperature in Celsius. Again, this is the definition of °C.

24.10 Clapeyron-Clausius relation revisited

For a pure substance, as we have seen, the chemical potentials of coexisting phases must be identical. Before and after the phase transition from phase I to II or vice versa, there is no change of the Gibbs free energy

$$\Delta G_{\rm CC} = 0, \tag{24.15}$$

where CC means "along the coexistence curve" and Δ implies the difference across the coexistence curve (say, phase I − phase II). From (24.15) we already obtained the *Clapeyron-Clausius relation*:

$$\left.\frac{\partial P}{\partial T}\right|_{\rm CC} = \frac{\Delta_{\rm I\to II} H}{T\Delta_{\rm I\to II} V}, \tag{24.16}$$

where $\Delta_{\rm I\to II}X$ denotes $X^{\rm II} - X^{\rm I}$.

24.11 Gibbs' phase rule

Consider a more general case of a system consisting of c chemically independent components (i.e., the number of components we can change independently). For example, H_3O^+ in pure water should not be counted, if we count H_2O among the independent chemical components.

Suppose there are ϕ coexisting phases. The equilibrium conditions are:
(1) T and P must be common to all the phases,
(2) The chemical potentials of the c chemical species must be common to all the phases.

To specify the composition of a phase we need $c-1$ variables, because we need only the concentration ratios. Thus, the chemical potential for a chemical species depends on T, P and $c-1$ mole fractions $(x^1, x^2, \cdots, x^{c-1})$, which are not necessarily common to all the phases (we must add a suffix to denote the phases). That is, μ's are $c+1$ variable functions, and we have $2+\phi(c-1)$ unknown variables. We have $\phi-1$ equalities among the chemical potentials in different phases for each chemical species, so the number of equalities we have is $(\phi-1)\times c$. Look at the following simultaneous equations:

$$\begin{aligned}
&\mu^1_{\mathrm{I}}(T,P,x^1_{\mathrm{I}},x^2_{\mathrm{I}},\cdots x^{c-1}_{\mathrm{I}}) = \mu^1_{\mathrm{II}}(T,P,x^1_{\mathrm{II}},x^2_{\mathrm{II}},\cdots x^{c-1}_{\mathrm{II}}) = \cdots = \mu^1_{\phi}(T,P,x^1_{\phi},x^2_{\phi},\cdots x^{c-1}_{\phi}),\\
&\cdots\\
&\mu^j_{\mathrm{I}}(T,P,x^1_{\mathrm{I}},x^2_{\mathrm{I}},\cdots x^{c-1}_{\mathrm{I}}) = \mu^j_{\mathrm{II}}(T,P,x^1_{\mathrm{II}},x^2_{\mathrm{II}},\cdots x^{c-1}_{\mathrm{II}}) = \cdots = \mu^j_{\phi}(T,P,x^1_{\phi},x^2_{\phi},\cdots x^{c-1}_{\phi}),\\
&\cdots\\
&\mu^c_{\mathrm{I}}(T,P,x^1_{\mathrm{I}},x^2_{\mathrm{I}},\cdots x^{c-1}_{\mathrm{I}}) = \mu^c_{\mathrm{II}}(T,P,x^1_{\mathrm{II}},x^2_{\mathrm{II}},\cdots x^{c-1}_{\mathrm{II}}) = \cdots = \mu^c_{\phi}(T,P,x^1_{\phi},x^2_{\phi},\cdots x^{c-1}_{\phi}),
\end{aligned} \tag{24.17}$$

Consequently, for the generic case we can choose $f = 2+\phi(c-1)-c(\phi-1) = c+2-\phi$ variables freely. This number f is called the number of *thermodynamic degrees of freedom*. We have arrived at the *Gibbs phase rule*:[388]

$$f = c + 2 - \phi. \tag{24.18}$$

24.12 How G behaves at the phase boundaries

What happens to the Gibbs free energy at the phase transition point under constant T and P ? You must be able to sketch it in the ordinary fluid case. Note the usual Gibbs relation:

$$dG = -SdT + VdP. \tag{24.19}$$

Under constant P, G may be sketched as follows:

[388] As astute readers have probably sensed already, the derivation is not water tight. We have assumed that there is no special functional relations among chemical potentials. Rigorously speaking, we *cannot* guarantee this and so we cannot derive the phase rule from the fundamental laws of thermodynamics (nor equilibrium statistical mechanics, either). Indeed, for example, by carefully preparing special mixtures the 'four corner' can be created on the PT-diagram.

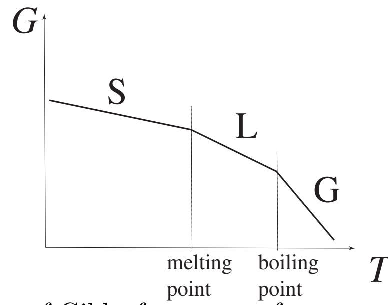

Figure 24.3: Typical behavior of Gibbs free energy for a pure substance. The free energy loses differentiability at first order phase transition points.

When P is the critical pressure, then the liquid-gas transition 'break' disappears: G becomes differentiable. However, the specific heat has a singular behavior at the critical temperature. That is, the LG transition becomes second order. We will discuss this later in more detail.

Try to sketch G under constant T as a function of P.

24.13 Classification of phase transitions

Usually, phase transitions are classified into *first order phase transitions* and the rest called continuous phase transitions or *second-order phase transitions*. In the first order phase transition at least one thermodynamic density (= extensive quantity per volume) changes discontinuously, but in the second order phase transitions there is no discontinuity in thermodynamic densities. The liquid-gas transition at the critical pressure is a second-order phase transition as noted just above.

Phase transitions in many interesting cases occur between more ordered and less ordered phases; it is between the low entropy state and the high energy (enthalpy) state. For example melting is the transition from low entropy solid to high energy liquid. Protein folding is the transition from higher energy random coil state to low entropy folded state.[389]

A first order phase transition occurs if the ordered phase loses its stability 'catastrophically.' In other words, the first order phase transition occurs when a slight loss of order favors further loss of order. Thus, there is no equilibrium state with reduced stability. In contrast, in the case of second order phase transitions reduction of order does not appreciably destabilize the order further. Thus, a phase with reduced stability of order can exist as an equilibrium state. You can intuitively understand a stable phase with reduced stability as an oscillator with a very weak spring. Fluctuation becomes very large near the second order phase transition; despite large thermal fluctuations the phase persists. The ordered phase persists until fluctuation becomes indefinitely large. Since the ordering of some sort is always the reason for phase

[389]However, do not have a prejudice that natural states of proteins are equilibrium states. Many large proteins are likely to be in metastable states when they function biologically normally. Think how you can prove experimentally that a particular protein is in equilibrium.

transitions, the second order phase transition is theoretically the most interesting. Therefore, we discuss the second order phase transition first.

24.14 Typical example of second order phase transition

A typical second order phase transition is the one from the paramagnetic to the ferromagnetic phase we can observe in magnets.

A magnet can be understood as a lattice of spins interacting with each other locally in space. The interaction between two spins has a tendency to align them parallelly. At higher temperatures, due to vigorous thermal motions, this interaction cannot quite make order among spins, but at lower temperatures the entropic effect becomes less significant, so spins order globally. There is a special temperature T_c below which this ordering occurs. We say an *order-disorder transition* occurs at this temperature.

The *Ising model* is the simplest model of this transition.[390] At each lattice point is a (classical) spin σ which takes only $+1$ (up) or -1 (down). A nearest neighbor spin pair has the following interaction energy:

$$-J\sigma_i\sigma_j, \tag{24.20}$$

where J is called the coupling constant, which is positive in our example (ferromagnetic case; if spins are parallel, interaction energy is lowered). We assume all the spin-spin interaction energies are superposable, so the total energy of the system for a lattice is given by

$$\mathcal{H} = -\sum_{\langle i,j\rangle} J\sigma_i\sigma_j - \sum_i h\sigma_i, \tag{24.21}$$

where $\langle\ \rangle$ implies the nearest neighbor pairs, and h is the external magnetic field.

The (generalized canonical) partition function for this system reads

$$Z = \sum_{\{\sigma_i=\pm 1\}} \mathrm{e}^{-\beta\mathcal{H}}. \tag{24.22}$$

---

[390]The Ising model was introduced by W. Lenz (1888-1957; different from the Lenz of Lenz's law). He was an important figure in the early development of quantum mechanics, known for the Lenz vector (Laplace-Runge-Lenz vector relevant to the O_4 symmetry of the Kepler problem). He was a student of and, later, a long-time assistant to Sommerfeld. Pauli, Jordan and others were his assistants. He was an important figure in the development of theoretical physics in Germany.

Lenz gave the model as a model of phase transition (although not restricted to the nearest neighbor interactions) to his PhD student, Ising, E 1900-1998. See https://web.archive.org/web/20160301212619/http://www.bradley.edu/academic/departments/physics/why/ising.dot Ising lived in Peoria (it is the town after next of the town where University of Illinois is) until mid 90s. He solved the 1D nearest neighbor version to show there is no phase transition and concluded that 3D was the same.

Here, the sum is over all spin configurations.[391]

24.15 Fundamental questions about phase transitions

So far phenomenologically, we accepted the existence of phase transitions, and discussed how to describe/handle them. From the statistical mechanics point of view, the most important question is why such qualitative changes can occur at all. Actually, a more fundamental question is: can statistical mechanics ever describe phase transitions? Up to early 1930s such doubts existed. Now, in the 21st century, we are sure that statistical mechanics correctly describes various phase transitions. HOWEVER, do not forget that we cannot yet explain statistical mechanically why ordinary molecules can make crystals below some finite temperature. Does the partition function contain a crystal? We believe so, but no one has demonstrated this.

24.16 Necessity of thermodynamic limit

If the system size is finite, the sum in (24.22) is a finite sum of positive terms. Each term in this sum is analytic[392] in T and h, so the sum itself becomes analytic in T and h (i.e., very smooth). Furthermore, Z cannot be zero, because each term in the sum is strictly positive. Therefore, its logarithm is real analytic in T and h; the free energy of the finite lattice system cannot exhibit any singularity. That is, there is no thermodynamic singularity, and consequently, there is no phase transition for this system.[393]

Even in the actual system we study experimentally, there are only a finite number of atoms, but this number is huge. Thus, the question of phase transitions from the statistical mechanics point of view is: is there any singularity in $A = -k_BT \log Z$ in the large system limit? The large system limit, with proper caution not to increase its surface area more than the order of $V^{2/3}$, where V is the system volume, is called the *thermodynamic limit*. Strictly speaking, phase transitions can occur only in this

[391] **Warning**. What is $F = -k_BT \log Z$ in this case? It is NOT the Helmholtz free energy in the original sense. That is why Z is (precisely speaking) called the generalized canonical partition function. Notice that dF is NOT given by $dF = -SdT + hdM$ (assuming the volume to be constant), but by $dF = -SdT - Mdh$.

Why does this happen? This is due to the term $-\sum_i h\sigma_i$ in the Hamiltonian (24.21). This is not a part of the proper energy of the system, but the potential energy of the spins stored between the magnet and the device creating the magnetic field.

[392] A more accurate mathematical term is 'holomorphic.'

[393] Strictly speaking, there is no phase transition for any finite system, unless each spin has infinitely many states.

limit.[394]

You may not wish to go into mathematics, but at least clearly recognize that qualitative changes require loss of analyticity.

[394]Does such a limit exist? This is also a fundamental question never considered till 1950s. This is a far easier question than the existence/non-existence question of phase transitions.

Q24.1 [Phase diagram of Ising magnet in thermodynamic space]
Consider an Ising magnetic system in 3-space. There is a second order order-disorder phase transition at $T = T_c$, if the magnetic field $h = 0$ (i.e., $h_c = 0$).
(1) What is the thermodynamic space for this system (or what are the thermodynamic coordinates for the system)?
(2) Sketch the phase diagram of this magnet in its thermodynamic space.

Solution.
(1) E and M must be the thermodynamic coordinates. h is intensive, and corresponds to P in fluids.
(2) We must draw a phase diagram on (E, M). The usual diagram is on (h, T).

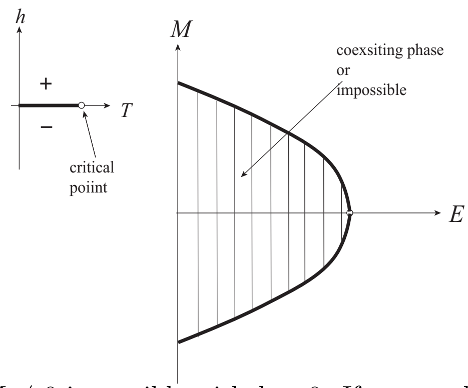

Figure 24.4: Below T_c $M \neq 0$ is possible with $h = 0$. If you apply nonzero h, one of the up or down phases remain as an equilibrium state. Thus, the 'lined' region is with $h = 0$; it is realizable if $d > 2$, but not in $d = 2$ (i.e., no actual equilibrium system can be in this region). Outside of this 'coexistence' region, for higher T of the temperature axis, magnetic field must be applied. Needless to say too large $|M|$ is not realizable, so the thermodynamic space is bounded vertically.

The rough sketch is shown here. However, accurate sketch is very hard.

Q24.2 [Latent heat of tetrachlorocarbon]
The melting temperature of tetrachlorocarbon (CCl_4) depends on the pressure as follows:

$$T_m = 250.56 + 4.005 \times 10^{-2} P - 2.15 \times 10^{-6} P^2, \tag{24.23}$$

where T is measured in K and P in atm. At $P = 1000$ atm, the melting causes the volume increase of $\Delta V = 3.06$ mℓ per mole. Find the latent heat of melting per mole of tetrachlorocarbon at 1000 atm. Notice that 1 atm = 101,325 P.

Solution.
We use the Clapeyron-Clausius relation

$$\left.\frac{\partial T_m}{\partial P}\right|_{\rm CC} = \frac{T_m \Delta V}{\Delta H}$$

or

$$\Delta H = T_m \Delta V \left(\left.\frac{\partial T_m}{\partial P}\right|_{\rm CC} \right)^{-1}$$

$$\left.\frac{\partial T_m}{\partial P}\right|_{\mathrm{CC}} = 4.005 \times 10^{-2} - 4.30 \times 10^{-6} P = 0.0358$$

in K/atm. Therefore, ($T_m = 288.5$ K)

$$\Delta H = 288.5 \times (3.06 \times 10^{-6}/0.0358)\ \mathrm{m}^3 \cdot \mathrm{atm} = 0.02466\ \mathrm{m}^3 \cdot \mathrm{atm} = 2498\ \mathrm{J},$$

or 597 cal/mol.

25 Spatial dimensionality and interaction range are crucial

Summary
∗ Statistical mechanics seems to be able to explain various phases and phase transitions rationally in the thermodynamic limit.
∗ Spatial dimensionality is crucial to the phase ordering and existence of the order-disorder phase transition. Peierls' argument tells us the importance of spatial dimensionality.
∗ If the interaction is long-ranged, phase transitions can happen even in 1-space. (Augmented) van der Waals gas in 1D is a typical example.
∗ The second order phase transition for magnets, fluids and binary fluid mixtures may be understood in a unified fashion.

Key words
Peierls' argument, Kac potential, van der Waals gas, Maxwell's rule, Tonks' gas

What you should be able to do
∗ Intuitively understand why spatial dimensionality matters.
∗ You must be able to explain Peierls' argument.
∗ Derivation of Tonk's equation of state should be a good exercise.

Whether statistical mechanics can understand phase transitions or not in the thermodynamic limit is a fundamental question. Peierls definitely settled the issue by demonstrating that the 2D Ising model has an ordered phase. His demonstration makes it clear that spatial dimensionality is crucial.

25.1 Magnet-lattice gas correspondence

The Ising model due to Lenz was introduced in the preceding lecture, whose Hamiltonian reads

$$H = -J \sum_{\langle i,j \rangle} \sigma_i \sigma_j - h \sum_i \sigma_i. \tag{25.1}$$

We can interpret this as a lattice model of a gas (lattice gas) with the following correspondence 'up' (resp., 'down') → lattice point 'occupied' (resp., 'empty'). h may be interpreted as the chemical potential (large positive h implies more up spins = more particles).

25.2 Order parameter

To characterize the order in the system we define an *order parameter* which is nonzero only in the ordered phase: magnetization per particle $m = \langle \sigma \rangle = M/N = (1/N)\sum \sigma_i$ is a good example. Thus, the fundamental question about the Ising model is whether M/N converges to zero or not in the thermodynamic limit.[395]

You can watch 2-Ising model here:
http://physics.weber.edu/schroeder/software/demos/IsingModel.html

25.3 Spatial dimensionality is crucial

For the existence of a phase transition, not only the system size but also the spatial-dimensionality of the system is crucial.

Let us consider a one-dimensional Ising model (Ising chain), whose total energy reads

$$H = -J \sum_{-\infty < i < +\infty} \sigma_i \sigma_{i+1}. \tag{25.2}$$

We have ignored the external magnetic field for simplicity. Compare the energies of the following two spin configurations (+ denotes the up spins and − down spins) (Fig. 25.1):

$$+ +$$
$$+ + + + \underbrace{- - - - - - - - -}_{\longleftarrow\; L \;\longrightarrow} + + + + + + + + +$$

Figure 25.1: Top: completely ordered state of 1-Ising model (+ implies up spins and − down spins); Bottom: Ising chain with a spin-flipped island of size L.

The bottom one has a larger energy than the top by $2J \times 2$ due to the existence of the two mismatching edges. However, this energy difference is independent of the size L of the island. Therefore, as long as $T > 0$ there is a finite chance of making big (= macroscopic) down spin islands amidst the ocean of up spins. If a down spin island becomes large, there is a finite probability for a large lake of up spins on it. This implies that no ordering is possible for $T > 0$.

As you can easily guess there is no ordered phase in any one dimensional lattice system with local interactions for $T > 0$.

25.4 There is an ordered phase in 2D: intuitive Peierls' argument

Consider the two-dimensional Ising model with $h = 0$. Imagine there is an ocean of up spins (Fig. 25.2). To make a circular down-spin island of radius L, we need $4\pi JL$

[395] This argument requires, honestly speaking, details about convergence of the distribution, etc. See the graduate course notes.

more energy than the completely ordered phase.

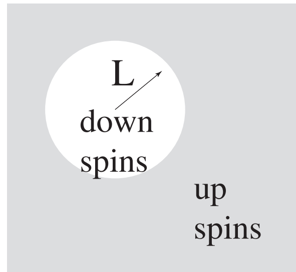

Figure 25.2: Peierls' argument illustrated.

This energy depends on L, making the formation of a larger island harder. That is, to destroy a global order we need a macroscopic amount of energy, so for sufficiently low temperatures, the ordered phase cannot be destroyed spontaneously. Of course, small local islands could form, but they never become very large. Hence, we may conclude that an ordered phase could exists at sufficiently low temperatures. Consequently, there must be a phase transition for a two-dimensional system with local short-range interactions. The above argument is known as *Peierls' argument* and can be made rigorous.[396]

25.5 Peierls' argument

What Peierls actually proved is the following. Prepare a $L \times L$ square lattice, and fix all the edge spins upward (Fig. 25.3). If L becomes large and if T is not low, eventually the probability $P(\sigma_0 = +1)$ of the center spin to be up converges to $1/2$. If this is always true for any T, it implies no spin ordering occurs. Peierls demonstrated that $P(\sigma_0 = +1) > 1/2$ at sufficiently low temperatures. An important idea used in the proof is basically the above intuitive argument.

Generally speaking, spatial dimensionality is crucial for the existence of phase transitions for the system with short-range interactions.[397]

25.6 Interaction 'range' is also crucial

What happens if the range of interactions is not finite and the intensity of interac-

[396] There is at least one more crucial factor governing the existence of phase transition. It is the *spin dimension*: the degree of freedom of each spin. Ising spins cannot point different directions, only up or down (their spin-dimension is 1). However, the true atomic magnets can orient in any direction (their spin dimension is 3). This freedom makes ordering harder. Actually, in 2D space ferromagnetic ordering at $T > 0$ by spins with a spin dimension larger than 1 is impossible.

[397] Here, 'short range' implies the interaction vanishes beyond some finite range, or the strength of the interaction decays sufficiently quickly (say, faster than $1/r^{d+1}$.

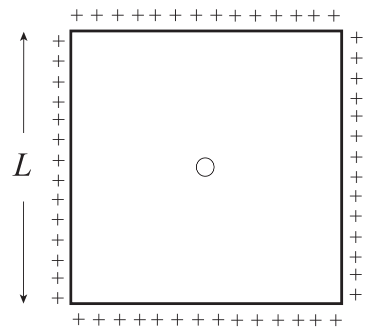

Figure 25.3: All the boundary spins are fixed to be up. What happens to the central spin in the circle in the $L \to \infty$ limit?

tion decays sufficiently slowly? Peierls' argument is still applicable. Obviously, if each spin can interact with all the spins in the system uniformly, an ordered phase is possible even in 1-space. If the coupling constant J decays slower than $1/r^2$, then an order-disorder phase transition is still possible at a finite temperature in one dimensional space.
Exercise. Intuitively explain the last statement. □

If the interaction is long-ranged, then the system may not behave thermodynamically normally (the fourth law may be violated). However, if interaction is infinitesimal, then thermodynamics may be saved even if the interaction does not decay spatially. As you see below such a system is essentially the system described by the van der Waals equation of state.

25.7 Van der Waals model: key ideas

Van der Waals proposed the following equation of state (*van der Walls equation of state*:

$$P = \frac{Nk_BT}{V - Nb} - \frac{aN^2}{V^2}, \tag{25.3}$$

where a and b are positive materials constants. Here, P, N, T, V have the usual meaning in the equation of state of gases. His key ideas are:
(1) The existence of the real excluded volume due to the molecular core should reduce the actual volume in which molecules can roam from V to $V - Nb$; this would modify the ideal gas law to $P_{HC}(V - Nb) = Nk_BT$. Here, subscript HC implies 'hard core.'
(2) The attractive binary interaction reduces the actual pressure from P_{HC} to $P = P_{HC} - a/(V/N)^2$, because the wall-colliding particles are actually pulled back by their fellow particles in the bulk.

25.8 Van der Waals model: 'derivation'

Let us 'derive' his equation of state from its entropy. We know that the entropy of a classical ideal monatomic gas **10.16** reads

$$S = S_0 + Nk_B \log \frac{V}{N} + \ \frac{3N}{2} k_B \log \frac{E}{N}. \tag{25.4}$$

Notice that E in this formula is just the kinetic energy K. For the van der Waals model,
(1) implies $V \to V - Nb$,
(2) implies $K = E + Nan$, where $n = N/V$ is the number density, because each particle receives stabilizing interaction from the surrounding 'mass' that must be proportional to n, so the real kinetic energy must be the actual E *minus* $-Nan$.

Therefore, the entropy of the van der Waals gas should read

$$S = S_0 + Nk_B \log \frac{(V - Nb)}{N} + \frac{3N}{2} k_B \log \frac{(E + aN^2/V)}{N}. \tag{25.5}$$

This gives

$$\frac{1}{T} = \left.\frac{\partial S}{\partial E}\right|_V = \frac{3}{2} \frac{Nk_B}{E + aN^2/V}, \tag{25.6}$$

and

$$\frac{P}{T} = \left.\frac{\partial S}{\partial V}\right|_E = \frac{Nk_B}{V - Nb} + \frac{3}{2} \frac{Nk_B}{E + aN^2/V} \left(-\frac{aN^2}{V^2}\right). \tag{25.7}$$

Combining these two, we obtain the van der Waals equation of state:

$$\frac{P}{T} = \left.\frac{\partial S}{\partial V}\right|_E = \frac{Nk_B}{V - Nb} - \frac{aN^2}{TV^2}. \tag{25.8}$$

25.9 Liquid-gas phase transition described by the van der Waals model

The most noteworthy feature of the equation is that liquid and gas phases are described by a single equation.

Let us study the general behavior of (25.8). The first term is $\propto 1/(V - Nb)$, so it blows up at $V = Nb$. It is basically the ideal gas equation translated by Nb along the V-axis. The second term becomes very important if T is small and is $\propto 1/V^2$. Since $1/V^2$ becomes larger more quickly than $1/(V - Nb)$ if V is not too close to Nb, (25.8) becomes non-monotonic as a function of V for sufficiently low T. That is, as in Fig. 25.4, the PV-curve wiggles. We know, however, thermodynamically, $(\partial P/\partial V)_T$ cannot be positive (it is a Le Chatelier's principle!). This 'wrong behavior' must be due to the attractive interactions. Van der Waals guessed that there is a gas-liquid phase transition. Thus, he proposed some ad hoc equilibrium condition to connect the gas and liquid branches of his equation.

25.10 Maxwell's rule

Maxwell was fascinated by the equation because of its possibility to describe the liquid and the gas phases in a unified fashion, and gave the liquid-gas coexistence condition (*Maxwell's rule*, see Fig. 25.4). As will be discussed below, this equation of state *reinforced by Maxwell's rule* can be obtained from statistical mechanics. Thus, the van der Waals model is an exact example exhibiting a phase transition.

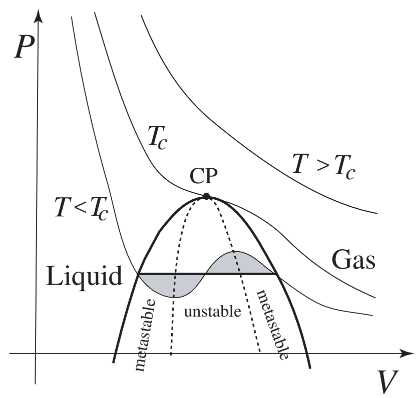

Figure 25.4: The thick curve is the *coexistence curve* below which no single phase can stably exist, and the dotted curve is the *spinodal curve* bounding the thermodynamically unstable states; the region between the spinodal and coexistence curves is the metastable region. When a high temperature state is quenched into the unstable region, it immediately decomposes into liquid and gas phases. If a high temperature state is quenched into the metastable region, after nucleation (of bubbles or droplets), phase separation occurs (see Lecture 28). The liquid-gas coexistence pressure for a given temperature is determined by *Maxwell's rule*: the two shaded regions have the same area.

Maxwell's rule is motivated by the calculation of the Gibbs free energy G: $dG = VdP$ (under constant T)[398] (see Fig. 25.5).

25.11 Kac potential and van der Waals equation of state

The van der Waals equation of state is heuristically derived, but what is really the microscopic model that gives it, if any? A proper understanding of van der Waals's idea is

$$P = P_{HC} - \frac{1}{2}\varepsilon n^2, \tag{25.9}$$

where P_{HC} is the hard core fluid pressure,[399] and the subtraction term is the average

[398] Since we cannot use thermodynamics where the system is unstable, the demo here (the original) is not a very respectable one. However, the obtained rule can even be thermodynamically justifiable (as explained in the graduate notes).

[399] For a collection of hard cores there is no gas-liquid transition at any temperature.

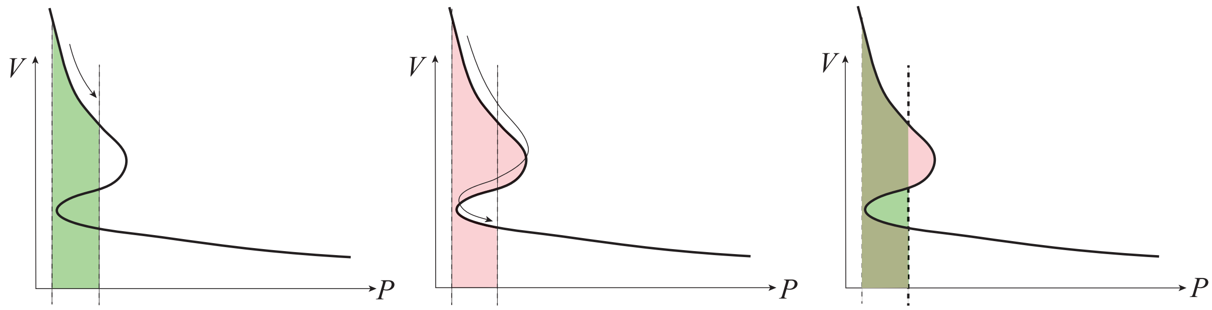

Figure 25.5: Maxwell's rule is derived from the equality of the Gibbs free energy along the coexisting line (the horizontal line in Fig. 25.4). The figure depicts the needed integral (signed area) $\int V dP$ along the curve. If the green area and the red area become identical, the vertical thick dotted line denotes the coexistence condition.

effect of attractive forces. As it is, this equation exhibits the non-monotonic (i.e., not thermodynamically realizable) PV curve just as the van der Waals equation of state, so there cannot be any microscopic model for (25.9).[400] However, this equation augmented with Maxwell's rule is thermodynamically legitimate, and indeed it is the equation of state of the gas interacting with the *Kac potential*:

$$\phi(r) = \phi_{HC}(r/\sigma) + \gamma^3 \phi_0(\gamma r/\sigma), \tag{25.10}$$

where $\phi_{HC}(x)$ is the hard core potential: 0 beyond $x = 1$ and ∞ for $x \le 1$, σ is the hard core diameter, and ϕ_0 is an attractive tail.[401] The parameter γ is a scaling factor; we consider the $\gamma \to 0$ limit (long range but infinitesimal interaction).

25.12 1D Kac potential system may be computed exactly

P_{HC} is not exactly obtainable if the spatial dimension is 2, 3, $\cdots$, but in 1-space, we can obtain it exactly. Therefore, the 1D Kac model (augmented van der Waals model) is exactly solvable, and exhibits a phase transition.

First, let us use the fact that the ideal gas law can be obtained purely mechanically as Bernoulli demonstrated long long ago. Look at the trajectories of the particles (diameter or length σ) (Fig. 25.6). Collisions are just exchange of velocities (the momentum conservation). Therefore, if we trace the trajectories of the centers of mass of the particles disregarding the particle sizes, then the trajectories behave just

[400] Roughly speaking, if the interaction potential is not too long-ranged, if it does not allow pushing infinitely many particles into a finite volume, and if the total interaction energy is bounded from below, then the normal thermodynamics is guaranteed.

[401] Notice that the second term of (25.10) is chosen so that

$$4\pi \int_0^\infty \gamma^3 \phi_0(\gamma r/\sigma) r^2 dr$$

converges in the $\gamma \to 0$ limit, a wide but shallow potential.

as shown in the right of Fig.25.6 (look at colored line examples in Fig. 25.6): point masses going through each other ballistically (ideal gas!). Therefore, the equation of state of the hard 'rods' must be identical to the ideal gas law in the space not covered by the particles, that is $L - N\sigma$ or, writing L as V the volume,

$$P(V - N\sigma) = Nk_BT. \tag{25.11}$$

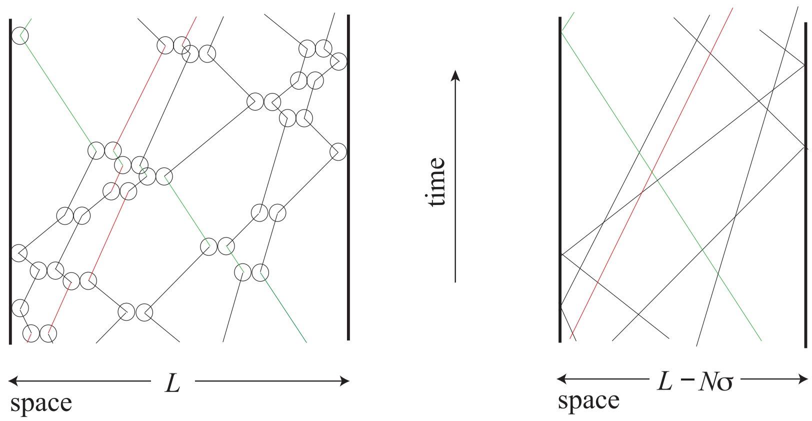

Figure 25.6: Trajectories of hard balls in 1D (Left) is just the trajectories of noninteracting point masses (Right).

So we have shown that statistical mechanics can describe phase transitions. Now, let us survey how to study the phase diagram for a given substance.

25.13 What are the key points to study the phases?

We wish to map out the equilibrium states in the space spanned by, say, T, P and other intensive parameters (usually) as we have seen in Fig. 24.1. To study an ordinary geographical map usually we pay attention to the territorial boundaries first. This means we must understand phase transitions. As we will learn near the phase transitions (esp., second order phase transitions) fluctuations become so big that any theory ignoring them does not make sense. However, far away from phase transition points, we may often ignore (at least qualitatively) fluctuations and simple theoretical methods often work.

Thus, the study of the phase diagram consists of two pillars: renormalization-group theory that can handle violent fluctuations and mean-field theory that is convenient if we may ignore fluctuations. We will discuss the mean field theory fairly in detail in this course. The basic idea of renormalization group theory and why it is important will be discussed in this course, but we will not have enough time to discuss its technical aspects.

25.14 Magnets, liquids and binary mixtures share some common features

The correspondence between the Ising model and the lattice gas model suggests that there are common features in the phase diagrams of a magnet and of a fluid system. Furthermore, we may interpret the Ising model as a lattice fluid mixture of 'up' molecules and 'down' molecules (or the fluid as a mixture of molecules and vacancies), so the phase diagram of a binary mixture must share some features with that of magnets (Fig. 25.7).

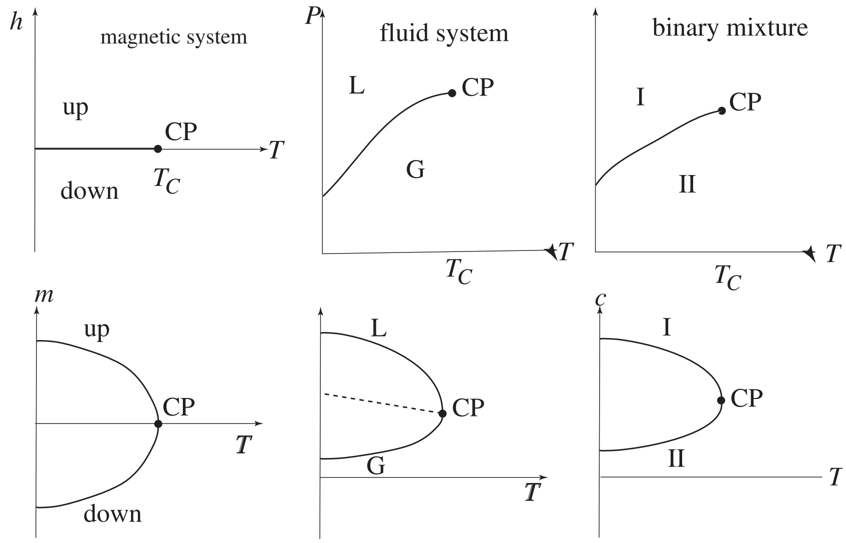

Figure 25.7: The correspondence of the phase diagrams among the magnet, the fluid, and the binary liquid mixture systems. T: temperature, T_c: the critical temperature, h: magnetic field, P: pressure, μ: chemical potential of one component, m: magnetization per spin, ρ: the number density, c: the concentration of a particular component. For the magnetic system, the spins are assumed to be the Ising spins (only two directions are allowed, up or down), and 'up' (resp., 'down') in the figure means majority of the spins point upward (resp., downward) (ferromagnetically ordered). L implies the liquid phase and G the gas phase. I and II denote different mixture phases. The following correspondences are natural: for the fields $h \leftrightarrow P \leftrightarrow \mu$; for the order parameters $m \leftrightarrow (\rho_L - \rho_G) \leftrightarrow (c_I - c_{II})$.

Thus, we can discuss the magnetic system as a representative example.

25.15 Ising model in d-space: a brief review

We already know spatial dimensionality is crucial for the existence/non-existence of phase ordering and consequently phase transitions. Phase ordering is possible because the order can resist thermal fluctuation. To this end microscopic entities must stand 'arm in arm.' The number of entities with which each entity directly interacts (cooperates) crucially depends on the spatial dimensionality. This is the intuitive reason why spatial dimensionality matters.

In short, the effect of fluctuations becomes severe and nontrivial, if the spatial dimensionality is not high.

Let us look at the effect of spatial dimensionality on the Ising model.

1-Ising model:
We can obtain the free energy (with magnetic field) exactly as we will see in Lecture 25 by, e.g., the transfer matrix method; the phase transition does not occur for $T > 0$ as we have intuitively seen above (Peierls' argument).[402]

2-Ising model:
(1) The Onsager solution gives the free energy without magnetic field.[403] There is a phase transition at $T_c > 0$ as we already know.
(2) Below the phase transition temperature T_c there are only two phases corresponding to the up spin phase and the down spin phase, and there is no phase coexistence.[404] That is, up and down phases cannot coexist (see Fig. 25.8).

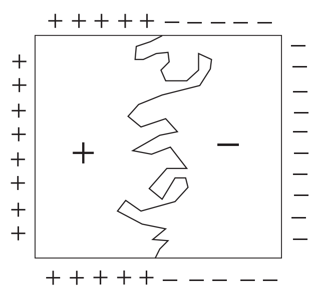

Figure 25.8: Even the half up and half down fixed boundary spin configuration cannot stabilize the interface location between up and down phases for 2D Ising model below T_c. The interface may be understood as a trajectory of a Brownian particle connecting the two phase boundary points at the boundary (Brownian bridge). If the system size is L, then its amplitude is $\sqrt{L}$. In the thermodynamic limit almost surely the observer at a fixed point (say, at the center) who can observe only a finite volume can observe only one of the phases, and can never see the spin flip in her lifetime.

(3) Near T_c there are various nontrivial *critical divergences*.[405]

3-Ising model:
(1) No exact evaluation of the free energy is known, but it is easy to demonstrate that $T_c > 0$ (see Peierls' argument).
(2) It is known that at sufficiently low temperatures there are phase coexistence.[406]
(3) The critical divergences are non-trivial just as in 2-space.

Beyond 3-space:
Although no exact free energy is known, the existence of positive T_c is easy to demonstrate, and the critical divergences around this point are believed to be the same for

[402] It is not hard to show that $T = 0$ is a phase transition point for this model.
[403] due to L. Onsager.
[404] Independently due to M. Aizenman and Y. Higuchi.
[405] Here, 'non-trivial' means that the fluctuation is so large that we cannot use mean-field theory to study the divergent behavior correctly.
[406] due to R. L. Dobrushin

all $d \geq 4$. This has been established for the dimension strictly greater than 4.[407]

25.16 Fluctuation can be crucial in $d < 4$

As you have seen above, near the critical point, or the point where 'strong order' disappears at last, fluctuation is quite important if the spatial dimensionality is less than 4. Beyond 4D, however, the effect of fluctuations may not be so pathological, and perhaps we may largely ignore fluctuation effects. This observation is relevant to the study of phase transitions as we will see soon.

[407]due to M. Aizenman. 4-Ising model still defies mathematical studies.

Q25.1 [Elementary questions]
Are the following statements correct or incorrect? If incorrect, you must explain why or give a counterexample for the statement. If correct, you must provide a brief supporting argument. However, if you can quote or point out the relevant statements in the lecture notes, you need not state your own. [Hint: all the answers are written somewhere in the lecture notes.]
(1) One of the thermodynamic densities must exhibit discontinuity for a phase transition to occur.
(2) When a solid phase melts to a liquid phase, the entropy always increases.
(3) No 1D system can exhibit phase transition if the interaction range is finite.
(4) When a first order phase transition occurs between phase I and II, these two phases can coexist.

Solution.
(1) No. This is required only for first order phase transitions.
(2) No. There is a counterexample. For ^{3}He, crystallization localizes atoms, so the spin-spin coupling due to exchange of particles is reduced, and the spin order that exists in liquid is lost.
(3) Yes. This is according to Peierls' argument or from the PF theorem.
(4) No. A counterexample is the 2-Ising model.

Q25.2 [Stability consequence]
When the temperature is raised under constant pressure, phase I changes into phase II through a first order phase transition. Show that the transition from I to II requires absorption of heat (latent heat).

Solution.
This is basically answerable with the aid of le Chatelier's principle, BUT, S is NOT differentiable at the phase transition point. However, the basis of the stability argument from which le Chatelier's principle is derived is the convexity of E as a function of S, and other extensive quantities. This means when $\Delta S \Delta T > 0$, so $\Delta S > 0$. The latent heat is this times the transition temperature, so it must be positive (absorbs heat).

Q25.3 [Reduce equation of state]
The van der Waals equation of state reads

$$P = \frac{Nk_BT}{V - Nb} - a\frac{N^2}{V^2}. \tag{25.12}$$

(1) Find the critical temperature T_c, volume V_c and pressure P_c in terms of a, b and k_B. [T_c is the temperature, where the PV-curve has an inflection point.]
(2) Van der Waals introduced the concept of reduced pressure $p = P/P_c$, reduced temperature $t = T/T_c$, and reduced volume $v = V/V_c$, and showed that p is a universal function of t and v (called the *reduced equation of state*). Find this relation.

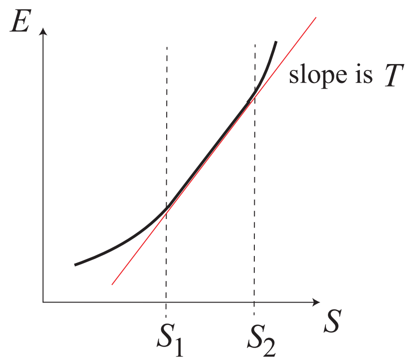

Figure 25.9: The slope is T. The straight portion of E is the coexisting phase of 1 and 2. Since E must be convex, the slope does not decrease. Therefore, the low temperature phase must correspond to the smaller-entropy phase.

Solution.
(1)

$$\left.\frac{\partial P}{\partial V}\right|_T = -\frac{Nk_BT_c}{(V_c - Nb)^2} + 2a\frac{N^2}{V_c^3} = 0, \tag{25.13}$$

$$\left.\frac{\partial^2 P}{\partial V^2}\right|_T = 2\frac{Nk_BT_c}{(V_c - Nb)^3} - 6a\frac{N^2}{V_c^4} = 0, \tag{25.14}$$

From this we get

$$\frac{k_BT_c}{(V_c - Nb)^2} = 2a\frac{N}{V_c^3}, \quad \frac{k_BT_c}{(V_c - Nb)^3} = 3a\frac{N}{V_c^4}. \tag{25.15}$$

Therefore (taking the ratio of the above equalities), we get

$$V_c - Nb = 2V_c/3 \;\Rightarrow\; V_c = 3Nb. \tag{25.16}$$

Therefore,

$$k_BT_c = \frac{2aN(2Nb)^2}{(3Nb)^3} = \frac{8a}{27b}. \tag{25.17}$$

Thus,

$$P_c = \frac{N}{(3Nb - Nb)}\frac{8a}{27b} - \frac{a}{9b^2} = \frac{a}{27b^2}. \tag{25.18}$$

(2) We have only to rewrite the van der Waals equation in terms of p, t, and v.

$$p\frac{a}{27b^2} = \frac{N8at/27b}{3vNb - Nb} - a\frac{N^2}{(3Nbv)^2}. \tag{25.19}$$

That is,

$$p = \frac{27b^2}{a}\frac{N8at/27b}{3vNb - Nb} - \frac{27b^2}{(3bv)^2} = \frac{8t}{3v - 1} - \frac{3}{v^2}. \tag{25.20}$$

26 Why critical phenomena are difficult; mean-field theory

Summary
∗ How order is lost upon changing T is discussed.
∗ It is explained why the second order phase transition is difficult to study.
∗ To understand the phase diagram we need renormalization group and mean-field theory.
∗ Why large fluctuations near the critical point imply universality is intuitively explained.
∗ Rushbrooke's inequality is demonstrated (as a review of thermodynamics).
∗ The mean field theory is formulated with the aid of conditional expectations.

Key words
correlation length, central limit theorem, renormalization group, (genuine and trivial) universality, mean-field theory, bifurcation.

What you should be able to do
∗ You must be able to illustrate what happens if you approach a second order phase transition by changing T.
∗ You must be able to set up the mean-field equation. There are many ways, but the formulation in terms of the conditional probability is the most elegant, so memorize the approach.
∗ How to solve (or qualitatively understand) mean-field equation graphically.
∗ You should clearly recognize the limitations of the mean field approach.
∗ You should be able to explain why critical fluctuations help universality.

26.1 Summary up to this point

What is the phase transition? If a thermodynamic variable is varied and if a mathematical singularity (loss of continuity, loss of differentiability, etc.; loss of analyticity[408] in short) in a thermodynamic potential is observed, we say there is a phase transition. That is, a phase transition is characterized by a mathematical singularity of a thermodynamic potential.

The existence of a singularity requires a very large system (strictly speaking, an infinitely large system). Thus, to formulate phase transitions mathematically, we need the *thermodynamic limit*. In the thermodynamic limit extensive quantities are

[408] holomorphy, precisely

all infinite, so we define *thermodynamic densities* (extensive quantities per particle). A phase transition may also be characterized by a mathematical singularity in a thermodynamic density. We have actually seen that statistical mechanics can describe phase transitions (2-Ising model, D Kac-model, although rather peculiar, the Bose-Einstein condensation).

Phase transitions are often studied by changing intensive parameters (e.g., temperature and pressure). When two phases coexist, they share the same intensive parameters (called *fields*). Therefore, a convenient thermodynamic potential is the *generalized Gibbs free energy* for a given amount of the material (N), that is, the (generalized) Gibbs free energy obtained by Legendre transformation of internal energy with respect to entropy, volume, magnetization, etc., except for the number of particles N. The Gibbs free energy may lose differentiability with respect to its natural independent variables (intensive parameters = fields).[409] If the differentiability is lost, we say a *first order phase transition* occurs. If the singularity in Gibbs free energy is less drastic, generally we say there is a *second order phase transition*.[410]

26.2 How is order lost in first order phase transition?

Let us consider how an order is lost upon changing temperature.[411] In the case of the first order phase transition, as briefly discussed in the preceding Lecture, decrease in order weakens cooperative interactions, accelerating further decrease of order.[412] For example, in the case of a liquid crystal in which slender molecules align in the (nematic) liquid crystal phase, increase of temperature randomizes the molecular alignment and make molecular packing harder, causing increase of the volume. Needless to say, this drastically helps randomization of molecular directions, and the liquid crystal-isotropic liquid phase transition is first order.

26.3 Typical second order phase transition

As a typical second order phase transition, let us consider the Ising model. Let us

[409] G must be continuous. Why?

[410] There is an infinite order phase transition, where G maintains to be C_∞ (infinite-times differentiable) but loses analyticity, that is, formal Taylor expansion ceases to converge. This actually happens in 2D XY model. Also such a singularity occurs between the stable and metastable branches of the free energy.

[411] **Warning**: This is NOT really a thermodynamic or equilibrium statistical-mechanical explanation.

[412] If a slight local loss of order could induce something like a domino effect of loss of global order, it is likely a first order phase transition. The *Lindemann criterion* illustrates this point; although the phase transition is determined by the equilibrium condition of the chemical potentials in the ordered and the disordered phases, instability in the ordered phase seems to occur sufficiently close to the equilibrium order-disorder phase transition point in the solid-liquid phase transition case.

approach the phase transition from the high temperature side. Up and down spin islands grow as T is reduced (see Fig. 26.1; the figure is constructed using http://www.pha.jhu.edu/~javalab/ising/ising.html (no more available?); the following site is also useful: http://physics.weber.edu/schroeder/software/demos/IsingModel.html).

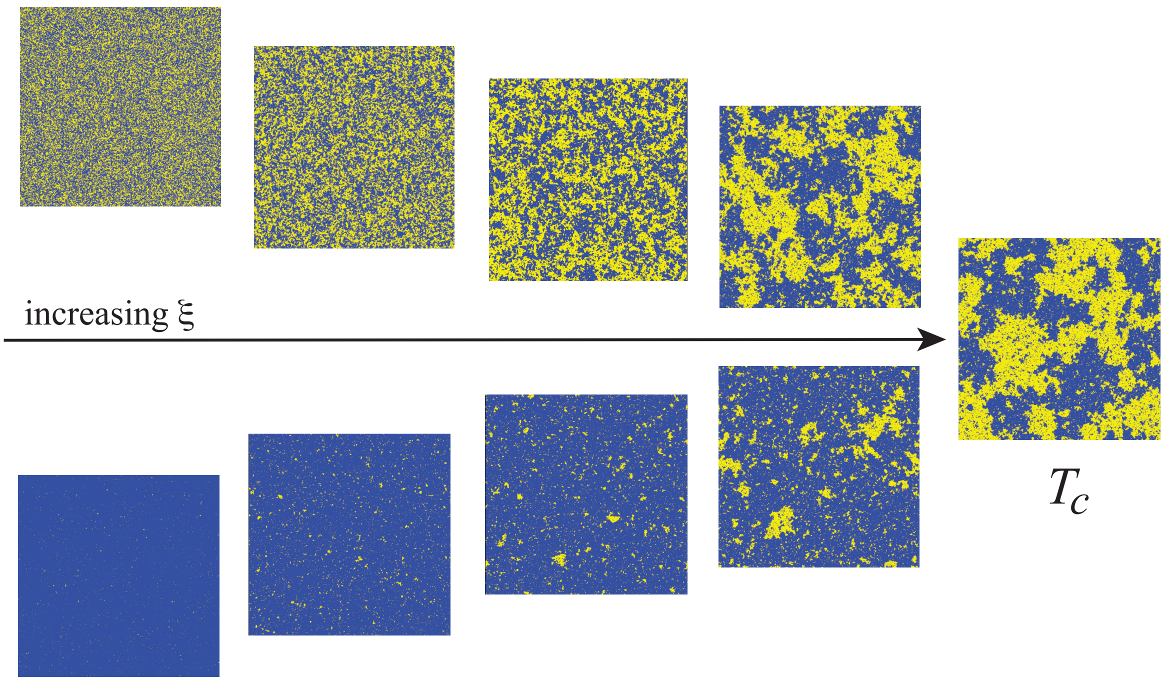

Figure 26.1: Temperature dependence of spin fluctuations. The right-most figure corresponds to the critical point. The upper half is the disordered high temperature phase, and the lower half is the ordered phase. The correlation length increases from left to right.

26.4 Correlation length

The typical size ξ of the islands is called the *correlation length*.[413] We see ξ grows and actually it diverges at T_c as $\xi \sim |T - T_c|^{-\nu}$, where ν is a positive universal constant (one of critical indices). From the low temperature side, in the almost completely ordered phase appear the opposite spins like blinking stars. They become spin-flipped islands, growing bigger and bigger as T increases (i.e., ξ grows). Eventually, these islands coalesce to make a supercontinent.

26.5 Critical fluctuations and slowing down

The patches (islands) of size $\sim \xi$ appear and disappear, so big fluctuations occur

[413] $\langle s(\boldsymbol{r})s(0)\rangle \sim e^{-|\boldsymbol{r}|/\xi}$ defines ξ.

near the critical point. This is the *critical fluctuation*. Since large scale change cannot be completed very quickly, we see increasing space-time scale fluctuations when T approaches T_c from its either side. That is, the dynamics becomes sluggish near the critical point (called *critical slowing down*). These fluctuations are not only big but also statistically highly correlated: the spins within ξ behave similarly, so as we approach T_c spin fluctuations become increasingly statistically correlated. Thus, even on the scale we can observe optically the system is not simply governed by the law of large numbers.

If such critical fluctuations occur in fluid, we see critical opalescence, which Einstein wished to understand (and created the thermodynamic fluctuation theory we have already learned in Section 19, esp., **19.4**):

`http://www.youtube.com/watch?v=cSliO89x7UU`

26.6 Scaling invariance of critical fluctuation

Critical fluctuations have a very special property of scaling invariance: from however large distance you observe the critical fluctuations, they look the same as you observe them from, say, 1m away. This is exhibited by the following two You Tube movies due to D. Ashton, excellent and wonderful:

`http://www.youtube.com/watch?v=lQxD1PinDbs`

`http://www.youtube.com/watch?v=MxRddFrEnPc`.

We will come back to the second movie soon.

26.7 Divergence of susceptibilities

We know the fluctuation-response relation **18.11**: generally,

$$\left.\frac{\partial X}{\partial x}\right|_{y,\cdots} = \beta\langle\delta X^2\rangle. \tag{26.1}$$

For example, the (isothermal) magnetic susceptibility χ is directly related to the variance of magnetization:

$$\chi_T = \beta\langle\delta M^2\rangle. \tag{26.2}$$

We just learned the big critical fluctuation, so we can expect that the susceptibilities become very large near the critical point.

26.8 Critical indices

Empirically the susceptibility diverges as (for $h = 0$, without magnetic field) (see Fig. 26.2)

$$\chi \sim |T - T_c|^{-\gamma} = |\tau|^{-\gamma} \ (h = 0), \tag{26.3}$$

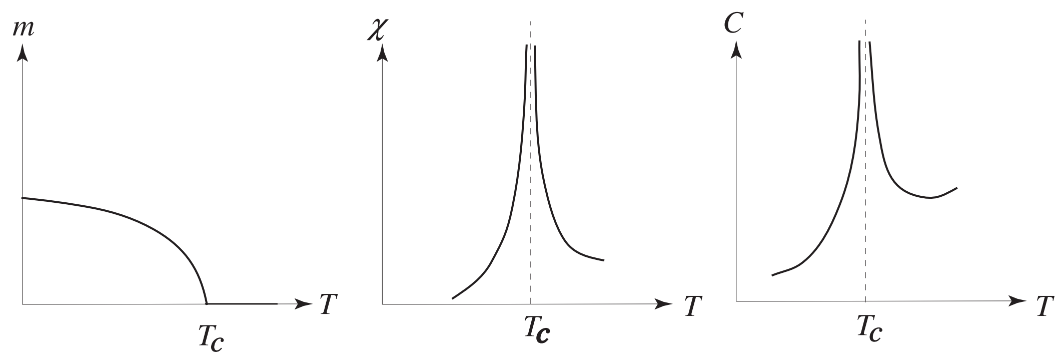

Figure 26.2: Schematic illustrations of singular behaviors near the critical point.

where $\tau = (T - T_c)/T_c$.

We cannot expect smooth increase of the magnetization m from zero below T_c:[414]

$$m \sim (-\tau)^\beta \ (h = 0, \tau < 0). \tag{26.4}$$

The divergence of energy (or entropy) fluctuation causes the divergence of specific heat as

$$C_B \sim |\tau|^{-\alpha} \ (h = 0). \tag{26.5}$$

α, β, γ, are positive numbers and are called *critical indices*. Representative values can be found in the table below. They are universal numbers. For example, for any fluid or binary mixture, or magnets (with an easy axis = Ising magnets) these numbers are common. They are determined by the nature of our world, not material-scientific trivial or fetish facts.

Ising critical exponents.

Exponents	2-space	3-space	$d(\geq 4)$-space
α	0 (log)	0.11	0 (jump)
β	1/8	0.325	1/2
γ	1.75	1.24	1
δ	15	4.8	3
ν	1	0.63	1/2

26.9 Critical index (in)equalities

It was empirically noted that several relations hold among these indices such as

$$\alpha + 2\beta + \gamma = 2. \tag{26.6}$$

Thermodynamically, we can prove

$$\alpha + 2\beta + \gamma \geq 2. \tag{26.7}$$

[414]Notice that there is no logical relation between the divergence of the susceptibility and the emergence of non-zero magnetization. For Ising models it is proved that these two occur simultaneously. The discrepancy seems to be possible only when long-range order is impossible.

Demonstration of this inequality gives us an excellent opportunity to review elementary thermodynamics.

26.10 Proof of index inequality (Rushbrooke inequality)

Even around the critical point the system does not become thermodynamically unstable. Therefore, inequalities required by the thermodynamic stability conditions remain valid. For example,[415] thermodynamic stability of a magnet implies (the Gibbs relation in this case is $dE = TdS + BdM$; **18.7**)

$$\frac{\partial(S, M)}{\partial(T, B)} \geq 0. \tag{26.8}$$

This inequality can be written explicitly, by expanding the determinant defining the Jacobian, as

$$\left.\frac{\partial S}{\partial T}\right|_B \left.\frac{\partial M}{\partial B}\right|_T \geq \left.\frac{\partial S}{\partial B}\right|_T \left.\frac{\partial M}{\partial T}\right|_B = \left.\frac{\partial M}{\partial T}\right|_B^2, \tag{26.9}$$

where a Maxwell's relation

$$\frac{\partial(S, T)}{\partial(B, M)} = 1 \tag{26.10}$$

has been used to obtain the second equality. This implies

$$\frac{1}{T} C_B \chi \geq \left.\frac{\partial M}{\partial T}\right|_B^2. \tag{26.11}$$

Introducing the definitions of the critical exponents given above, we obtain

$$|\tau|^{-\alpha} |\tau|^{-\gamma} \geq |\tau|^{2(\beta-1)}. \tag{26.12}$$

Here, we have ignored all the finite coefficients near the critical point (such as T^{-1}).[416] (26.12) implies that

$$|\tau|^{-(\alpha+2\beta+\gamma-2)} \geq 1 \tag{26.13}$$

is required for $\tau \to 0$. Therefore, the quantity in the parentheses must be nonnegative:

$$\alpha + 2\beta + \gamma \geq 2. \tag{26.14}$$

This is called *Rushbrooke's inequality*.

[415] This requires twice differentiability of the potential, so it does not hold exactly at the critical point, but we may use it in its any neighborhood.

[416] We have assumed that the critical point is not zero; The 1-Ising model has $T_c = 0$, but this is a pathological example.

26.11 Fluctuation and universality

Watch Dr Ashton's movie again. Large scale fluctuations seems to dominate the scene, and the phenomenon looks the same from however far away you observe it. Thus, we could guess that microscopic details should not be very important. That is, we expect the *universality*: microscopic details do not matter for salient features of the phenomena (in this case critical phenomena). Indeed, the critical indices for fluids, binary mixtures, and 3D Ising magnets are identical (cf. Fig. 25.7). The point is impressively illustrated by Dr Ashton.

26.12 Universality, nontrivial and trivial

A typical and good example of universality is the osmotic pressure of polymer solutions. Irrespective of the polymers and solvents, as long as the polymers are long enough, and the solvent dissolves polymers well, Fig. 26.3 is quantitative:

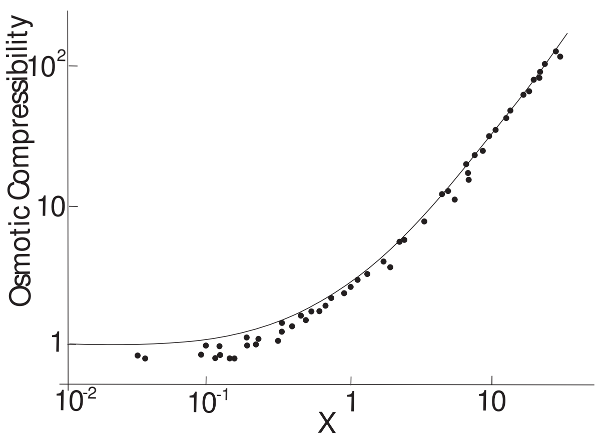

Figure 26.3: The osmotic compressibility $\partial\pi/\partial c$ as a function of $X \propto$ the polymer concentration c. In this case the proportionality constant X/c is the only adjustable parameter representing the specificity of a particular polymer-solvent pair. The curve is the renormalization group result. All the data for any polymer solution must be on the curve. [based on T. Ohta and A. Nakanishi, J. Phys. A 16, 4155 (1983); T. Ohta and Y. Oono, Phys. Lett. **89A**, 460 (1982). The points are experiments due to I. Noda, N. Kato, T. Kitano and M. Nagasawa, Macromolecules 14, 668 (1981).].

Here is one parameter we cannot theoretically compute, i.e., the proportionality constant between X and c. However, notice that except for this one parameter, there is no freedom left: even if you change, solvents, polymers, or temperature, Fig. 26.3 is quantitatively correct. That is, an (uncountably) infinite dimensional space of polymer solutions is subsumed to a 1-dimensional (one-parameter) world.

You might say we already know examples of universality. For example, we know (**21.13**)

$$PV = \frac{2}{3}E \tag{26.15}$$

for any ideal gas irrespective of statistics: if the spatial dimensionality is 3, and the dispersion relation is $\varepsilon \propto p^2$, this is true. Or we know $PV = E/3$ for phonons and photons in 3-space. This is quite universal. However, it is due to the universality (common quantitative feature) of the elementary entities (without interaction!) making up the system. In this sense, universality is unsurprising, and trivial. Furthermore, if you modify a system a bit with interactions, the PV relation changes sensitively. That is, infinite ways of changing the system result in infinitely different modifications of the resulting equation of state.

In contradistinction, the universality discussed in the preceding paragraph is obviously not due to some common quantitative features at the microscopic level. Of course, the system must be a polymer system, but we use only two features: a polymer is very long, and cannot cross itself; nothing quantitative is required. In this case, there are infinitely many ways to modify polymer-solvent systems (by simply changing polymers and solvents), but only one parameter is modified in consequence (i.e., only X/c is modified) as emphasized above. That is, this universal feature is quite stable against materialistic perturbations. Thus, the above mentioned universality is deserved to be called the *genuine universality*.

Elementary statistical mechanics is boring because it emphasizes trivial universality only.

26.13 Study of phase diagram

The purpose of statistical mechanics is to understand various macroscopic properties of a given equilibrium system. We know this is equivalent to mapping out its thermodynamic space. Just as the ordinary maps we are interested in two things: where the borders are and what each territory looks like. The former corresponds to the study of phase transitions and the latter to characterized each phase. As we have already seen in Fig. 24.2 the phase diagram on the thermodynamic space is complete, but usually we are contented with the diagram on, say, the PT-space such as Fig. 25.7. Let us look at it again:

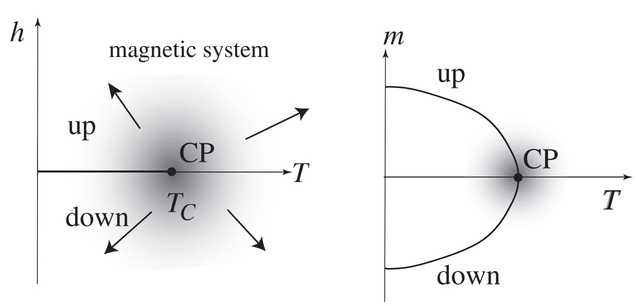

Figure 26.4: The shaded area is dominated by fluctuations; if you go away from it along the arrows, the correlation length diminishes and mean field theory becomes respectable.

To understand boundaries (phase transitions) if you are close to the critical point or the second order phase transition point, you must deal with fluctuations and high correlation (statistical dependence). There, many things would be universal as we have seen briefly. If away from the critical point, the phase transitions become first order. The phase transition locations are determined by the equality of the chemical potentials of the phases between which the transition occurs. Thus, many small details including small fluctuations that sensitively modify the chemical potentials really matter. If you are away from the critical point (and phase transitions in general) along the arrows in the figure, then the correlation length reduces and fluctuation becomes less significant (i.e., microscopic entities are more statistically independent).

At this juncture watch Ashton's 'zooming out' movie again. Since there is no qualitative difference along the arrows, to understand the general feature of various phases, we can study the regions where the correlation length is small and fluctuations are small (i.e., the zoomed-out states). Then, at least qualitatively what happens at the first order phase transition can also be understood. For example, to understand ice we could study sufficiently low temperature perfect crystal ice, and to understand vapor, we can study very high temperature gas (almost an ideal gas).

Thus, the study of the phase diagram consists of two strategies: to roughly understand the nature of phases we may largely ignore fluctuations and to understand phase boundaries we need a means to cope with fluctuations. The former is represented by the mean field theory we will discuss below and the latter by renormalization group theory. We cannot go into the latter in this course, but in the following its crucial mathematical core will be explained. Then, in Section 28 how to explain the scaling index equality (26.6) using scaling invariance (Kadanoff construction) will be outlined.

26.14 Central limit theorem

We have realized that near the second order phase transition/critical point, fluctuation becomes large, and also strongly correlated. How can we handle such a strongly correlated fluctuating system? We wish to know the distribution of fluctuations on the mesoscopic scale (because the correlation lengths are on the mesoscopic scale). If we understand the mesoscopic fluctuation statistics, we should be able to compute macroscopic observables. How can we study the mesoscopic fluctuation statistics? We encounter the third pillar of probability theory: *central limit theorem* (CLT); recall that the law of large numbers and large deviation theory are the two of the three pillars we have already utilized.

The law of large numbers may be understood as the statement that the density distribution function of $(1/N)\sum_{i=1}^{N} X_i$ is concentrated to a single point $m = \langle X_1 \rangle$, if X_i are iid. Here comes the other refinement of LLN: the central limit theorem. Instead of N if we divide the partial sum $S_N = \sum X_i$ with a smaller quantity, say $N^{3/4}$, which must be chosen just right, the density distribution of $S_N/N^{3/4}$ might converge to a nice function. In the case of iid stochastic variables, we know the size of the fluctuation of S_N is $\sqrt{N}$,[417] so perhaps $\sqrt{N}$ is the right factor.

If X_i are iid[418] with the distribution not too broad, this guess is correct. We have the

[417]Recall $S_N = N\langle X \rangle + O[\sqrt{N}]$.

[418]The CLT in this form holds more generally even if X_i's are not iid, but are correlated. If the

central limit theorem:

> **Central Limit Theorem**
> If X_i are assumed to be iid with a finite variance, the density distribution function of $(S_N - Nm)/\sqrt{N}$ converges to a Gaussian function $N(0, V)$, where $m = \langle X_1 \rangle$ and $V = \langle (X_1 - m)^2 \rangle$.

This allows us to calculate expectation values of quantities dependent on fluctuations.[419]

26.15 We need much more general CLT to understand critical phenomena
Unfortunately, the system we are interested in are strongly interacting systems, so X_i are not at all statistically independent, but strongly correlated rather globally. Therefore, to understand second-order phase transition, we need a vast generalization of the usual CLT to the case with strong correlations. This extension is the *renormalization group theory.* Let X_i be the ith spin. Then, $M = \sum X_i$ is the magnetization. Let us consider this in the paramagnetic phase (i.e., $M = 0$ on the average). We are interested in its fluctuation. Due to strong correlation, now we cannot choose $y = 1/2$ in M/N^y to have a nice distribution function in the thermodynamic limit; we must choose y in a highly nontrivial fashion, which is related to the critical indices.[420]

26.16 Misunderstanding of CLT
In elementary thermal physics courses, CLT is invoked to explain intuitively why the existence of many particles makes macroobservables almost deterministic. However, as clearly noted in this course, the law of large numbers is the fundamental reason. If you know how to prove CLT, you will agree that CLT is much more sophisticated and restricted. Usual use of CLT to explain why statistics works is like showing continuity by showing differentiability.

This abuse of math is likely to be caused by misunderstanding of CLT. The main claim of CLT is, after scaling, the nontrivial distribution emerges that is system-size (sample-size) independent. This is renormalization group!

We need only LLN in elementary statistical mechanics. Every instructor should understand this.

26.17 Mean field Idea

Sufficiently away from critical points/second order phase transition points, the equilibrium average of a function of several spins $f(s_0, s_1, \cdots, s_n)$ may be computed

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correlation decays sufficiently quickly or if X_i make a Markov process, the CLT with $\sqrt{N}$ holds. However, the variables we are interested in here behave much more strongly correlated, and the factor $\sqrt{N}$ is not appropriate.

[419] ⟪**Central limit theorem vs. large deviation**⟫ The reader might claim that it has already been used to understand fluctuations: isn't the Gaussian nature of fluctuation the sign of central limit theorem? This is only accidental for systems with finite variances. Fluctuation studies the deviation of the average from the true average, when the system size is small. We ask how the fluctuation *of* the mean *disappears* as the system size increases. In contrast, the central limit theorem is concerned with small deviations *from* the mean that appropriately scales with the system size. Fortunately (or unfortunately), for iid with finite variance they give the same conclusion about fluctuations.

[420] Beyond this point, you can go to my graduate school lecture notes (Chapter 5) or "Informal Notes on Renormalization and Phase Transitions" (both downloadable). A more elementary explanation may be found in *The Nonlinear World* (Springer 2012) (Chapter 3).

through separately averaging all the spins. Furthermore, if we assume $\langle s_i^k \rangle \sim \langle s_k \rangle^k$ (i.e., if we assume that fluctuations are not large), we arrive at

$$\langle f(s_0, s_1, \cdots, s_n) \rangle \simeq f(\langle s_0 \rangle, \langle s_1 \rangle, \cdots, \langle s_n \rangle). \tag{26.16}$$

This is the basic idea of the *mean field* approach. Here, let us proceed slightly more systematically.

26.18 Quantitative formulation of mean field theory: fundamental equation

Let us look at an elementary identity of probability theory. If $\cup_i B_i = \Omega$ and $B_i \cap B_j = \emptyset$ for $i \neq j$ (i.e., $\{B_i\}$ is a partition of the sample space Ω), then (Fig. 26.5)

$$E\left(E(A|B_i)\right) = \sum_i P(B_i) E(A \,|\, B_i) = E(A). \tag{26.17}$$

That is, the average of a conditional expectations over all the conditions is equal to the unconditional average.

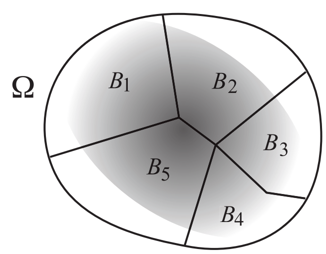

Figure 26.5: (26.17) is illustrated. Suppose A is something (shade in the figure) distributed on the sample space Ω which is partitioned into $B_1, \cdots, B_5$. In each partition we can define the average on it $E(A \,|\, B_i)$. If the probability for event B_i to happen is $P(B_i)$, the average of A over Ω is given by (26.17).

Let us choose as B_i a particular configuration 'i' $\{s_1, \cdots, s_{2d}\}$ of all the spins interacting with the 'central spin' s_0 on a d-cubic lattice (Fig. 26.6). Notice that if $s_1, \cdots, s_{2d}$ are fixed, the central s_0, which is interacting only with these neighboring spins, is totally decoupled from the rest of the world.

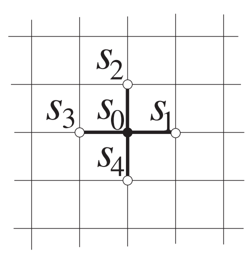

Figure 26.6: The central spin s_0 and its nearest neighbor surrounding spins $s_1, \cdots, s_{2d}$. If $s_1, \cdots, s_{2d}$ are fixed, s_0 is walled by them and is decoupled from the rest of the world.

Therefore, to study the distribution of $s_0 = \pm 1$, we have only to compute its energy in the given environment and to make Boltzmann factors to average as follows:

$$E(s_0|s_1, \cdots, s_{2d}) = \frac{\sum_{s_0} s_0 e^{\beta J s_0(s_1+\cdots+s_{2d})+\beta h s_0}}{\sum_{s_0} e^{\beta J s_0(s_1+\cdots+s_{2d})+\beta h s_0}} = \tanh[\beta h + \beta J(s_1 + \cdots + s_{2d})]. \tag{26.18}$$

Because $E(s_0) = E\left(E(s_0|s_1, \cdots s_{2d})\right)$, we obtain

$$\langle s_0 \rangle = \langle \tanh\left[\beta h + \beta J(s_1 + \cdots + s_{2d})\right] \rangle. \tag{26.19}$$

This is an *exact* relation into which we may introduce various approximations to construct mean field approaches.

26.19 The crudest version of the mean-field theory

Now, to compute the RHS of (26.19), we must introduce some approximation. The most popular (and simple-minded) version is (26.16) or more concretely for the present example:

$$\langle \tanh[\beta h + \beta J(s_1 + \cdots + s_{2d})] \rangle \simeq \tanh[\beta h + \beta J \langle s_1 + \cdots + s_{2d} \rangle]. \tag{26.20}$$

Therefore, for $m = \langle s_0 \rangle$, we obtain a closed equation (consistency equation)

$$m = \tanh[\beta(2dJm + h)]. \tag{26.21}$$

$2dJm + h$ may be understood as an effective magnetic field acting on s_0, so this is called the *mean field* (sometimes called the *molecular field* as well). This is the etymology of the name of the approximation method being considered.

26.20 How to solve the consistency equation

Let $2d\beta Jm = x$. (26.21) reads

$$x = 2d\beta J \tanh(x + \beta h). \tag{26.22}$$

For simplicity, let us assume $h = 0$. We have to solve

$$x = 2d\beta J \tanh x. \tag{26.23}$$

This may be graphically solved (Fig. 26.7).

The bifurcation[421] from the case with a single solution to that with 3 solutions

[421] ⟪**Bifurcation**⟫ A phenomenon that the solution (or the solution set) changes its character is called *bifurcation*. There are many types, and the one we encounter here is a *pitchfork bifurcation*; if we know this, the exchange of the stability of the branches immediately tells us the stabilities of the branches as illustrated in the text.

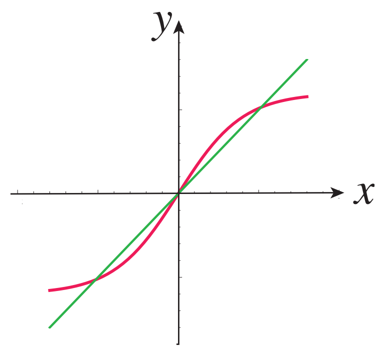

Figure 26.7: The solution to (26.23) may be obtained graphically.

occurs at $2d\beta J = 1$. That is, this gives the phase transition temperature T_c. m increases as $|T - T_c|^{1/2}$ (i.e., the critical exponent $\beta = 1/2$).

To conclude that the bifurcation actually signifies the phase transition (within the mean-field approximation), we must check that the nonzero solutions are the equilibrium solutions. That is, we must demonstrate that the $m \neq 0$ solutions have a lower free energy than the $m = 0$ case. The best way may be to study the bifurcation diagram and check the stability of the solution under small perturbations; if the state is a stable equilibrium, small deviation from the state will decay. The stability of $m \neq 0$ state is obvious.

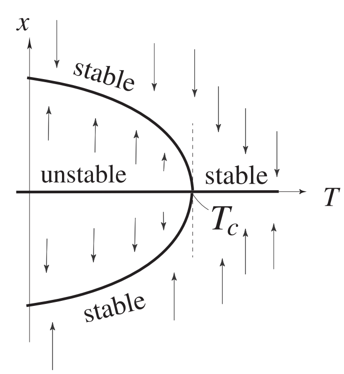

Figure 26.8: The stability of the solution to (26.23) may also be understood graphically.

26.21 How reliable is the mean field theory?

We have introduced the idea of mean field theory to study the system thermodynamics sufficiently away from critical points. Therefore, the mean field theory cannot generally assert anything about the phase transition. It cannot guarantee the existence of phase transition (esp., second order phase transition) even if it concludes that there is one. Recall that even for $d = 1$, the mean field theory (a simple version we just discussed) asserts that there is a second order phase transition at some finite T. We know this cannot be true. Even in the case where a phase transition occurs, it cannot reliably predict whether the phase transition is continuous or not. However, if fluctuation effects are not serious, then the mean field results become qualitatively reliable. Thus, it is believed that if $d \geq 4$ (especially $d > 4$), for fluids and magnets, the simplest mean field results are generally qualitatively correct.

However, if a mean field theory concludes that there is no ordering phase transition, this conclusion sounds very plausible. Since mean field theory ignores fluctuations, it should overestimate the ordering tendency and if a mean field theory still tells us that there is no ordering, this assertion is likely to be true. For the ferromagnetic Ising model this expectation has been vindicated. The same idea tells us that the mean field critical temperature should be the upper bound of the true critical temperature: $T_c \leq T_{c,\ \mathrm{mean}}$.

26.22 Use of mean-field approach: practical guide

Generally speaking, mean-field approaches may be relied upon, if the fluctuation effect is not decisive:
(1) If the spatial dimensionality is sufficiently high, then 'spins' gang up against thermal fluctuations;
(2) If the first order phase transition is with a big 'jump,' then fluctuations may not easily be able to fill the gap that must be jumped.
Thus, these cases are (often) amenable to mean-field approaches (at least qualitatively).

Perhaps, practically, we may summarize the use of mean field method as follows: we should not swallow the results of the method uncritically (especially as to the phase transitions), but since the method is easy to use in many cases, it is worth trying first.

27 Improving mean field and transfer matrix

Summary
$*$ Mean field theory can be somewhat improved, if the constraints imposed on the spin variables are honestly taken into account.
$*$ Transfer matrix technique is outlined.

Key words
mean-field theory, transfer matrix, Perron-Frobenius' theorem, Perron-Frobenius eigenvalue

What you should be able to do
$*$ Remember that we should respect the algebraic structure inherent in the system.
$*$ You must be able to set up the self-consistency equation for mean field approaches.
$*$ You must practically be able to set up transfer matrices for 1D finite range models.
$*$ Memorize the Perron-Frobenius theorem.

27.1 Naive mean field approach: a review

Let us review the simplest mean-field approach in detail: the 1D Ising chain whose Hamiltonian is

$$H = -J\sum_i s_i s_{i+1} - h\sum_i s_i. \tag{27.1}$$

We have derived the fundamental equality, which reads for the present case as

$$\langle s_0\rangle = \langle \tanh[\beta J(s_{-1}+s_1)+\beta h]\rangle. \tag{27.2}$$

The naivest mean-field approach is to use the following type of approximation: $\langle f(x)\rangle \simeq f(\langle x\rangle)$. Since we may assume that the equilibrium single phase is translationally symmetric, $\langle s_0\rangle = \langle s_{\pm 1}\rangle = m$. Then, with the above mentioned approximation (27.2) becomes

$$m = \tanh[2\beta Jm + \beta h]. \tag{27.3}$$

(27.3) reads

$$2\beta Jm + \beta h = 2\beta J\tanh[2\beta Jm+\beta h] + \beta h \tag{27.4}$$

or

$$x = 2\beta J\tanh x + \beta h. \tag{27.5}$$

Here, we will not discuss h, so let us set $h = 0$. Then,

$$x = 2\beta J\tanh x. \tag{27.6}$$

Thus, $2\beta J = 1$ determines the critical point: $T_c = 2J/k_B$.

Everyone knows this is wrong. Intuitively, ordering is hindered by fluctuations, so, if you ignore the effect of fluctuations, then ordered phases tend to be stable at higher temperatures. Therefore, the order-disorder transition point estimated by a mean-field approach tends to be an overestimation at best; the predicted phase transition may not even exist as in this case.

27.2 Improving mean field approach

There is, however, a room to improve the mean field theory. We know $s^2 = 1$. Using this, we can handle fluctuations in a better way. Let us expand (27.2). Notice that $\tanh x$ can be expanded into an odd power series:

$$\tanh x = x - \frac{1}{3}x^3 + \frac{2}{15}x^5 + \cdots. \tag{27.7}$$

In our case $h = 0$, so we need odd powers of $s_{-1} + s_1$. For example,

$$(s_{-1}+s_1)^3 = s_{-1}^3 + 3s_{-1}^2 s_1 + 3s_{-1}s_1^2 + s_1^3 = s_{-1} + 3s_1 + 3s_{-1} + s_1 = 4(s_{-1}+s_1). \tag{27.8}$$

Analogously, any odd power of $s_{-1} + s_1$ is proportional to $s_{-1} + s_1$. Therefore, we must have the following identity if s_i takes only ± 1 with an appropriate constant A:

$$\tanh[\beta J(s_{-1} + s_1)] = A(s_{-1} + s_1). \tag{27.9}$$

A is determined by substituting ± 1 to the spins:

$$\tanh(2\beta J) = 2A. \tag{27.10}$$

Therefore, (27.2) reads (with $h = 0$)

$$\langle s_0 \rangle = \frac{\tanh 2\beta J}{2} \langle s_{-1} + s_1 \rangle. \tag{27.11}$$

That is, we have obtained an exact relation:

$$m = m \tanh(2\beta J). \tag{27.12}$$

We know $|\tanh(2\beta J)| < 1$, so unless $T = 0$, $m = 0$. Therefore, there is no phase transition for $T > 0$. Mean field theories may not be that bad![422]

At this juncture, reread **26.22**, especially, when mean-field approaches may be OK.

[422]However, this seems to be a very lucky case; we have an exact formula! Generally speaking, you must not trust mean field theoretical results too much as to the phase transitions.

27.3 Transfer matrix method

To conclude the second-order phase transition, let us discuss one general method to get the free energy exactly. Let us consider a 1D-Ising model with the Hamiltonian[423] given by

$$H = -J\sum_{i=1}^{N-1} s_i s_{i+1} - h\sum_{i=1}^{N} s_i. \tag{27.13}$$

Let us define the partition function $Z_N(+)$ for the length N spin chain with the Nth spin up:

$$Z_N(+) = \sum_{\{s_n\}_{n=1}^{N-1}} e^{\beta[J(+1)s_{N-1}+h(+1)]} e^{\beta[Js_{N-1}s_{N-2}+hs_{N-1}]}\cdots e^{\beta[Js_2s_1+hs_2]}e^{\beta hs_1}. \tag{27.14}$$

We can analogously define the partition function $Z_N(-)$ for the length N spin chain with the Nth spin down. In terms of these, we can make $Z_{N+1}(\pm)$ as

$$Z_{N+1}(\pm) = \sum_{s=\pm 1} e^{\pm\beta[Js+h]} Z_N(s). \tag{27.15}$$

Therefore, if we introduce the vector

$$\boldsymbol{Z}_N = \begin{pmatrix} Z_N(+) \\ Z_N(-) \end{pmatrix}, \tag{27.16}$$

we can write

$$\boldsymbol{Z}_{N+1} = \boldsymbol{T}\boldsymbol{Z}_N, \tag{27.17}$$

where $\boldsymbol{T}$, called the *transfer matrix*,[424] is defined as

$$\boldsymbol{T} = Matr(e^{\beta[Jss'+hs]}) = \begin{pmatrix} e^{\beta J+\beta h} & e^{-\beta J+\beta h} \\ e^{-\beta J-\beta h} & e^{\beta J-\beta h} \end{pmatrix}. \tag{27.18}$$

Notice that

$$Z_N = (1,1)\boldsymbol{Z}_N. \tag{27.19}$$

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[423] Strictly speaking, the term proportional to J is the Hamiltonian of the system itself, and the term proportional to h is the potential energy the system has between the system making the magnetic field h.

[424] ⟪**The origin of the transfer matrix method**⟫ The method was devised by Kramers and Wannier: Phys. Rev. **60**, 252 (1941). For a continuum model, an integral equation approach can be used and was devised by H. Takahashi almost simultaneously in 1942 (Proc. Phys-Math. Soc. Japan **24**, 60 (1942)). He showed that 1D short-range systems cannot have any phase transition for $T > 0$. [In 1941 Japan attacked Pearl Harbor; in 1942 Fermi and collaborators succeeded in nuclear chain reaction.]

Repeated use of the recursion (27.17) results in

$$\boldsymbol{Z}_N = \boldsymbol{T}^N \begin{pmatrix} e^{\beta h} \\ e^{-\beta h} \end{pmatrix}. \tag{27.20}$$

In this case the first spin is free to point up or down. For a ring of N spins ($s_1 = s_{N+1}$), as we see immediately, $Z_N = Tr\, \boldsymbol{T}^N$.

27.4 How to compute the product of matrices

The easiest method to compute (27.20) is to use an orthogonal transformation (or more generally unitary transformation) to convert $\boldsymbol{T}$ into a diagonal form:[425]

$$\boldsymbol{T} = U^{-1} \begin{pmatrix} \lambda_1 & 0 \\ 0 & \lambda_2 \end{pmatrix} U, \tag{27.21}$$

where λ_1 and λ_2 are eigenvalues of $\boldsymbol{T}$, and U is the orthogonal transformation needed to diagonalize $\boldsymbol{T}$. Introducing (27.21) into (27.20), we obtain

$$\boldsymbol{Z}_N = U^{-1} \begin{pmatrix} \lambda_1^N & 0 \\ 0 & \lambda_2^N \end{pmatrix} U \begin{pmatrix} e^{\beta h} \\ e^{-\beta h} \end{pmatrix}. \tag{27.22}$$

Therefore, we finally have the following structure:

$$Z_N = a\lambda_1^N + b\lambda_2^N, \tag{27.23}$$

where a and b are nonzero real numbers. If we assume $\lambda_1 > |\lambda_2|$, a is positive, and, since $N \gg 1$, the first term dominates Z_N. Therefore, the free energy per spin is given by

$$f = -k_B T \log \lambda_1. \tag{27.24}$$

Depending on the boundary conditions, the exact formula for the partition function changes, but the free energy per spin (this is the only quantity meaningful in the thermodynamic limit $N \to \infty$) depends only on the largest eigenvalue of the transfer matrix that is not dependent on the boundary condition.

27.5 Why there is no phase transition in 1-space

Let us discuss why there is no phase transition for $T > 0$ in 1D finite-range interaction systems from the transfer matrix point of view. The free energy could exhibit singularity if $Z \le 0$, but this does not happen, because Z is a sum of positive terms.

[425]if impossible, in a Jordan normal form. A necessary and sufficient condition for a matrix $\boldsymbol{T}$ to be diagonalizable is that it is *normal*: $\boldsymbol{T}^*\boldsymbol{T} = \boldsymbol{T}\boldsymbol{T}^*$. If all the eigenvalues are distinct, the matrix is normal. In the present case, the eigenvalues are distinct, so the matrix is diagonalizable.

As long as $T > 0$, K is finite, so all the elements of the transfer matrix are without any singularity as a function of T[426] (and h), and eigenvalues are *algebraic functions*[427] of the entire functions of T and h. Therefore, as long as eigenvalues are finite, their singularities are branch points.[428] The branch points of the eigenvalues occur when they change their multiplicities (digeneracies), so the multiplicity of the largest eigenvalue is of vital importance. The key theorem we need is the following famous and important theorem:

Theorem [Perron and Frobenius][429]
Let A be a square matrix whose elements are all non-negative, and there is a positive integer n such that all the elements of A^n are positive. Then, there is a non-degenerate real positive eigenvalue λ such that
(i) $|\lambda_i| < \lambda$, where λ_i are eigenvalues of A other than λ,[430]
(ii) the elements of the eigenvector belonging to λ may be chosen all positive. □
This special real eigenvalue giving the spectral radius is called the *Perron-Frobenius eigenvalue*.

Since the transfer matrix is with positive elements, the logarithm of its Perron-Frobenius eigenvalue gives the free energy per spin. If the number of states for each 1D element is finite and the interaction range is finite, then no phase transition occurs for $T > 0$, because the transfer matrix is finite dimensional.

27.6 Onsager obtained the exact free energy of 2-Ising model

Onsager used the transfer matrix method to evaluate the partition function of the 2-Ising model on the square lattice exactly.[431,432] There are people who say that

[426]The elements of the transfer matrix are entire functions; a function that is holomorphic (= no singularities) except at infinity is called an *entire function*.

[427]An algebraic function of $\{x_i\}$ is a function that can satisfy a polynomial whose coefficients are polynomials of $\{x_i\}$. An entire function is a function whose singularity is only at infinity.

[428]For example, consider $\sqrt{z}$. This is real if $z > 0$ and have two values, but for $z = 0$ there is only one value. In this case, $z = 0$ is an example of the branch point. Take $x^2 - 2zx + 1 = 0$. The roots are algebraic functions of z: $x = z \pm \sqrt{z^2 - 1}$. Therefore, $z = 1$ is a branch point for x. Notice that $dx/dz = 1 \pm z/\sqrt{z^2 - 1}$, so at the branch point, the derivative ceases to exist (for this example).

[429]For a succinct proof, see the P504 course note.

[430]That is, λ gives the spectral radius of A.

[431]⟪**Onsager's biography**⟫ See C. Longuet-Higgins and M. E. Fisher, "Lars Onsager: November 27, 1903-October 5, 1976," J. Stat. Phys., **78**, 605 (1995). This is an Onsager's biography everyone can enjoy. According to this, Onsager applied the transfer matrix method to the strip of width 2, 3 and 4 lattice points, and constructed a conjecture from these results, then confirmed it for the width 5 strip and closed in on the general formula.

"His statistical mechanics were popularly known as 'Advanced Norwegian I' and 'Advanced Norwegian II'." He was fired more than once for his poor teaching, and his Nobel-prize winning dissertation intended for his PhD was rejected as insufficient from his alma mater.

[432]Onsager's much greater contribution to statistical physics is his contribution to nonequilibrium

Onsager's result for the first time demonstrated that the equilibrium statistical mechanics framework could capture phase transition, but Peierls' work was far before the exact solution.

Exact solutions are very useful of course, but the reasons for the possibility of exact solutions could be rather unimportant peculiarities from the physics point of view. Therefore, it is not productive to rely on exact solutions to construct general theories.

theory, which we have glanced at already. This point seems often ignored as we read explicitly in S. G. Brush, *Statistical Physics and the Atomic Theory of Matter, from Boyle and Newton to Landau and Onsager* (Princeton UP, 1983).

Q27.1 [Ising on diamond lattice]
Consider Ising spins on the diamond lattice (without an external magnetic field h). The interactions of the spins are restricted to the nearest neighbor pairs.
(1) Write down the fundamental equation for this system corresponding to

$$\langle s_0 \rangle = \langle \tanh [\beta J(s_1 + \cdots + s_{2d})] \rangle \tag{27.25}$$

on the d-cubic lattice.
(2) What is the critical point, if you use the simplest mean-field theory that uses the approximation $\langle \tan(\cdots) \rangle = \tan(\langle \cdots \rangle)$?
(3) This is a three-dimensional system, so there is definitely a positive critical temperature T_c. What can you say about this true T_c from your result in (2)?

Solution.
(1) This is quite the same as is explained in the notes. On the diamond lattice one spin has only 4 nbh spins, so

$$\langle s_0 \rangle = \langle \tanh [\beta J(s_1 + \cdots + s_4)] \rangle, \tag{27.26}$$

where $s_1, \cdots, s_4$ are the spins connected to s_0 with the C-C bonds.
(2) The naivest approach gives

$$\langle s_0 \rangle = \tanh [\beta J \langle s_1 + \cdots + s_4 \rangle] \,. \tag{27.27}$$

Expecting the translationally symmetric magnetization,

$$m = \tanh 4\beta J m \tag{27.28}$$

is the crudest mean-field equation. This means $x = 4\beta J \tanh x$, so $T_c = 4J/k_B$.
(3) Thermal fluctuation tends to be against ordering, so theories ignoring fluctuations overestimate the ordering effect, pushing the critical point up. Thus, we may conclude that the critical temperature of the Ising model on a diamond lattice must not be higher than $4J/k_B$. Actually, we may guess the true T_c is far less than this. ($T_c = 2.7J/k_B$[433])

Q27.2 [Improving diamond lattice]
We have derived in **Q26.1** the fundamental equation for the starting point of the mean field approaches for the diamond lattice as

$$\langle s_0 \rangle = \langle \tanh[\beta J(s_1 + \cdots + s_4)] \rangle. \tag{27.29}$$

Let us be better than **Q27.1**. We wish to exploit the fact that $s^2 = 1$.
(1) Expanding tanh in a power series, show that

$$\tanh[\beta J(s_1 + \cdots + s_k)] = A(s_1 + s_2 + s_3 + s_4) + B(s_1 s_2 s_3 + s_1 s_3 s_4 + s_2 s_3 s_4 + s_1 s_2 s_4). \tag{27.30}$$

[433] J W Essam and M F Sykes, Physica 29, 378 (1963).

That is, any odd power of $(s_1+s_2+s_3+s_4)$ is written as a sum of $(s_1+s_2+s_3+s_4)$ and $(s_1s_2s_3+s_1s_3s_4+s_2s_3s_4+s_1s_2s_4)$.
(2) Determine A and B by setting $s=\pm 1$ so that (28.46) holds, or show that

$$A = \frac{1}{8}(\tanh 4\beta J + 2\tanh 2\beta J). \tag{27.31}$$

(3) Now, introducing (28.46) into (28.45), we get the following equation

$$\langle s_0\rangle = A\langle s_1+s_2+s_3+s_4\rangle + B\langle s_1s_2s_3+s_1s_3s_4+s_2s_3s_4+s_1s_2s_4\rangle. \tag{27.32}$$

$\langle s_0\rangle = \langle s_1\rangle = \cdots = m$ is the magnetization per spin, so (28.48) reads

$$m = 4Am + 4B\langle s_1s_2s_3\rangle. \tag{27.33}$$

Notice that up to this point there is NO APPROXIMATION, but, unfortunately, we cannot solve (28.49). Now, let us introduce the approximation

$$\langle s_1s_2s_3\rangle = m^3. \tag{27.34}$$

Then, our 'approximate' mean field equation is

$$m = 4Am + 4Bm^3. \tag{27.35}$$

What is the condition that determines the phase transition? [Hint. At what value of A is there a bifurcation[434]?]

Solution.
(1) Checking first 2 or three terms in the expansion of tanh is practically all right.

However, if we wish to 'prove' (28.46), we can proceed as follows. Generally we have an odd power $(s_1+s_2+s_3+s_4)^m$, where m is an odd positive integer. If we expand this, (e.g., multinomial theorem) we obtain for $a+b+c+d=m$ ($a,\cdots,d$ are nonnegative integers)

$$s_1^a s_2^b s_3^c s_4^d.$$

There is a perfect permutation symmetry among $s_1,\cdots,s_4$, so we have only to consider the types of terms as follows [Do not honestly expand tanh.]

$$\begin{aligned}
s_1^m &= s_1 \\
s_1^{m-1}s_2 &= s_2, \\
s_1^{m-2}s_2^2 &= s_1, \\
s_1^{m-2}s_2s_3 &= s_1s_2s_3. \\
s_1^{m-3}s_2^3 &= s_2, \\
s_1^{m-3}s_2^2s_3 &= s_3 \\
s_1^{m-3}s_2s_3s_4 &= s_2s_3s_4
\end{aligned}$$

[434]Recall 'bifurcation' implies the change of number of (real) roots.

Therefore, summing all these terms, we must have (28.46).
(2) For all s being $+1$ case:

$$\tanh(4\beta J) = 4A + 4B.$$

For one -1

$$\tanh(2\beta J) = 2A - 2B.$$

Other possibilities do not give any new relation. From these, we get

$$A = (1/8)(\tanh 4\beta J + 2\tanh 2\beta J), \ \ B = (1/8)(\tanh 4\beta J - 2\tanh 2\beta J).$$

(3) We must solve $m = 4Am + 4Bm^3$. One way is to follow the lecture notes, i.e., a graphical method. This tells us that when the slope of $4Am + 4Bm^3$ at $m = 0$ is 1, bifurcation occurs. Hence, $4A = 1$ or

$$\tanh 4\beta J + 2\tanh 2\beta J = 2. \tag{27.36}$$

You need not solve this, but notice that the T_c obtained from this must be smaller than that obtained from $4\beta J = 1$ (due to a better approximation).

Q27.3 [Interacting particles on lattice]
At each lattice site of 1D lattice is a particle which can take the ground state and excited state. Only nearest neighbor excited state can interact and the excitation energy required is ε (> 0). The Hamiltonian may be written as

$$\mathcal{H} = -J\sum_i \sigma_i\sigma_{i+1} + \varepsilon\sum_i \sigma_i, \tag{27.37}$$

where $\sigma_i = 0$ denotes the ground state, and $\sigma_i = 1$ the excited state. Find the free energy per particle (i.e., write down the transfer matrix and compute its eigenvalues).

Solution.
The transfer matrix can be made as follows.

$$T = \begin{array}{c|cc} & 0 & 1 \\ \hline 0 & 1 & 1 \\ 1 & e^{-\beta\varepsilon} & e^{\beta J - \beta\varepsilon} \end{array}$$

Therefore, the characteristic equation reads

$$(1-\lambda)(e^{\beta J - \beta\varepsilon} - \lambda) - e^{-\beta\varepsilon} = \lambda^2 - \lambda(1 + e^{\beta(J-\varepsilon)}) + e^{\beta(J-\varepsilon)} - e^{-\beta\varepsilon} = 0.$$

Hence,

$$\lambda = \frac{1}{2}\left(1 + e^{\beta(J-\varepsilon)} \pm \sqrt{(1 - e^{\beta(J-\varepsilon)})^2 + 4e^{-\beta\varepsilon}}\right).$$

+ gives the Perron-Frobenius eigenvalue, so we can read off the free energy.

Q27.4 [Adsorption with interactions]
There is a long 1D lattice of adsorption points. Each adsorption point can accommodate at most one gas particle. The state of the lattice may be described by the adsorption pattern $\{\sigma_i\}$, where $\sigma_i = 1$ if the ith adsorption point is occupied, and $\sigma_i = 0$, otherwise. The adsorbed particles interact with each other if they are adjacent; the system energy $\mathcal{H}$ may be described as

$$\mathcal{H} = -\varepsilon \sum_i \sigma_i \sigma_{i+1}. \tag{27.38}$$

This adsorbing 1D lattice is put in a very large box containing a gas that may be used as a chemostat for the adsorbing particles. The chemical potential of the gas may be assumed to be μ, a constant. We wish to determine the average coverage θ of the lattice by the gas particles.
(1) Write down the grand canonical partition function Ξ_M for the 1D lattice system of length M (do not try to compute the sum). Notice that the total number of the particles on the lattice may be written as $N = \sum_i \sigma_i$. The temperature is maintained at T. You may use the standard abbreviations as β.
(2) The grand canonical partition function of the length M 1D lattice described above may be written as

$$\Xi_M = (1,1)\boldsymbol{T}^M \boldsymbol{a} \tag{27.39}$$

with the aid of a transfer matrix $\boldsymbol{T}$, where $\boldsymbol{a}$ is a certain 2 dimensional vector.
(3) Find the limit q

$$q = \lim_{M\to\infty} \frac{1}{M} \log \Xi_M. \tag{27.40}$$

(4) From q obtain θ.

Solution.
(1)

$$\Xi_M = \sum_{\sigma_1,\cdots,\sigma_M \in \{0,1\}} \exp[\beta\epsilon(\sigma_M\sigma_{M-1} + \sigma_{M-1}\sigma_{M-2} + \cdots + \sigma_2\sigma_1) + \beta\mu N] \tag{27.41}$$

$$= \sum_{\sigma_1,\cdots,\sigma_M \in \{0,1\}} \exp[\beta\epsilon\sigma_M\sigma_{M-1} + \beta\mu\sigma_M + \cdots + \beta\epsilon\sigma_2\sigma_1 + \beta\mu\sigma_2 + \beta\mu\sigma_1]. \tag{27.42}$$

(2) We rewrite (27.42) as

$$\Xi_M = \sum_{\sigma_1,\cdots,\sigma_M \in \{0,1\}} e^{\beta\epsilon\sigma_M\sigma_{M-1} + \beta\mu\sigma_M} e^{\beta\epsilon\sigma_{M-1}\sigma_{M-2} + \beta\mu\sigma_{M-1}} \cdots e^{\beta\epsilon\sigma_2\sigma_1 + \beta\mu\sigma_2} e^{\beta\mu\sigma_1}. \tag{27.43}$$

$e^{\beta\epsilon\sigma_M\sigma_{M-1}+\beta\mu\sigma_M}$ can take the following values:

$$\begin{array}{c|cc} & 1 & 0 \\ \hline 1 & e^{\beta\epsilon+\beta\mu} & e^{\beta\mu} \\ 0 & 1 & 1 \end{array} \tag{27.44}$$

Therefore, (27.42) may be written as

$$\Xi_M = (1,1)\boldsymbol{T}^{M-1}\begin{pmatrix} e^{\beta\mu} \\ 1 \end{pmatrix} \tag{27.45}$$

with

$$\boldsymbol{T} = \begin{pmatrix} e^{\beta\epsilon+\beta\mu} & e^{\beta\mu} \\ 1 & 1 \end{pmatrix} \tag{27.46}$$

Since $M \gg 1$, you need not distinguish M and $M \pm 1$.

(3) The characteristic equation for $\boldsymbol{T}$ is

$$\begin{vmatrix} e^{\beta\epsilon+\beta\mu} - \lambda & e^{\beta\mu} \\ 1 & 1-\lambda \end{vmatrix} = (e^{\beta\epsilon+\beta\mu}-\lambda)(1-\lambda)-e^{\beta\mu} = \lambda^2-(1+e^{\beta\epsilon+\beta\mu})\lambda+4e^{\beta\epsilon+\beta\mu}-e^{\beta\mu} = 0. \tag{27.47}$$

Therefore, the Perron-Frobenius eigenvalue is

$$\begin{aligned} \lambda &= \frac{1+e^{\beta\epsilon+\beta\mu}+\sqrt{(1+e^{\beta\epsilon+\beta\mu})^2-4e^{\beta\epsilon+\beta\mu}+4e^{\beta\mu}}}{2} \\ &= \frac{1+e^{\beta\epsilon+\beta\mu}+\sqrt{(1-e^{\beta\epsilon+\beta\mu})^2+4e^{\beta\mu}}}{2}. \end{aligned} \tag{27.48}$$

If $\mu \to -\infty$, then $\lambda = 1$ as expected.

(4) To obtain the coverage, we need the expected value of N.

$$N = \frac{\partial}{\partial\beta\mu}\log\Xi_M \tag{27.49}$$

$$\theta = \lim_{M\to\infty}\frac{N}{M} \tag{27.50}$$

Therefore, we conclude[435]

$$\theta = \frac{\partial}{\partial\beta\mu}q = \frac{\partial}{\partial\beta\mu}\log\lambda \tag{27.51}$$

That is

$$\theta = \frac{e^{\beta\epsilon+\beta\mu}+(2e^{\beta\mu}+e^{2\beta(\epsilon+\mu)}-e^{\beta(\epsilon+\mu)})/\sqrt{(1-e^{\beta\epsilon+\beta\mu})^2+4e^{\beta\mu}}}{1+e^{\beta\epsilon+\beta\mu}+\sqrt{(1-e^{\beta\epsilon+\beta\mu})^2+4e^{\beta\mu}}}. \tag{27.52}$$

This indeed goes to 1 if μ or ϵ is large enough.

[435] You might worry about exchanging the limit and the differentiation, but since $\beta\mu$ is usually very negative, the convergence is swift, and the procedure is quite legitimate.

28 Kadanoff's explanation of scaling

Summary
$*$ Near critical points all the length scales couple and thermal fluctuations build up into large scale fluctuations.
$*$ The large scale fluctuation is scale invariant and implies universality.
$*$ Scaling + coarse-graining is the key ingredient of renormalization group approach.

Key words
scaling invariance, coarse-graining, renormalization, Kadanoff construction

What you should be able to do
$*$ Intuitively understand Kadanoff construction.
$*$ Explain why critical divergences (singularities) occur.
$*$ To understand the scaling index equality.

28.1 Kadanoff construction

Without any simulation Kadanoff (1937-2015) completely understood the structure exhibited in Ashton's video and succeeded in elucidating the general features of critical phenomena with an ingenious intuitive picture Fig. 28.1.

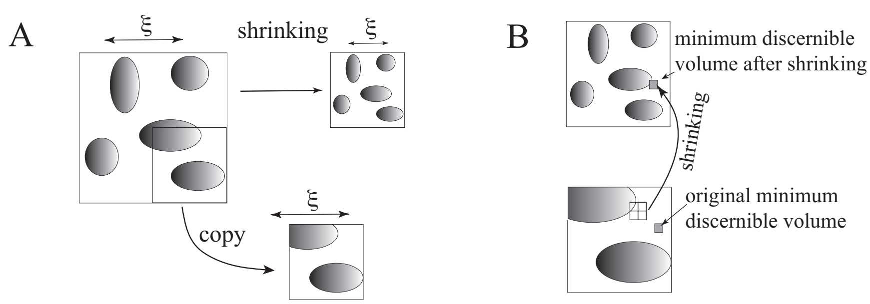

Figure 28.1: **A**: The Kadanoff construction. 'Shrinking' corresponds to looking at the system from distance with fixed eyesight, that is, scaling + coarse-graining. The outcome corresponds to the system away from the critical point; the correlation length ξ becomes smaller. **B**: If we step back and the distance between us and the sample becomes ℓ times as large as the original distance (in the figure $\ell = 2$), the actual linear dimension of the minimum discernible volume becomes ℓ-times as large as the original minimum discernible volume.

If the original system has a temperature $\tau = (T - T_c)/T_c$ and magnetic field h, then from our stepped-back point of view the system looks as if it has these parameters scaled (increased; farther away from the critical point) to $\tau\ell^{y_1}$ and $h\ell^{y_2}$; the exponents y_1 and y_2 must be positive, where ℓ is the shrinking rate (> 1). This is a *guess* or *hypothesis*, but seems to explain everything neatly as we will see below.

28.2 Scaling law

Let us write $m = \mathcal{M}(\tau, h)$ (this is the equation of state for the magnetic system). After one stepping-back, the volume of the region recognized as a unit cube to us would be actually the cube with edge ℓ (see Fig 28.1 Right) before stepping back.

Let us put $'$ to the quantities observed after stepping back. We look at the magnetic energy stored in the minimum discernible block $h'm'$ (after shrinking). The energy should be a much better additive quantity than the local magnetic moment (since energy is additive even microscopically), so we expect

$$h'm' = \ell^d hm. \tag{28.1}$$

Since $h' = h\ell^{y_2}$, we obtain[436]

$$m = \ell^{-d}(h'/h)m' = \ell^{y_2-d}\mathcal{M}(\tau', h') = \ell^{y_2-d}\mathcal{M}(\tau\ell^{y_1}, h\ell^{y_2}). \tag{28.2}$$

This is the *scaling relation* for the equation of state. It should be clearly recognized that this is an *identity* that holds for any positive number ℓ. Therefore, we may set $|\tau|\ell^{y_1} = 1$. Thus, we obtain from (28.2) ($\tau < 0$ to have non-zero magnetization)

$$m(\tau, 0) = |\tau|^{(d-y_2)/y_1} m(-1, 0). \tag{28.3}$$

That is,

$$\beta = \frac{d - y_2}{y_1}. \tag{28.4}$$

We can also conclude from the derivative of (28.2) with respect to h:

$$\gamma = \frac{2y_2 - d}{y_1}. \tag{28.5}$$

28.3 Critical exponent equality

To obtain α we must compute the specific heat, which is available as the second derivative of the free energy with respect to T (recall **17.12**). The (singular part of the) free energy[437] $f_s = \mathcal{F}_s(\tau, h)$ per minimum discernible volume unit scales as

$$f_s = \mathcal{F}_s(\tau, h) = \ell^{-d}\mathcal{F}_s(\tau\ell^{y_1}, h\ell^{y_2}). \tag{28.6}$$

[436] B. Widom [(1965) Equation of State in the Neighborhood of the Critical Point, *J. Chem. Phys.*, **43**, 3898] realized that if we assume this generalized homogeneous function form of the equation of state, critical phenomena can be understood. The Kadanoff construction explains this [Kadanoff, L. P. (1966). Scaling laws for Ising models near T_c, *Physics* **2**, 263-272].

[437] The free energy itself has a large nonsingular part that does not contribute to the singular behaviors near the critical point (**D13.4**).

This comes from $f_s' = \ell^d f_s$ due to the extensivity of the free energy. If we differentiate (28.6) with h, we get (28.2). Differentiating (28.6) twice with respect to τ (that is, T), we obtain

$$C(\tau, h) = \ell^{2y_1-d} C(\tau \ell^{y_1}, h\ell^{y_2}). \tag{28.7}$$

Therefore,

$$\alpha = \frac{2y_1 - d}{y_1}. \tag{28.8}$$

From (28.4), (28.5) and (28.8) we obtain Rushbrooke's equality:

$$\alpha + 2\beta + \gamma = 2. \tag{28.9}$$

28.4 Renormalization group transformation

Kadanoff's idea (Kadanoff construction) consists of two parts: coarse-graining and scaling (shrinking). The crux of the idea is: if the system is at the critical point, the configuration is invariant under coarse-graining $\mathcal{K}$ with an appropriate scaling $\mathcal{S}$. That is, if we define $\mathcal{R} = \mathcal{K}\mathcal{S}$, then thermodynamic observables (densities and fields) are invariant under the application of $\mathcal{R}$ at T_c. To apply $\mathcal{R}$ is to observe the system from distance with a fixed eyesight. Fig. 28.2 Left illustrates how iterative operations of $\mathcal{R}$ drive the statistical configurations at various temperatures.

Operating $\mathcal{R}$ is called a *renormalization group transformation*. We can understand its iterative applications as multiplication of $\mathcal{R}$; doing nothing corresponds to the unit element. Therefore, the totality of the renormalization group transformations is informally called a *renormalization group*.[438] According to Kadanoff's original idea, the image due to $\mathcal{R}$ is the same system under a different condition (e.g., at a different temperature), so we may understand that $\mathcal{R}$ transforms a thermodynamic state into another (of the same system); then, we may imagine that successive applications of $\mathcal{R}$ define a flow on the phase diagram of the same materials system under study. This view is illustrated in Fig. 28.2 Right.[439]

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[438] The inverse may not be defined, so it is usually a monoid. For the concept of 'group' see Section 28

[439] As we will see soon, this flow does not generally flow on the phase diagram (of a given material). In terms of Fig. 28.2 Left, the flow diagram exhibits what happens to the 'actual' configurations. The renormalization flows move as $n = 1, 2, \cdots$ to the left, starting from the 'actual slice'; note, however, the obtained configurations are generally not exactly realized by any state in the phase diagram of the system under study. The flows in Fig. 28.2 Right are, intuitively, an approximate projection of these RG flow lines onto the actual system.

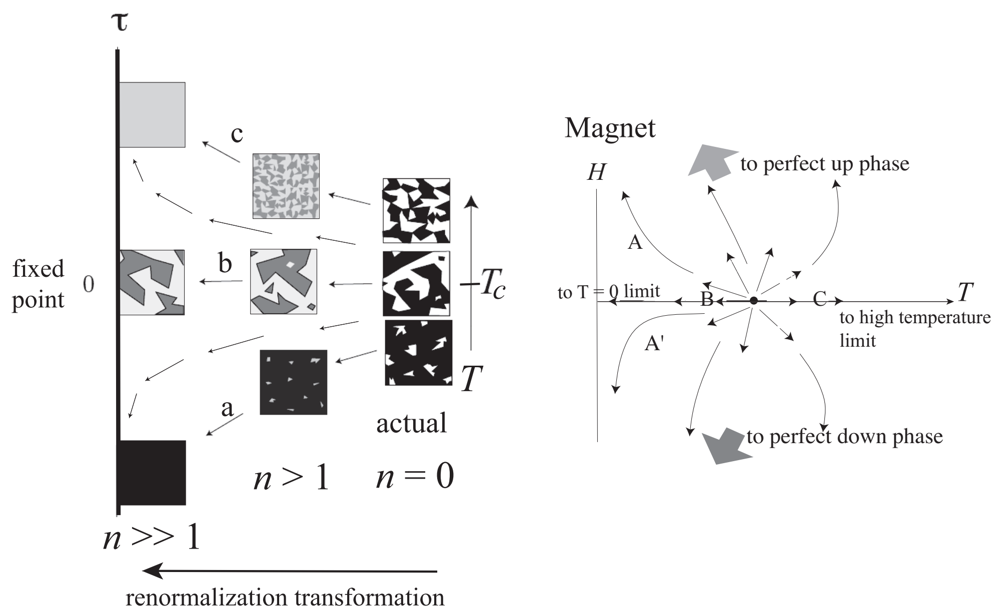

Figure 28.2: **Left**: The result of Kadanoff construction, or the real space renormalization group transformation. For simplicity, $h = 0$ (i.e., on the right phase diagrams we study the system only along the curve BC in Upper Right). Here, $\tau = (T - T_c)/T_c$ and n is the number of times we operate the renormalization group transformation $\mathcal{R}$; we start from the actual configurations ($n = 0$) at various temperatures. As $\mathcal{R}$ is applied successively, the configurations are transformed as the arrows indicate. The leftmost vertical line denotes the destination after many applications of $\mathcal{R}$. a, b, c correspond to the trajectories a, b, c in Fig. 28.3. Only when the starting point is just right, the system can stay at $\tau \sim 0$. The low temperature states are driven to one of the ordered phases at $T = 0$; in the illustration it happens to be totally 'down.' If the starting point is $T > T_c$, the state is driven to $T = \infty$ state. **Right**: RG flows 'projected' (see the text) on the phase diagram of the (Ising) magnet. There are five ultimate destinations (high temperature limit, phase boundary, critical point, all up and all down low temperature states).

28.5 Renormalization group fixed point

At the fixed point $\mathcal{R}\xi = \xi$ should hold for the correlation length ξ. Since $\mathcal{S}$ definitely shrinks the system, this condition is satisfied only if $\xi = 0$ or $\xi = \infty$. That is, the phases without spatial correlation at all or critical points are the only possible fixed points. Notice that if we understand these fixed points, we understand the general structure of the phase diagram. The ordinary bulk phases from our macroscopic point of view do not have any appreciable correlation distance, so they are close to the $\xi = 0$ fixed points. To understand their macroscopic properties we need not worry (qualitatively) about spatial correlations of fluctuations (see footnote 9). This is the reason why the so-called mean-field theory (see Section 26) is useful. Thus, to understand the phase diagram, we use mean field theory to understand the bulk phases not too close to the critical points,[440] and use renormalization group theory

[440] This does not mean that we can use the original microscopic Hamiltonian when we utilize a mean-field approach; we must use an appropriately renormalized Hamiltonian. Therefore, a precise

to understand the features near the critical points.

28.6 Renormalization group flow (RG flow)

We may interpret the renormalization group transformation as a map from a (generalized) canonical distribution μ to another (generalized) canonical distribution $\mu' = \mathcal{R}\mu$. We can imagine effective Hamiltonians H and H' (it is customary that β is absorbed in H's) according to

$$\mu = \frac{1}{Z}e^{-H}, \ \mu' = \frac{1}{Z'}e^{-H'}. \tag{28.10}$$

We may write $H' = \mathcal{R}H$. Therefore, we can imagine that successive applications of $\mathcal{R}$ defines a flow (RG flow) in the space of Hamiltonians (or models or systems). This idea is illustrated in Fig. 28.3 (Fig. 28.2 Left actually illustrates the pattern changes along a, b or c in Fig. 28.3). In Fig. 28.3 H^* is a fixed point with an infinite correlation length of the RG flow. Its stable manifold[441] is called the *critical surface*. The Hamiltonian of the actual material, say, magnet A, changes (do not forget that β is included in the definition of the Hamiltonian in (28.10)) as the temperature changes along the trajectory denoted by the curve with 'magnet A.' It crosses the

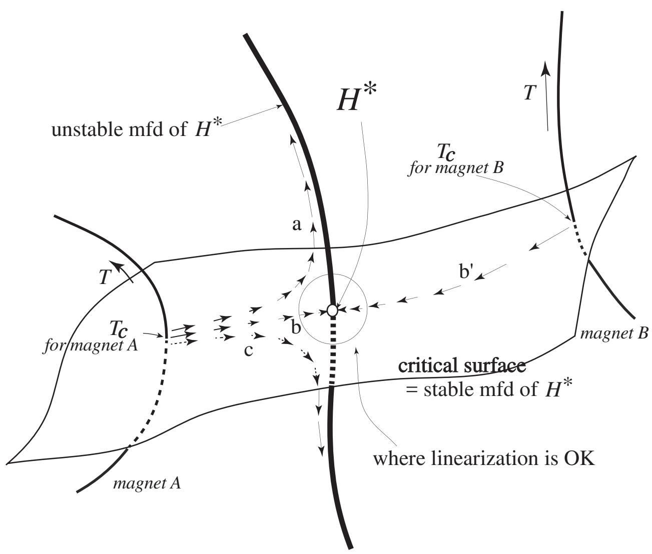

Figure 28.3: A global picture of renormalization group flow in the Hamiltonian space $\mathcal{H}$. The explanation is in the text. 'mfd' = manifold. The thick curves emanating from H^* denote the direction that the Hamiltonians are driven away from the fixed point by renormalization. This curve corresponds to the leftmost thick line in Fig. 28.2 Left.

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statement is: there is a (model) Hamiltonian (with short-range interactions) that can be used to describe the macroscopic features of a bulk phase with the aid of a mean-field approach.

[441]⟪**Stable manifold**⟫ For a fixed point x, the totality of points y flowing into x is called the *stable manifold* of x.

critical surface at its critical temperature. The renormalization transformation uses the actual microscopic Hamiltonian of magnet A at various temperatures as its initial conditions. Three representative RG flows for magnet A are depicted. 'a' is slightly above the critical temperature, 'b' exactly at T_c of magnet A ('b$'$' is the corresponding RG trajectory for magnet B, a different material; both b and b$'$' are on the critical surface), 'c' slightly below the critical temperature (these a, b, c correspond to those in Fig. 28.2 Left). Do not confuse the trajectory (black curve) of the actual microscopic system as temperature changes and the trajectories (successive arrows; RG flow) produced by the RG transformation.

If we understand H^*, we understand all the universal features of the critical behaviors of all the magnets crossing its critical surface.

Let us have a taste of quantitative realization of the renormalization idea.

28.7 Detailed illustration of real space renormalization group calculation[442]

Kadanoff's idea, which may be summarized as follows, allows us to compute, e.g., critical exponents: Introduce some method $\mathcal{K}$ to coarse-grain the system. This method also dictates the spatial scale reduction rate ℓ. The coarse-graining method $\mathcal{K}$ may be understood as a map from a configuration S (this may be a field or spin configuration $\{s_i\}$) of the original system to a configuration of the reduced system. Fig. 28.4 illustrates two examples. The important point of $\mathcal{K}$ is that it is a map: given a configuration S, $\mathcal{K}(S)$ is unique. However, it is not an injection (one-to-one map), since it is a kind of coarse-graining.

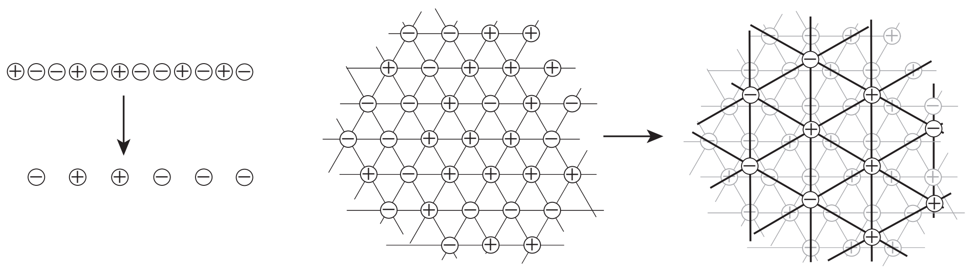

Figure 28.4: **Left**: Decimation of 1-Ising model, $\ell = 2$ (see **Q33.1**); **Right**: Blocking of 3 spins of the triangular lattice 2-Ising model. $\ell = \sqrt{3}$. The value of the block spin is determined by the majority rule: the block spin is up (down) if two or more spins being blocked are up (down).

Triangular lattice 2-Ising coarse-graining:

Let us study the triangular lattice Ising model. It is generally the case that coarse-graining produces multi-spin interactions, even if the original model contains only binary spin interactions as in the present example. However, we wish to be as simple as possible, so we use a (crude but still interesting) approximation that under $\mathcal{K}$ illustrated in Fig. 28.4 Right, the Hamiltonian preserves its shape (that is, we assume that the RG flow does not leave the phase diagram of this particular system; Recall Fig. 28.2):[443]

$$H = \sum K s_i s_j + h s_i \rightarrow H' = \sum K' s'_\alpha s'_\beta + h' s'_\alpha, \tag{28.11}$$

where s'_α, etc. denote the block spins defined by the majority rule: if two or more spins are up (down) in the block, the block spin is up (down).

[442] To understand renormalization group approaches the best way is to follow a few examples to nurture the reader's intuition; Leo Kadanoff told the author that it was easy to invent an RG if we knew the answer (= the system behavior). Chaikin, P. M. and Lubensky, T. C., (1995). *Principles of condensed matter physics*, Cambridge, Cambridge University Press contains excellent explanations and examples.

[443] More accurate handling of this problem can be seen in Niemeijer, Th. and van Leeuwen, J. M. J. (1973). Wilson theory for spin systems on a triangular lattice, *Phys. Rev. Lett.*, **31**, 1411-1414.

How to specify block spins:
Fig. 28.5 explains the block spins more explicitly. For simplicity, let us study the small h case; we ignore its effect on the coarse-grained coupling constant. Since we are interested in the macroscopic global behavior of the mode, we need not worry about the intrablock spin interactions.[444] Therefore, the 'block spin α'-'block spin β' interaction energy must be equal to the sum of the interaction energies among the original spins belonging to different blocks. As can be seen from Fig. 28.5, we may

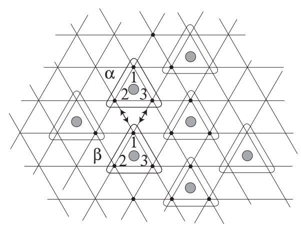

Figure 28.5: Triangular lattice and the block spins α and β. 1, 2, 3 denote the original spins (small black dots). The rounded triangles denote block spins, and small gray disks indicate the positions of the block spins.

demand

$$K's'_\alpha s'_\beta = K(s_{\alpha 2}s_{\beta 1} + s_{\alpha 3}s_{\beta 1}) \tag{28.12}$$

on the average (we cannot demand this exactly). That is, the block spin α-β interaction is supported by two 'actual' interactions: interactions between $\beta 1$ spin and $\alpha 2$ and $\alpha 3$ spins.

Spin-block spin relation:
If we wish to relate K and K', we must relate s and s'. The basic idea is that near the critical point the correlation length ξ is large, so

$$K's'_\alpha s'_\beta = K(\langle s_{a2}\rangle_{s'_\alpha}\langle s_{\beta 1}\rangle_{s'_\beta} + \langle s_{a3}\rangle_{s'_\alpha}\langle s_{\beta 1}\rangle_{s'_\beta}), \tag{28.13}$$

where $\langle s\rangle_{s'}$ is the average of the original spin s in the block spin whose value is s' (a conditional average), and

$$s'_\alpha = \mathrm{sgn}(\langle s_{\alpha 1}\rangle_{s'_\alpha}). \tag{28.14}$$

The following table tells us the original spin configuration compatible with $s'_\alpha = +1$ (i.e., the majority up; $s_{\alpha 1}$ spin is circled). The last line in the table is the intra-block

	⊕ + +	⊕ − +	⊕ + −	⊖ + +
$S_{\alpha 1}$	+1	+1	+1	−1
intra-block energy	$-3K$	$+K$	$+K$	$+K$

[444]They shift the origin of the free energy, but it has nothing to do with the correlation length, so they correspond to the non-singular part of the free energy. Recall that we discussed the singular part of the free energy; we are picking up the singular part only. See **28.3**.

energy of the block spin that determines how a particular internal configuration is likely. Therefore, we obtain

$$\langle s_{\alpha 1}\rangle_{+} = \frac{e^{3K}+e^{-K}+e^{-K}-e^{-K}}{e^{3K}+e^{-K}+e^{-K}+e^{-K}} = \frac{e^{3K}+e^{-K}}{e^{3K}+3e^{-K}} \equiv \phi(K). \tag{28.15}$$

By symmetry $\langle s_{\alpha 1}\rangle_{-} = -\langle s_{\alpha 1}\rangle_{+}$, so we can write

$$\langle s_{\alpha 1}\rangle_{s'_\alpha} = \phi(K)s'_\alpha. \tag{28.16}$$

***K* → *K′* relation**:
(28.13) now reads

$$K's'_\alpha s'_\beta = 2K\phi(K)^2 s'_a s'_\beta, \tag{28.17}$$

or

$$K' = 2K\phi(K)^2. \tag{28.18}$$

***h* → *h′* relation**:
Since we have assumed that h is small, we may simply ignore its effect on K', and we require

$$h's'_\alpha = h(s_{\alpha 1}+s_{\alpha 2}+s_{\alpha 3}), \tag{28.19}$$

so we immediately obtain

$$h' = 3h\phi(K). \tag{28.20}$$

$\mathcal{R}$ has been constructed:
This completes our construction of $\mathcal{R}$: $(K,h) \to (K',h')$ with $\ell = \sqrt{3}$ (from the geometry: Fig. 28.5).

Fixed points of $\mathcal{R}$:
Let us look for fixed points of $\mathcal{R}$, (K_F, h_F), determined by

$$K_F = 2K_F\phi(K_F)^2,\ h_F = 3h_F\phi(K_F). \tag{28.21}$$

$K_F = 0$ is certainly a solution, but $\phi = 1/\sqrt{2}$ gives $K^* = (1/4)\log(1+2\sqrt{2}) \simeq 0.3356\cdots$. For all K_F $h_F = 0$ is a solution. There is no other finite solution.[445]* That is, $(K,h) = (0,0)$ or $(K^*,0)$ is the fixed point.[446] From the correspondence explained in Fig. 28.6 the unstable fixed point $(K^*,0)$ in the (K,h)-plane corresponds to the critical point seen from far away; The thick K axis corresponds to the thick curve through H^* in Fig. 28.3. **Flow near the fixed point; linear approximation to $\mathcal{R}$** :
Although we studied both τ and h, let us study $h = 0$ as before and the flow along the unstable manifold of H^* (the thick curve in Fig. 28.3). As can be seen from

[445] Don't divide the equation with zero.
[446] $K_F = \infty$ is a fixed point corresponding to the ordered phases or $T = 0$.

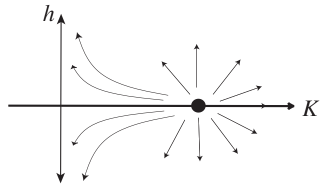

Figure 28.6: The RG flow for the triangular lattice Ising model in the (K, h)-plane. The black dot denotes the location of the nontrivial fixed point $(K^*, 0)$. The origin is also a fixed point. This figure corresponds to Fig. 28.2 Right; larger K corresponds to lower temperature. The black dot corresponds to H^* and the K axis to the thick curve through H^* in Fig. 28.3.

$\mathcal{R}\tau = \tau\ell^{y_1}$ and since $K - K^*$ is essentially τ, we must study the local behavior of $\mathcal{R}$ near the critical fixed point. Let $K = K^* + \delta K$ and $K' = K^* + \delta K'$. Then the linear approximation of $\mathcal{R}$ along the K curve is

$$\mathcal{R}(K^* + \delta K) = K^* + \left(\frac{d\mathcal{R}}{dK}\right)_{\text{at } K^*} \delta K = K^* + \delta K'. \tag{28.22}$$

We may identify (K' is given by (28.18))

$$\ell^{y_1} = \left.\frac{dK'}{dK}\right|_{K=K^*} = 1.634\cdots. \tag{28.23}$$

Therefore, since $\ell = \sqrt{3}$,

$$y_1 = \log 1.634/\log\sqrt{3} \simeq 0.8939\cdots. \tag{28.24}$$

Its exact value is 1 (related to the critical exponent α).[447] The reader may think the result is not impressive (the mean field theory gives 2).

28.8 Universality, trivial and nontrivial

The reader might say we already know examples of universality. For example, we know $PV = 2E/3$ for any ideal gas irrespective of statistics, if the spatial dimensionality is 3, and the dispersion relation is $\varepsilon \propto p^2$ (Section 28). Or we know $PV = E/3$ for phonons and photons in 3-space. This is quite universal. However, it is due to the universality (common quantitative feature) of the elementary entities making up the systems. In this sense, universality is unsurprising, and trivial.

In contradistinction, the universality near the critical point is obviously not due to some common quantitative features at the microscopic level. Of course, the system must exhibit a critical phenomenon, but we use only three features: the interaction is short-ranged, the order parameter is a scalar, and the system is 3D. Thus, the reason for the universality is not in the common nature of the system constituents.

[447] Actually, $1/y_1 = \nu$, the exponent for the correlation length.

Furthermore, the response to system changes is quite different from the trivial case above. If one adds certain interactions, the 'trivial' universality is lost in infinitely different ways according to the infinitely different perturbations. In contrast, in the case of the critical phenomena, if one turns on perturbations modifying interactions, T_c changes sensitively and also the actual values of susceptibilities are altered, but the main features (e.g., critical exponents) do not change. Thus, the universality of the second-order phase transition deserves to be called the *genuine universality*.

28.9 What is statistical mechanics for?

The phase transition points (e.g., T_c) and the values of susceptibilities sensitively depend on materialistic details as mentioned above. We also noted that there is no use of theory to study chemical equilibrium constants in **20.18**. Generally speaking, it is impossible to calculate materials constants very accurately through implementing the theoretical formalism of statistical thermodynamics. Then, what is statistical mechanics for? Statistical mechanics should try to understand (and compute) universal features of many-body systems that are insensitive to quantitative details. Needless to say, demonstrating the existence of some features (say, a phase transition) is an important target of statistical mechanics. As we will see soon in the case of critical phenomena there is a hope that statistical mechanics can obtain universal features quantitatively. Actually, it is fair to say that the true role of statistical mechanics was consciously recognized as the study of universality and not of fetish details (as the actual value of T_c) through the study of critical phenomena.

Discussion 13

D13.1 [Pomeranchuk effect]
The low temperature phase diagram of ^{3}He is illustrated in Fig. 28.7.

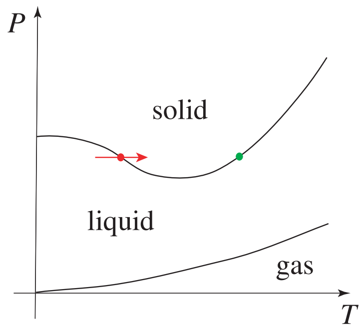

Figure 28.7: A schematic phase diagram of ^{3}He.

(1) Under constant pressure at low temperatures (below ~ 0.3 K), heating (the red arrow in Fig. 28.7) solidifies ^{3}He liquid. Which entropy is larger, the solid phase or the liquid phase? You must provide a supporting argument for your assertion.

(2) If solidification occurs by heating along the red arrow, does the density increase or decrease? You must provide a supporting argument for your assertion.
(3) ^{3}He atom is a spin 1/2 particle, so we must take the magnetic order into account. The so-called spin exchange is the cause of spin spin coupling. In the usual magnet this exchange is mediated by the electron exchange among atoms, but in ^{3}He it is mediated by the positional exchange of the atoms. In the solid phase atoms cannot move easily so positional exchange does not occur. In contrast, in the liquid phase, atoms exchange positions easily, so we must pay attention to the spin-spin coupling. What do you guess is the reason for the 'strange' phase diagram?
(4) If you increase the pressure of ^{3}He reversibly and adiabatically across the liquid-sold phase transition line, what happens to the system temperature?

Solution.
(1) Since the phase diagram is on the PT-plane, the Gibbs free energy G is the thermodynamic potential governing this phase diagram. The Gibbs relation is

$$d(-G) = SdT - VdP. \tag{28.25}$$

Therefore, where G is differentiable (i.e., without any first-order phase transition), we can identify the slopes. Since E is convex and $-G$ is obtained from E by a Legendre transformation:

$$-G = \max_{S,V}[ST + (-P)V - E], \tag{28.26}$$

$-G$ is a convex function of T and $(-)P$. $-G$ is qualitatively illustrated as a function of T and P in Fig. 28.8.

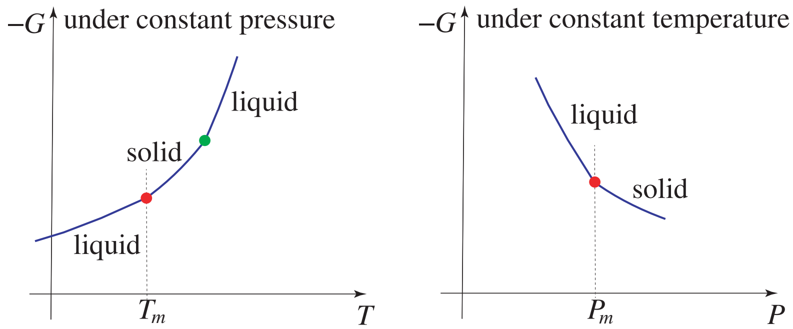

Figure 28.8: $-G$ is a convex function of T (and P).

Thus, around the red point $S(T_m - 0) < S(T_m + 0)$ (i.e., the slope increases, although may not do so smoothly). Therefore, the solid state has larger entropy than the liquid phase (the *Pomeranchuk effect* predicted by him).
(2) As you see from Fig. 28.8 at the red point volume jumps and the density increases by solidification under constant T. Notice that in each phase the density is smooth.[448] Therefore, the discrepancy in density persists even along the T constant line, if you cross the phase transition line. Thus, volume shrinks upon heating.
(3) We can expect that spin ordering (actually antiferromagnetism[449]) in liquid reduces the system entropy sufficiently to compensate the entropy increase due to the particle position disorder.
(4) If you increase the pressure and cross the phase transition line from the liquid to the solid phase isothermally, we know entropy increases (you can use a similar argument as in (3)). However, the actual change in the problem is isentropic (S constant), so we must cool the system. Thus, adiabatic reversible compression can cool the system.

D13.2 [Grand canonical approach to 1D van der Waals gas]
Let us study the 1D Kac model **25.11** with the aid of the grand canonical approach. Here, to make the calculation easy, let us cheat a bit, replacing the interaction portion as the limiting form $-an$, where n is the number density:[450]
(1) If there are N particles in the container of volume V, the canonical partition function reads

$$Z_N(V) = \frac{1}{h^N}\int_{(N-1)\sigma}^{V-\sigma} dx_N \cdots \int_{\sigma}^{x_3-\sigma} dx_2 \int_0^{x_2-\sigma} dx_1 \int dp_1 \cdots dp_n e^{-\sum_{i=1}^N p_i^2/2mk_BT + aN^2/k_BTV}. \tag{28.27}$$

[448]That is, C^ω.
[449]These spins order into an antiferromagnetic state only at around 10^{-3} K.
[450]The honest approach must study the finite systems with the true Kac potential (25.10). After computing the partition function, we take the thermodynamic limit and then take the Kac limit $\gamma \to 0$.

Here, σ is the particle hard core diameter. Check that, indeed, this is the right canonical partition function (with the afore-mentioned cheating). Then, actually compute the canonical partition function $Z_N(V)$. [You virtually know the answer, if you consult Fig. 25.6 in the notes.]
(2) Using the result of (1) write down the grand canonical partition function. Since you cannot perform the summation over N, you have only to write down the formula.
(3) The grand canonical partition function written down in (2) has the following structure:

$$\Xi = \sum_{N=0}^{M} e^{F(N,V)}, \tag{28.28}$$

where M is the maximum number of particles we can push into volume V. Use $\Lambda = 1 + (1/2)\log(2\pi m k_B T/h^2) + \mu/k_B T$ to simplify the result.

Show that if the temperature is sufficiently high, there is only one $n = N/V$ that maximizes $A(n) = F(N,V)/V$.

Also demonstrate that if the temperature is sufficiently low, there can be three extrema for $A(n)$.
(4) What does the grand partition function look like, if n that maximizes $A(n)$ are not unique?
(5) There is a text book[451] which writes explicitly as follows:

$$\Xi = e^{\beta PV} + e^{\beta P' V}. \tag{28.29}$$

Here, we have assumed that $A(n)$ have two maxima, and the two terms correspond respectively to the two maxima. Is this correct?

Solution.
(1) Let us start with the $N = 2$ case:

$$Z_2(V) = \frac{1}{h^2}\int_{\sigma}^{V-\sigma} dx_2 \int_0^{x_2-\sigma} dx_1 \int dp_1 dp_2 e^{-\sum_{i=1}^{2} p_i^2/2mk_BT + aN^2/2k_BTV} \tag{28.30}$$

$$= \left(\frac{2\pi m k_B T}{h^2}\right)^{2/2} \int_0^{V-2\sigma} dy_2 \int_0^{y_2} dy_1 e^{2a/Vk_BT} \tag{28.31}$$

$$= \left(\frac{2\pi m k_B T}{h^2}\right)^{2/2} \frac{1}{2}(V-2\sigma)^2 e^{2a/Vk_BT}. \tag{28.32}$$

In the above calculation the interparticle distances $y_2 = x_2 - x_1$ and $y_1 = x_1 - 0$ have been introduced.

For $N = 3$, introducing $y_3 = x_3 - x_2$ as well we get

$$Z_3(V) = \frac{1}{h^3}\int_{2\sigma}^{V-\sigma} dx_3 \int_{\sigma}^{x_3-\sigma} dx_2 \int_0^{x_2-\sigma} dx_1 \int dp_1 dp_2 dp_3 e^{-\sum_{i=1}^{3} p_i^2/2mk_BT + aN^2/k_BTV}$$

[451] by Kardar

$$(28.33)$$

$$= \left(\frac{2\pi m k_B T}{h^2}\right)^{3/2} \int_0^{V-3\sigma} dy_3 \int_0^{y_3} dy_2 \int_0^{y_2} dy_1 e^{9a/2Vk_BT} \tag{28.34}$$

$$= \left(\frac{2\pi m k_B T}{h^2}\right)^{3/2} \frac{1}{3!}(V-3\sigma)^3 e^{9a/2Vk_BT}. \tag{28.35}$$

Now, it is easy to guess the following general formula:

$$Z_N(V) = \frac{1}{N!}\left(\frac{2\pi m k_B T}{h^2}\right)^{N/2} (V-N\sigma)^N e^{aN^2/2Vk_BT}. \tag{28.36}$$

This is the result you can read off from Fig. 25.6 in the notes.
(2)

$$\Xi = \sum_{N=0}^{M} \frac{1}{N!}(V-N\sigma)^N (2\pi m k_B T/h^2)^{N/2} e^{aN^2/2Vk_BT} e^{\mu N/k_BT}. \tag{28.37}$$

(3) From (28.37) we obtain

$$F(N,V) = N\log(V-N\sigma) - N\log N + N + \frac{N}{2}\log(2\pi m k_B T/h^2) + aN^2/2Vk_BT + \mu N/k_BT \tag{28.38}$$

(actually, this is $\log Z_N(V)$ + the chemical potential term), so

$$A(n) = n\log(1/n-\sigma) + n + \frac{n}{2}\log(2\pi m k_B T/h^2) + an^2/2k_BT + \mu n/k_BT \tag{28.39}$$

$$= n\log(1/n-\sigma) + n\Lambda + an^2/2k_BT, \tag{28.40}$$

where $\Lambda = 1 + (1/2)\log(2\pi m k_B T/h^2) + \mu/k_BT$. Differentiating this wrt to n, we get the condition for a maximum:

$$\frac{\partial A(n)}{\partial n} = \log\left(\frac{1}{n}-\sigma\right) - \frac{1}{1-n\sigma} + \Lambda + an/k_BT = 0. \tag{28.41}$$

The first two terms are

$$\log(1/n) + \log(1-n\sigma) - \frac{1}{1-n\sigma}. \tag{28.42}$$

This is a monotone decreasing function of n from $+\infty$ (at $n=0$) to $-\infty$ (at $n=1/\sigma$, the maximum packing density). Therefore, if T is sufficiently large, there is only one solution to (28.41).

We see there could be three solutions for this equation, if T is sufficiently small, because $A(n)$ has the following form:

$$\log(1/n) + \log(1-n\sigma) - \frac{1}{1-n\sigma} + \left[\frac{(a+\mu)n}{k_BT} + \frac{n}{2}\log T + \text{ constant}\right]. \tag{28.43}$$

For sufficiently small T the term proportional to $1/T$ dominates in [ ], so the monotonic decreasing nature of (28.42) is lost for intermediate values of n. Therefore, there can be three extrema (with an appropriate chemical potential); two maxima and one minimum. Recall that $A(n)$ is essentially negative free energy, so there are two stable local minima for the free energy, if T is sufficiently low.
(4) At high temperatures there is only one maximum for $A(n)$, so we may use the maximum term to estimate (28.28). This is just as we have seen in the proof of ensemble equivalence in the text:

$$\Xi = e^{PV/k_BT} \simeq e^{VA(n)}. \tag{28.44}$$

If T is sufficiently low (with an appropriate chemical potential), as noted in (3) there are two maxima. If the heights of these maxima are different, then thanks to the multiplicative V in the exponent of (28.28) only one maximum can contribute. Only when these two maxima have exactly the same heights can they both contribute to the grand partition function, and this corresponds to the phase coexistence temperature.
(5) As already explained in (4) this form holds only exactly at the phase transition temperature. At other temperatures one term is overwhelmingly smaller than the other, and around the taller maximum are numerous higher $A(n)$'s than the secondary maximum, so literally, the equation is nonsensical; however, if you compute the log of the right-hand side, the difference from $\log \Xi$ is likely to be $O[\log N]$.

D13.3 [Square lattice Ising model: mean field approach].[452]
We have derived the fundamental equation (the consistency equation) for the starting point of the mean field approaches:

$$\langle s_0 \rangle = \langle \tanh[\beta J(s_1 + \cdots + s_k)] \rangle \tag{28.45}$$

for an Ising model on a lattice with k nearest-neighbor spins around s_0. Let us take a lattice with $k = 4$ (square lattice, for example).
(1) Let us use the naivest approach as (26.21). Obtain the critical point T_c with this crude approximation.

Then, using a more accurate mean field theory explained in **27.2**, we wish to exploit the fact that $s^2 = 1$. First, we expand tanh in power series.
(2) Show that

$$\tanh[\beta J(s_1 + \cdots + s_k)] = A(s_1 + s_2 + s_3 + s_4) + B(s_1s_2s_3 + s_1s_3s_4 + s_2s_3s_4 + s_1s_2s_4). \tag{28.46}$$

That is, any odd power of $(s_1 + s_2 + s_3 + s_4)$ is written as a sum of $(s_1 + s_2 + s_3 + s_4)$ and $(s_1s_2s_3 + s_1s_3s_4 + s_2s_3s_4 + s_1s_2s_4)$.

[452]= **Q27.2**, because HW13 is related.

(3) Determine A and B by setting $s = \pm 1$ so that (28.46) holds, or show that

$$A = \frac{1}{8}(\tanh 4\beta J + 2\tanh 2\beta J). \tag{28.47}$$

(4) Now, introducing (28.46) into (28.45), we get the following equation

$$\langle s_0 \rangle = A\langle s_1 + s_2 + s_3 + s_4 \rangle + B\langle s_1 s_2 s_3 + s_1 s_3 s_4 + s_2 s_3 s_4 + s_1 s_2 s_4 \rangle. \tag{28.48}$$

$\langle s_0 \rangle = \langle s_1 \rangle = \cdots = m$ is the magnetization per spin, so (28.48) reads

$$m = 4Am + 4B\langle s_1 s_2 s_3 \rangle. \tag{28.49}$$

Notice that up to this point there is NO APPROXIMATION, but, unfortunately, we cannot solve (28.49). Now, let us introduce the approximation

$$\langle s_1 s_2 s_3 \rangle = m^3. \tag{28.50}$$

Then, our 'approximate' mean field equation is

$$m = 4Am + 4Bm^3. \tag{28.51}$$

What is the condition that determines the phase transition? [Hint. At what value of A is there a bifurcation[453]?]

Solution.
(1) Exchanging tanh and averaging (and assuming spatial uniformity), we get

$$m = \tanh(k\beta J m). \tag{28.52}$$

or

$$x = k\beta J \tanh x. \tag{28.53}$$

If the tangent at $x = 0$ of the right-hand side is larger than 1, there are three solutions; below that there is one solution (see Fig. 26.7 in the notes). Thus, the bifurcation point is $k\beta J = 1$ or $T_c = kJ/k_B$.
(2) Checking first two or three terms in the expansion of tanh is practically enough.
However, if you wish to 'prove' (28.46), you can proceed as follows. Since the convergence radius of the power series is infinite, we need not worry about the size of the terms. Generally we have an odd power $(s_1 + s_2 + s_3 + s_4)^m$, where m is an odd positive integer.
If we expand this, (e.g., multinomial theorem tells us) we obtain the terms of the following form:

$$s_1^a s_2^b s_3^c s_4^d \tag{28.54}$$

[453] Recall 'bifurcation' implies the change of the number of (real) roots.

for $a+b+c+d=m$ ($a, \cdots, d$ are nonnegative integers).

There is a perfect permutation symmetry among $s_1, \cdots, s_4$ and only one or three of $a, \cdots, d$ must be odd. The even powers of s_i is one, and the odd powers s_i itself, so we have only two types of terms s_1 or $s_1 s_2 s_3$. Taking the perfect permutation symmetry into account, we get (28.46).

If you wish to be a bit more pedestrian, look at

$$
\begin{aligned}
s_1^m &= s_1, && (28.55)\\
s_1^{m-1} s_2 &= s_2, && (28.56)\\
s_1^{m-2} s_2^2 &= s_1, && (28.57)\\
s_1^{m-2} s_2 s_3 &= s_1 s_2 s_3, && (28.58)\\
s_1^{m-3} s_2^3 &= s_2, && (28.59)\\
s_1^{m-3} s_2^2 s_3 &= s_3, && (28.60)\\
s_1^{m-3} s_2 s_3 s_4 &= s_2 s_3 s_4. && (28.61)
\end{aligned}
$$

There is no other case (modulo permutation of the suffixes). [Do not honestly expand tanh.] Therefore, summing all these terms,[454] we must have (28.46).
(3) For all s being $+1$:

$$\tanh(4\beta J) = 4A + 4B. \tag{28.62}$$

For one -1:

$$\tanh(2\beta J) = 2A - 2B. \tag{28.63}$$

Other possibilities do not give any new relation. From these, we get

$$A = (1/8)(\tanh 4\beta J + 2\tanh 2\beta J),\ \ B = (1/8)(\tanh 4\beta J - 2\tanh 2\beta J). \tag{28.64}$$

(3) We must solve $m = 4Am + 4Bm^3$. When the slope of $4Am + 4Bm^3$ at $m = 0$ is 1, bifurcation occurs. Hence, $4A = 1$ or

$$\tanh 4\beta J + 2\tanh 2\beta J = 2 \tag{28.65}$$

is the equation for the critical point.

You need not solve this, but notice that the T_c obtained from this must be smaller (I got $\beta J = 0.33$) than that obtained from $\beta J = 0.25$ (due to a better approximation). The exact result (due to Onsager) is $\beta J = [\log(1+\sqrt{2})]/2 = 0.440$.

D13.4. [Simple 1D renormalization (decimation)]
Let us study 1-Ising model with the aid of *decimation* illustrated in Fig. 28.9. This procedure thins the spins through summing over a subset of spins, keeping the rest

[454] Since the original power series is absolutely convergent, we can do this.

fixed.

The original canonical partition function reads (here, $K = \beta J$)

$$Z = \sum_{s,\sigma} \cdots e^{Ks_{-1}\sigma_0 + \sigma_0 s_1} \cdots, \tag{28.66}$$

where spins at the even lattice positions are written as σ.

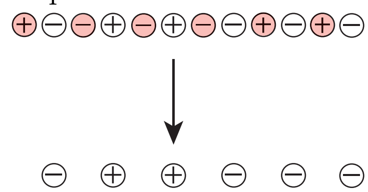

Figure 28.9: Decimation: we sum over the red spins.

(1) Summing over all σ states, the original Z now reads

$$Z = C \sum_{s} \cdots e^{K'(s_{-1}s_1)} \cdots, \tag{28.67}$$

where C is a constant. This can be understood as (C times) the canonical partition function of the chain consisting of the remaining odd lattice spins $\{s_i\}$. Actually, each term in the sum is a product of the factors (proportional to)

$$\sum_{\sigma_0 = \pm 1} e^{K(s_{-1}\sigma_0 + \sigma_0 s_1)}, \tag{28.68}$$

so to compute K' we should study

$$\sum_{\sigma_0 = \pm 1} e^{K(s_{-1}\sigma_0 + \sigma_0 s_1)} = e^{A + K' s_{-1} s_1}, \tag{28.69}$$

where A is a constant (and C is the product of e^As). Find A and K'.

(2) Since we do not care for C, the result of (1) may be understood as the transformation of the system Hamiltonian from H to $H' = \mathcal{D}H$ (decimation transformation):

$$H = \sum_{i \in \mathbb{Z}} K s_i s_{i+1} \to H' = \mathcal{D}H = \sum_{i \in \mathbb{Z}/2} K' s_i s_{i+2}. \tag{28.70}$$

The macroscopic observables of a very big system governed by H should be understood from the behavior of the system governed by $\mathcal{D}^n H$ for large n. Using this observation, show that there is no finite temperature phase transition in 1-space.

Solution.

(1) Let us solve (28.69). If the spin sum is zero: $s_{-1} + s_1 = 0$,

$$2 = e^{A - K'}; \tag{28.71}$$

otherwise,

$$2\cosh(2K) = e^{A+K'}, \tag{28.72}$$

so we obtain

$$e^{2K'} = \cosh(2K), \tag{28.73}$$

or

$$K' = \frac{1}{2}\log\cosh 2K. \tag{28.74}$$

Thus, we have constructed a map $\mathcal{D}$ from the original Hamiltonian to the coarse-grained Hamiltonian:

$$H = \sum_{i\in\mathbb{Z}} K s_i s_{i+1} \to H' = \mathcal{D}H = \sum_{i\in\mathbb{Z}/2} K' s_i s_{i+2}. \tag{28.75}$$

(2) Starting from some positive K and iterating (28.74), we see (e.g., graphically) clearly that $K \to K' \to \cdots \to 0$ quickly (that is, the system is driven to the high-temperature disordered fixed point), consistent with the fact that there is no phase transition for $T > 0$.

E13.1 [Elementary questions]
(1) The density of a gas is usually less than the liquid of the same substance. Why?
(2) Does a triple point correspond to a single thermodynamic state?
(3) At the triple point (solid-gas-liquid coexistence; cf. Fig. 24.1 in the notes) of a pure substance, three coexistence curves, the LG, GS and LS curves, meet at the tricritical point on the PT-plane (P the vertical axis). Which curve is the steepest, and which the least steep around the triple point? You must justify your answers.
(4) When a magnetic field is applied in the z-direction, a phase transition from phase I to phase II occurs. What can you say about the change of the magnetization?

Solution.
(1) We can make a gas phase by reducing the pressure of the corresponding liquid, usually, so the gas phase is a low pressure phase. The convexity of $-G$ implies that $V(P-0) > V(P+0)$, because $-V$ is the conjugate variable of P. Thus, the gas phase has a larger volume (or a less density).
(2) No. In the thermodynamic space it occupies a triangular domain (or see Fig. 24.2 in the notes).
(3) We use the Clapeyron-Clausius equation:

$$\left.\frac{dP}{dT}\right|_{\text{coex line}} = \frac{\Delta S}{\Delta V}. \tag{28.76}$$

Because of the general placement of these three phases on the PT diagram, obviously

$$\left|\left.\frac{dP}{dT}\right|_{s\to l}\right| \gg \left.\frac{dP}{dT}\right|_{s\to g} \text{ or } \left.\frac{dP}{dT}\right|_{l\to g}. \tag{28.77}$$

Notice that ΔV between the gas phase and the condensed phases are similar, but $\Delta S_{s\to g}$ is larger than $\Delta S_{l\to g}$, so usually

$$\left.\frac{dP}{dT}\right|_{s\to g} > \left.\frac{dP}{dT}\right|_{l\to g}. \tag{28.78}$$

(4) This is a (generalized le Chatelier). Or the convexity of $-A$, where $A = E - M_z B_z$. Thus, M_z must be monotone increasing with respect to B_z. That is, II has a bigger magnetic moment in the z-direction than I.

E13.2 [Phase coexistence]
There is a mixture of two chemicals A and B. This mixture can have 4 phases, solid (S), liquid I (L), liquid II (L') and gas (G) phases. In the gas phase A and B mix freely, but the solid phase consists only of A (i.e., B cannot get into the solid phase). Can you have a quadruple point (T_Q, P_Q) where these 4 phases coexist? You may assume any reasonable functional equation can be solved.

Solution.

Let x_ϕ be the mole fraction of A in phase $\phi = L$, L' or G. The equilibrium condition of 4 phase-coexistence reads

$$\mu_S^{\mathrm{A}}(P,T) = \mu_L^{\mathrm{A}}(P,T,x_L) = \mu_{L'}^{\mathrm{A}}(P,T,x_{L'}) = \mu_G^{\mathrm{A}}(P,T,x_G), \tag{28.79}$$

$$\mu_L^{\mathrm{B}}(P,T,x_L) = \mu_{L'}^{\mathrm{B}}(P,T,x_{L'}) = \mu_G^{\mathrm{B}}(P,T,x_G). \tag{28.80}$$

There are five (5) unknowns, P, T, x_L, $x_{L'}$ and x_G, and we have five (5) equations, so, generically, there can be a four-phase coexisting point.

Notice that if B can go into the solid phase, this is the standard case, and the answer is yes, according to the Gibbs phase rule.

E13.3 [2-Ising model on the honeycomb lattice; mean-field approach]
Let us consider a 2-Ising model on the honeycomb lattice whose coupling constant is J. Assume there is no magnetic field.
(1) Find the equation corresponding to (26.19) [consistency equation] in the notes.
(2) Find T_c with the aid of the approximation corresponding to (26.20) [the naivest approximation] in the notes.
(3) Then, using a more accurate mean field theory explained in **27.2** of Discussion 13.3, compute T_c. Which T_c obtained by (2) or by this question should be lower? Is your result consistent with your expectation?

Solution
(1) The coordination number of the honeycomb lattice is 3, so

$$\langle s_0 \rangle = \langle \tanh[\beta J(s_1 + s_2 + s_3)] \rangle. \tag{28.81}$$

(2) The approximation gives

$$m = \tanh 3\beta J m. \tag{28.82}$$

That is,

$$x = 3\beta J \tanh x. \tag{28.83}$$

This gives $\beta_c J = 1/3$ or $T_c = 3J/k_B$.
(3) The equation corresponding to (5.8.10) is

$$\tanh \beta J(s_1 + s_2 + s_3) = a(s_1 + s_2 + s_3) + b s_1 s_2 s_3, \tag{28.84}$$

and the coefficients are determined by the following simultaneous equation

$$\tanh 3\beta J = 3a + b, \tag{28.85}$$

$$\tan \beta J = a - b. \tag{28.86}$$

We get

$$a = \frac{1}{4}(\tanh \beta J + \tanh 3\beta J), \quad b = \frac{1}{4}(\tanh 3\beta J - 3\tanh \beta J). \tag{28.87}$$

Thus, the mean-field equation reads

$$m = 3am + bm^3, \tag{28.88}$$

The bifurcation point is given by the slope of the right-hand side at $m = 0$ to be 1, i.e., $3a = 1$ or, more explicitly, solving the equation

$$m = \pm\sqrt{\frac{1-3a}{b}} \text{ or } 0, \tag{28.89}$$

so T_c is determined by $a = 1/3$:

$$\tanh \beta J + \tanh 3\beta J = 4/3. \tag{28.90}$$

A more accurate calculation is expected to take the effect of fluctuations more accurately into account. Fluctuations oppose ordering, so better approximation should give lower T_c. That is, we can expect that the T_c from the current approximation method is lower than that obtained in (3), i.e., $T_c = 3J/k_B$.

It is not hard to prove that the T_c according to the 'better' approximation is indeed lower than $3J/k_B$, but here let us use a numerical result: $\beta_c J = 0.48$ or $T_c = 2.08J/k_B$.

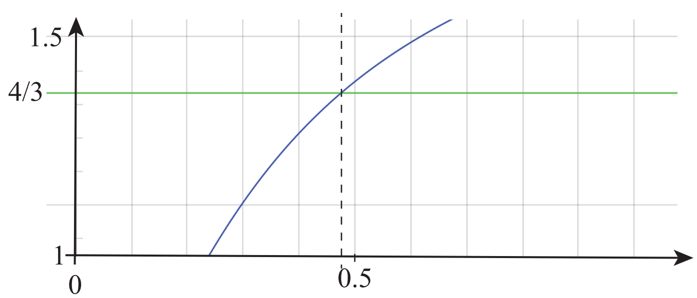

Figure 28.10: Solving (28.90) graphically.

The exact answer is known to be $\beta J = 0.658$ or $T_c = 1.52J/k_B$; thus our improvement is considerable.

29 Symmetry breaking

Summary
∗ Spontaneous symmetry breaking and two important consequences are discussed.

Key words
(spontaneous) symmetry breaking, rigidity, Nambu-Goldstone boson

What you should be able to do
∗ Be able to explain intuitively why rigidity and NG bosons emerge upon spontaneous symmetry breaking.

29.1 Ordering means lowering the system symmetry

So far we discussed phase transitions. It is very often the transition between ordered and not-so-ordered states. Ordering means the system has less symmetry: in a gas phase molecules can sit anywhere, so the system has the full 3D translational and rotational symmetry, but if a crystal is formed (ordered!), we know the molecules cannot sit everywhere they wish; they must make a crystal lattice, so translational and rotational symmetries are lost.

29.2 How to describe the symmetry

The symmetry of a system may be understood through *symmetry operations* (Fig. 29.1).

It is clear that more highly symmetric objects allow more symmetry operations that keep the objects intact (invariant). The totality G of the symmetry operations that keep an object intact is called the *symmetry group* of the object.[455]

29.3 Spontaneous breaking of symmetry

[455] ⟪**Group**⟫ If $a, b \in G$, and if we write operating b first and then a next as the product ab, then $ab \in G$, so we can have an algebraic structure on G (as illustrated in http://demonstrations.wolfram.com/C3vGroupOperations/. We know (i) the identity $e \in G$ and (ii) the inverse operation a^{-1} of any operation $a \in G$ is again in G. Furthermore, (iii) $(ab)c = a(bc)$. If G satisfies these three conditions, G is called a *group*. If a subset $H \subset G$ is again a group, it is called a *subgroup* of G. Lowering of the symmetry of a system corresponds to restricting the original symmetry group to its genuine subgroup.

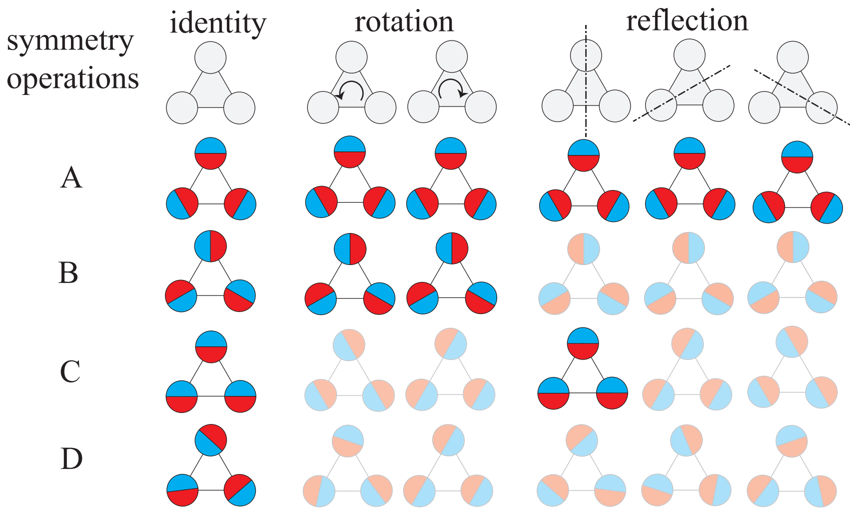

Figure 29.1: Symmetry illustrated. There are two kinds of rotational operations and three kinds of reflection operations that keep A intact (symmetry group C_{3v}). With lowering the symmetry allowed symmetry operations become restricted. For B only rotations are allowed (symmetry group C_3), and for C only one reflection is allowed (C_σ). Without any symmetry (case D) only identity I keeps the figure intact.

If an equilibrium state has a symmetry group which is a genuine subgroup of the symmetry group of the system Hamiltonian, we say the symmetry is *spontaneously broken*. Certainly, the symmetry is spontaneously broken below T_c for 2-Ising model. In this case the symmetry that is broken is described by a discrete group (up-down symmetry).[456]

Crystallization mentioned above is another example. The Hamiltonian of the system is something like

$$H = \sum_i \frac{\boldsymbol{p}_i^2}{2m} + \sum_{i<j} \phi(\boldsymbol{r}_i - \boldsymbol{r}_j), \tag{29.1}$$

where ϕ is usually a binary interaction potential. Thus, the Hamiltonian has a full translation symmetry: nothing happens even if translation $\boldsymbol{r}_i \to \boldsymbol{r}_i + \boldsymbol{a}$ is applied to all the particles; H is invariant.[457] However, we believe this system crystallizes, losing its translational symmetry, if the interaction potential is something like the Lenard-Jones potential.[458] Thus, crystallization is a typical spontaneous symmetry breaking. In contrast to the 2-Ising model, the symmetry group in this case is continuous. That is, any $\boldsymbol{a}$ is allowed or any small angle rotation can keep the Hamiltonian intact. Really interesting phenomena due to spontaneous symmetry breaking occur if the broken symmetry is continuous.

[456] Z_2 group.

[457] You might ask how the boundary of the system is taken care of. We take a huge system (eventually the thermodynamic limit), or we may impose a periodic boundary condition.

[458] As already noted previously, we have not been able to prove this within statistical mechanics.

29.4 Symmetry breaking in Heisenberg magnet

Consider a Heisenberg magnet as an example (cf. Fig. 29.2). In this case the system Hamiltonian

$$H = -J \sum_{\langle i,j \rangle} \boldsymbol{s}_i \cdot \boldsymbol{s}_j \tag{29.2}$$

has a full 3D rotational symmetry of spins.[459] The disordered phase (paramagnetic phase) has no magnetization $\boldsymbol{m} = 0$, so indeed the system is fully rotationally symmetric. However, below T_c, when ferromagnetic order emerges, then $\boldsymbol{m}$ is a definite non-zero vector. Thus, the system symmetry is no more 3D rotational but only the 2D rotation around the axis parallel to $\boldsymbol{m}$ (in the spin space). Thus, the symmetry is lowered, a typical example of spontaneous symmetry breaking[460] (Fig. 29.2).

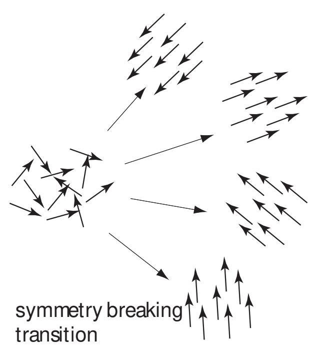

Figure 29.2: Symmetry breaking results in an ensemble of symmetry broken phases collectively representing the whole symmetry of the system. (This illustration corresponds to a transition from a paramagnetic phase to a ferromagnetic phase.)

29.5 Consequences of symmetry breaking: rigidity

Now, take a Heisenberg magnet below its T_c with magnetization $\boldsymbol{m}$ being in the $+z$-direction. Let us choose one spin in front of us and rotate it by 90° to point in the $+x$-direction, and hold it. What happens? The spins around the rotated spin do not like this, because the interaction is energetically unfavorable. Thermal fluctuation occasionally flip them and align them to the held spin. Needless to say, then, these reoriented spins will have uncomfortable relations with further outside spins, BUT this outside relation is 'better'; the central spin never moves, so the discomfort is

[459] O_3-symmetry, needless to say, it is a continuous symmetry. The spins live on a lattice, so there is no spatial rotational symmetry. Do not confuse the rotations in the spin space and in the actual space.

[460] In this case, the macroscopic states with different $\boldsymbol{m}$ are understood as distinct phases just as gas and liquid phases in fluids. If $\boldsymbol{m}$ changes to $\boldsymbol{m}'$, this is a first order phase transition between two distinct ordered phases.

steady, but in the outer layers it is ameliorated by thermal fluctuations. Thus, the flipped x-oriented domain gradually widens, and eventually the macroscopic magnet changes its direction of magnetization. Since this state has the same energy as the original state (H, the system Hamiltonian, is symmetric!), the final state will last forever, even if you stop holding the central spin. If we do not pay attention to what was actually happening between the two equilibrium states, what happens is just the rotation of the magnetization. This property— the whole system following the modification of its part—is called (generalized) *rigidity*.[461]

The rigidity the most familiar to us is the rigidity of a solid. If we push one end of a solid, the other end also moves accordingly. You cannot do this for fluids. Only after translational symmetry is spontaneously broken can we have this ordinary rigidity of solid. If one end is twisted, the other end follows as well. This is due to the breaking of the rotational symmetry by crystallization.

Rigidity also occurs in 2D Ising model: if you flip the central spin and hold it, eventually the magnetization would change its sign. Thus, whenever symmetry is spontaneously broken, rigidity emerges. However, symmetry breaking of continuous symmetries is much more dramatic, because any local small change (which is impossible for discrete symmetry cases) propagates to the other end.

29.6 Nambu-Goldstone bosons: a consequence of breaking of continuous symmetry

If the spontaneously broken symmetry is continuous, and if the system interactions are short-ranged, we have another universal feature: the *Nambu-Goldstone bosons* (NG bosons). The NG bosons refer to long wave length collective excitations in the ordered phase (like acoustic phonons = sound waves in solids) whose excitation energy tends to zero in the long-wavelength limit.

All possible symmetry broken phases (see Fig. 29.2) have the same energy, because they can be transformed into each other with an element of the symmetry group of the system Hamiltonian. Consider a 3D rectangular parallelepiped, and assume that the phase changes continuously along its one axis (x-axis) (Fig. 29.3)

Let us estimate the needed energy for such deformation of the magnetization per cross section perpendicular to the x-axis. The spin interaction energy is given by the scalar product of spins, so if the angle between the neighboring spins is a small angle θ, the energy increases by $1 - \cos\theta \propto \theta^2$ relative to the perfect parallel case. Suppose the spin-spin angle changes by $d\theta$ if they are apart by dx along the x-axis. The energy change per dx is proportional to $d\theta^2$, so the total energy change due to

[461] The change in a 'small part' is in this case kept by an external means (by us). Then, the change eventually propagates to the whole system (i.e., any indefinitely large finite domain follows). Notice that an equilibrium state is stable under any perturbation of any finite domain, if the perturbation is left unconstrained. Do not mix up these different situations.

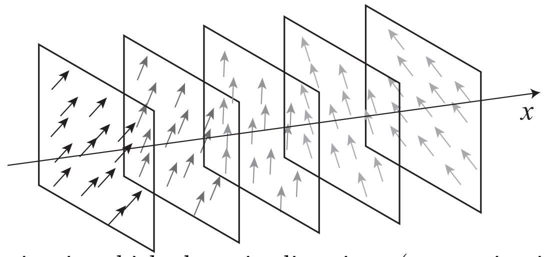

Figure 29.3: The situation in which the spin directions (magnetizations) in the planes perpendicular to an axis (x-axis) change gradually

this twisting of spins from one end 0 to the other end L is given by

$$(d\theta)^2 \frac{L}{dx} \simeq \int_0^L \frac{d\theta^2}{dx} = \int_0^L \left(\frac{d\theta}{dx}\right)^2 dx. \tag{29.3}$$

Here, the L/dx in the leftmost expression is the number of slices. The formula implies that if the total twist angle is θ, then the total energy cost for this deformation is proportional to θ^2/L. That is, if we can deform the system continuously, longer wave deformation (fluctuation) requires less energy to realize. Thus, the Nambu-Goldstone bosons become possible.

In the case of the Heisenberg ferromagnet, precession of spins can propagate as a wave (*spin waves*) and its quantum is called *magnons*. In a crystal the vibration due to the mutual displacement of lattice cells can propagate as a wave and its quantum is our familiar (acoustic) phonons. They are the NG bosons due to crystallization.

29.7 NG bosons do not exist for long-range interaction systems

However, as can be guessed from the above explanation, if there is a long-range interaction, then the energy required by a long-wavelength excitation may not vanish. This indeed happens in plasmas. Suppose we displace + charges relative to − charges as in Fig. 29.4. The Coulomb interaction energy between the charge density fluctuations does not decrease with distance (remember the parallel plate capacitor). Therefore, the excitation energy has a lower cut off and the long-wave frequency does not converge to zero.[462]

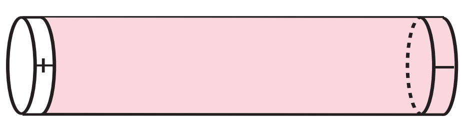

Figure 29.4: However far away the + and − charges are apart, in this case (recall a parallel plate capacitor) the Coulomb interaction between the separated charges does not decay.

29.8 Summary of symmetry breaking

We can summarize representative examples. Although not discussed superfluidity of

[462]Plasma oscillation is these excitations.

^{4}He is also added.[463]

	solid	Heisenberg ferro	superfluid
Broken Symmetry	3D translational	rotational	phase
Order	3D periodicity	ferromagnetism	superfluidity
NG boson	acoustic phonons	spin wave	second sound
Rigidity	rigidity	ferromagnetism	superfluidity

29.9 Symmetry breaking requires big systems

If the system is finite, there is no symmetry breaking.[464] Fig. 29.2 implies the following difficulty: if we compute the partition function of a system as usual

$$Z = \sum e^{-\beta H}, \tag{29.4}$$

because the sum is over all the possible microscopic states, the resultant Z or the free energy of the system is completely symmetric, that is, its symmetry group is identical to that of the microscopic Hamiltonian. This statement is true if the system is finite, because the sum is a finite sum. Thus, taking the thermodynamic limit is absolutely needed to make a rational and simple framework to understand spontaneous symmetry breaking.

29.10 What actually selects a particular symmetry broken state?

When the intrinsic symmetry is broken, how is a particular phase selected in the real world? This is selected by extremely small fortuitous external effects or even without such effects by intrinsic thermal fluctuations. If there is a weak external field (stray field), the system would react very sensitively to it. Therefore, if one wishes to study a particular phase with the aid of statistical mechanics an appropriate weak field conjugate to the order parameter is introduced to the system Hamiltonian to select the phase. After computing its thermodynamic limit, the field is set to zero. This limit must be performed after the thermodynamic limit; if performed before the thermodynamic limit, the symmetry breaking field effect disappears. Symmetry breaking means that the thermodynamic limit and the conjugate-field zero limit are not commutative.

[463] About this section, a strongly recommended reference is: P. W. Anderson, *Basic Notions of Condensed Matter Physics* (Westview Press 1984, 1997), Chapter 2.

[464] To state more practically, the state with a broken symmetry has a life time. For example, for a very small crystal, thermal fluctuation could spontaneously rearrange the crystal axes. Needless to say, if a crystal is not very small such fluctuations occur only very rarely. The agreement of its behavior to the behavior in the thermodynamic limit is practically perfect, because the life-time of a given orientation is very long. However, mathematically, or theoretically, it is still not a true equilibrium state, so thermodynamic limit is taken.

30 First order phase transition

Summary
∗ How the first order phase transition becomes possible is explained.
∗ Even if phase transition occurs, the ensemble equivalence of statistical mechanics holds. That is, to study thermodynamics even with singularities, we can use any convenient statistical ensemble we like.

Key words
metastable state, unstable state, nucleation, spinodal decomposition

What you should be able to do
∗ Get familiar with the use of bifurcation diagram to understand phase transitions
Clearly recognize that E is once continuously differentiable with respect to S, V and other work coordinates.
∗ You must be able to illustrate why ensemble equivalence is all right.

30.1 First order phase transition example: nematic-isotropic liquid crystal transition

As already discussed briefly, in the case of liquid crystals, the ordering and volume change are coupled, and isotropic liquid-nematic liquid phase transition is (weakly) first order. As has already been mentioned, liquid crystal consists of slender molecules, which orient in the random directions at higher temperatures but tend to align at lower temperatures. This ordered phase is called the nematic liquid crystal phase. If we increase its temperature, due to thermal expansion, the distance between molecules increase slightly. This enhances disorganization of the molecular orientation, weakening molecular interactions further. This in turn enhances volume expansion and enhances disorder. In this way catastrophically order is lost, and a first order phase transition — nematic-isotropic phase transition — happens.

In this case, if there were no volume change, then the order would last more stably and the first order phase transition would be much closer to the second order phase transition or would become a second order phase transition itself.

30.2 Caricature model of first order phase transition

The above observation suggests a caricature model of first order phase transition within the mean field approximation. For a Ising magnet model, suppose that if the (magnitude of the) magnetization per spin m (i.e., the order parameter) becomes smaller, J in (26.23) decreases as illustrated in Fig. 30.1.

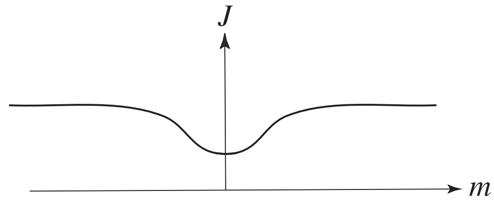

Figure 30.1: Order-dependent coupling constant that induces a first order phase transition. If the order parameter becomes small, the spin-spin interaction becomes weak. In such a model the order would precipitously decrease.

Let us review the mean field approach for a square lattice. Our starting point is the following equation

$$\langle s_0 \rangle = \langle \tanh[\beta J(s_1 + s_2 + s_3 + s_4)] \rangle. \tag{30.1}$$

The naivest mean-field approach is

$$m = \tanh 4\beta J m \tag{30.2}$$

or

$$4\beta J m = 4\beta J \tanh 4\beta J m, \tag{30.3}$$

that is, we must solve

$$x = 4\beta J \tanh x. \tag{30.4}$$

We replace J with the $J(x)$ in Fig. 30.1:

$$x = 4\beta J(x) \tanh x. \tag{30.5}$$

This modification is illustrated in Fig. 30.2.

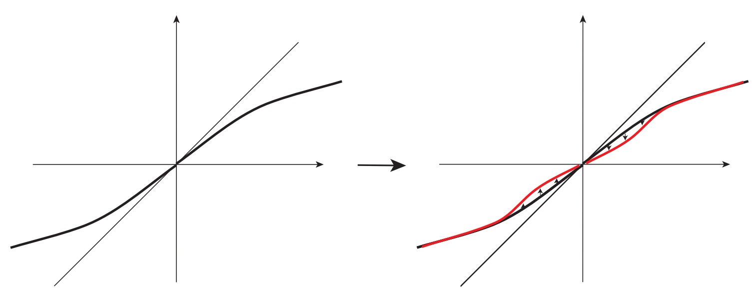

Figure 30.2: Introduction of the m-dependent coupling constant: Replacing J with $J(x)$ illustrated in Fig. 30.1 corresponds to the modification from Left to Right.

30.3 Bifurcations exhibited by the caricature model

Let us study what happens if we lower the temperature. As β increases, the curve in Fig. 30.2 becomes steeper and eventually crosses the diagonal line at three, and then five places as shown in Fig. 30.3; At T_b new non-zero fixed points appear.

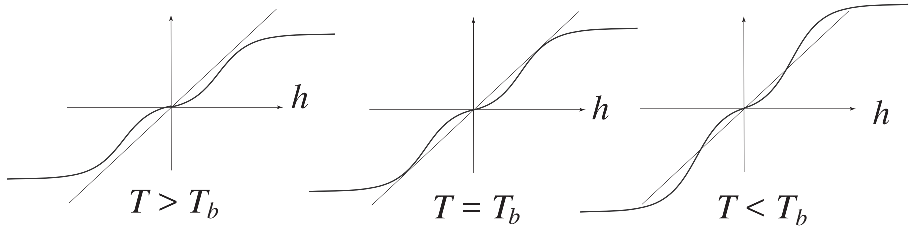

Figure 30.3: A first order phase transition occurs slightly below T_b. To determine the exact phase transition temperature, we need an analogue of Maxwell's rule.

The stability of solutions may be read off from the bifurcation diagram Fig. 30.4. Below T_b there is a branch where m is not zero. The possibility of hysteresis (e.g., supercooling) can also be found. An equilibrium phase transition (or the coexistence of two phases) occurs somewhere the branches corresponding to the coexisting phases are stable. To determine the exact phase transition point requires an analogue of Maxwell's rule, which would choose a transition point (the thick vertical line) somewhere between T_b and T_X in Fig. 30.4.

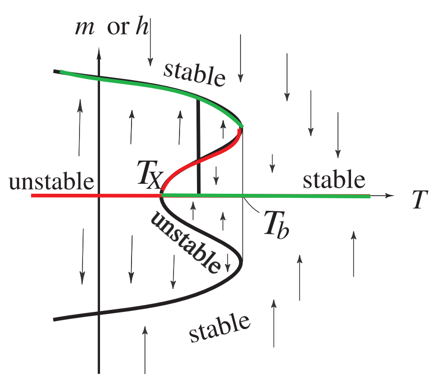

Figure 30.4: The bifurcation diagram for the model that allows a first order phase transition. The vertical arrows denote the evolving direction of perturbation to the fixed point values of m at various temperatures. We can at once see the stability of the fixed points from the exchange of stability occurring at every bifurcation. To determine the exact phase transition temperature (denoted by the thick vertical line in the figure; within the mean-field theory) we need a rule parallel to Maxwell's rule.

30.4 Metastable and unstable states

In Fig. 30.4 the green curves denote stable solutions (roots) and red unstable solutions (in the sense that small perturbations added to the solution grow). Above T_b without any question $m = 0$ disordered phase is the equilibrium phase, and below T_X again without doubt the ordered (i.e., $m \neq 0$) phase is stable. Between T_b and T_X the situation looks complicated. Thermodynamically, we expect there must be a phase transition from $m = 0$ branch to $m \neq 0$ branch somewhere between these two temperatures. The situation is analogous to the van der Waals gas; there should be a counterpart of Maxwell's rule that determines the equilibriums phase transition point.[465] Thus, if we come from the high temperature side slowly to T_X a first order phase transition occurs at the vertical thick line position in Fig. 30.4.

If we rapidly cool the system, it is possible that we can stay on the green line below the phase transition point, which is the supercooled disordered phase, which is *metastable*: it is stable against small perturbations but it is not really globally stable (does not correspond to the global free energy minimum). If we heat the system in an ordered phase (say, $m > 0$ phase) gradually, at the phase transition point order is lost and the $m = 0$ phase appears. However, if we heat the system rapidly, we can continue to stay on the green curve, which is the superheated ordered state, and is metastable.

If we cool the disordered state really rapidly (temperature quench), then we could move the state on the green line left to T_X. This state is unstable, so it rapidly organizes into an ordered phase.

30.5 Phase ordering kinetics: nucleation and spinodal decomposition

How phases changes into each other is an interesting question both pure and materials scientifically, because we could make various textures by arresting the transition process at an appropriate stage. When a metastable state orders, we expect seeds of ordered phases appear in the ocean of disordered phase as nuclei. The formation of nuclei is the rate-determining step. Once nuclei are formed, they grow rapidly and the phase transition is completed.

If a disordered phase is quenched into its unstable state, then immediately ordered domains appear everywhere in the space. However, ordered phases are usually not unique (in the figure we have $\pm$ phases), so initially fine mosaic state is formed. Then, each domain of a particular ordered phase tries to increase its domain.[466]

30.6 First order phase transition due to external field change

[465] Honestly speaking, we must make a mean-field approximation of the free energy and find the equilibrium condition.

[466] If the order parameter is conserved, it is called the *spinodal decomposition*.

Phase transition can occur even if T is constant due to changes of other variables (say, P in the case of fluid; look at the PT diagram). Again, this phase transition can be understood intuitively with the aid of magnets.

Below T_c 2-Ising model is in the up phase or down phase. If a small magnetic field is applied, then the direction of the spins of one phase is stabilized relative to the other phase. This means one phase is no more a true equilibrium state but only a metastable state. Let us discuss the phase transition induced by this change with the aid of a mean field theory. Let us assume J is constant, and we consider (26.22), i.e.,

$$m = \tanh(2d\beta Jm + \beta h). \tag{30.6}$$

Multiplying $2d\beta J$ and then adding βh, we get

$$2d\beta Jm + \beta h = 2d\beta J \tanh(2d\beta Jm + \beta h) + \beta h \tag{30.7}$$

or we have only to study

$$x - \beta h = 2d\beta J \tanh x \tag{30.8}$$

To solve this equation we again use a graphic method (Fig. 30.5, the corresponding bifurcation diagram is in Fig. 30.6):

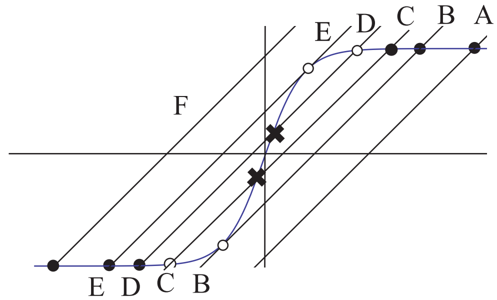

Figure 30.5: Reducing h corresponds to A $\to$ F. If the magnetic filed intensity is positively large (A), the up phase is stable. Between A and B even if h is reduced virtually nothing happens. If h is reduced further a metastable down spin state (white disk on the negative domain) becomes possible. Also there is an unstable state (cross mark). If h is reduced, then the metastable down phase becomes stable, and the stable up phase becomes metastable. Look at the bifurcation diagram in Fig. 30.6 Left.

In Fig. 30.5 A $\to$ E describes the effect of reducing magnetic field favoring the up phase while keeping the temperature $T < T_c$. The corresponding bifurcation diagram (Left of Fig. 30.6) may be easier to understand. Below B once the down phase domain is formed, it is *metastable* (i.e., if it is large enough, it lasts for a very long time). The stability exchanges between the up and down phases at $h = 0$ can be understood intuitively. If h is further reduced (i.e., becomes larger in the opposite direction) at E the up phase becomes *unstable*. If there are remaining domains of the up phase, they disappear quickly.

Suppose the system is initially in the down phase. If an upward magnetic field

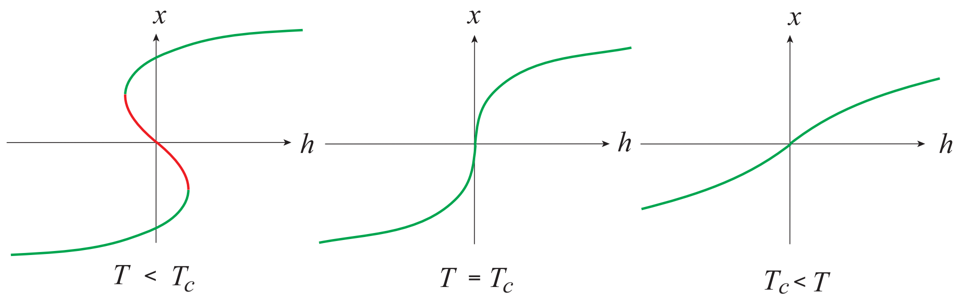

Figure 30.6: Bifurcation diagram for (30.8). Green curves denote locally stable solutions; thermodynamically (i.e., globally) stable or metastable states. Red portion denotes locally unstable solutions; thermodynamically unstable states.

($h > 0$) is applied, it becomes metastable, because the up phase is thermodynamically more stable (its free energy is less than that of the down phase). However, until B is realized, big enough down spin domains persist. If the magnetic field is suddenly increased to A, the down phase becomes unstable and goes into the up phase locally in avalanches.

The picture just explained applies to many first order phase transitions when the intensive variable is changed that is conjugate to a density that jumps at the first order phase transition. As can be guessed from the illustration in Fig. 25.7 for a fluid system (or a binary mixture system), pressure (or chemical potential) may be regarded as the intensive variable to induce first order phase transitions.

We know there is no phase transition above T_c for fluids. This corresponds to the bifurcation diagram on the right of Fig. 30.6. Smoothly, just as the up phase turns into the down phase and vice versa, in the case of the fluid, very high density states may be converted into very low density states through changing the pressure.

30.7 Phase transition and ensemble equivalence

To conclude this introductory course, let us review the meaning of 'ensemble equivalence': you may use any convenient ensemble that can produce a certain thermodynamic potential (generalized free energy) to compute any thermodynamic potential (especially E and S) you wish.

In these lectures it has been stressed that the most fundamental macroscopic description of a macrosystem in equilibrium is in terms of thermodynamic coordinates. The entropy as a function of the thermodynamic coordinates gives the most complete thermodynamic description of the system. In other words, if we know the internal energy as a function of entropy and work coordinates as $E = E(S, V, \cdots)$, we have a complete thermodynamic description of the system. Therefore, it is natural to guess that even if we compute the Helmholtz free energy A, we may not be able to obtain $S = S(E, X)$ in its generality. But, actually, it is not the case: from A we can fully reproduce E. If A is differentiable, of course we know the Gibbs-Helmholtz relation, but no differentiation is needed.[467]

However, since the thermodynamic coordinates are privileged variables, we should lose something. Indeed, we lose some detailed information. Let us see what we can preserve and what we lose when we move from the thermodynamic coordinate system (in terms of $E = E(S, V, \cdots)$) to something else (in the illustration below, to $A = A(T, V, \cdots)$).

30.8 *E* must always be continuously differentiable

In terms of internal energy, a phase transition occurs where the convex function $E = E(S, V, \cdots)$ loses its smoothness. Here 'smoothness' implies the holomorphy as a multivariable function. Since a convex function is continuous, E cannot have any jump. Furthermore, as we see from the Gibbs relation,

$$dE = TdS - PdV + xdX + \cdots, \tag{30.9}$$

so its continuous differentiability must be satisfied in the region of thermodynamic space meaningful to the system.[468] Thus, internal energy must be a C^1 (= continuously differentiable) convex function of entropy and work coordinates. Consequently, the worst singularity is the loss of twice differentiability. For example, the constant volume specific heat can become not definable. We know at the critical point this indeed happens.

30.9 What if *E* is not twice differentiable?

If a C^1 convex function loses twice differentiability, what can happen? Let us look at one variable S of E. Let us assume that work coordinates (such as the volume) are kept constant. Here we pay attention to the case in which the singularity is isolated. We will not discuss more general cases.

Fig. 30.7 illustrates E as a function of S. The slope of this curve is temperature T. Something happening to the second derivative implies that the temperature derivative of S (the constant volume specific heat) has a singularity.

In (A) phase I and phase II have the same extensive variable values (the values of thermodynamic densities) at 'a', so these two phases do not coexist. In this case the order parameter may change continuously. In contrast, in (B) phase I and phase II coexist at 'a' temperature T (= given by the slope of the straight portion between 'a' and 'b'). These two phases are distinct and have different densities. As we already know very well, if some density changes discontinuously at the phase transition, it

[467] It is solely due to the convexity of $-A$ as we discussed briefly long ago.

[468] P and T never jump when we change thermodynamic variables. Why? It is a deep question.

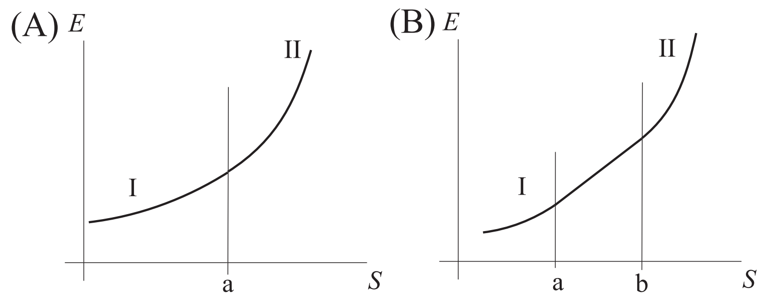

Figure 30.7: When twice differentiability is lost: In (A) it is assumed that the second-order differentiability has a problem at a single point a. In (B) this happens at two points a and b.

is called a first order phase transition. Otherwise, it is generally called a higher order (usually second order) phase transition; if two phases can coexist, the transition is first order. This happens for (B) (however, even if the transition is first order, phases may not coexist; recall the 2D Ising model below T_c). In case (A) a crude sketch of the energy function cannot tell whether the transition is first order or higher.

30.10 What do we lose by Legendre transformation?

To understand the coexistence of two phases under constant temperature discussed above, it is convenient to use the thermodynamic potential one of whose independent variables is temperature, that is, the Helmholtz free energy. It is obtained by the Legendre transformation with respect to entropy. We have already seen a general introduction to convex analysis. Here, let us see some detail when there is a phase transition. We know $A = \min_S[E - ST]$. If this is rewritten in the form standard to convex analysis, it reads $-A = \max_S[ST - E]$ (i.e., $E^* = -A$). Thus, the free energy is convex upward as a function of temperature (In Fig. 30.8 the convex function $-A$ is illustrated).

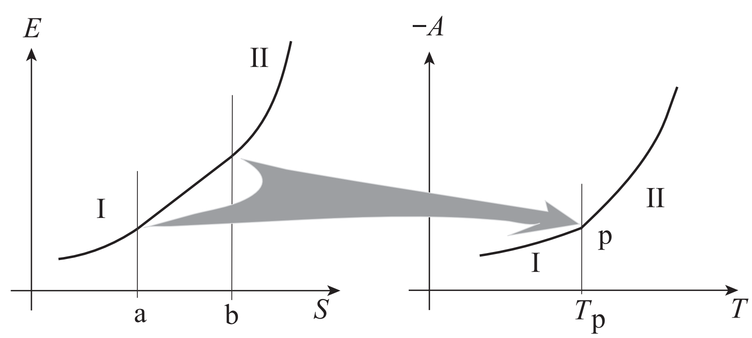

Figure 30.8: Legendre transformation E to A (or $-A$).

Fig. 30.8 **Left** is just the same as Fig. 30.7 (B) and depicts E as a continuously differentiable function of S. E is linear between a and b, and the slopes at a and at b agree with the slope of the linear portion. Phase I occupies left of a, and phase II right of b, and the linear portion describes the coexistence of these phases. The slope of the linear portion is the coexistence temperature T_p, corresponding to the break point p of the free energy graph on the right. All the coexisting phases between a and b are mapped to a point p by the Legendre transformation.

If a first order phase transition happens and if two phases can coexist, there is a 'linear' portion in the graph of internal energy. This is mapped to a single point by the Legendre transformation (Fig. 30.8). As can be seen from this, when two phases coexist, thermodynamic states that can be distinguished by thermodynamic coordinates (intuitively, the states distinguishable by different ratios of two phases) are identified and mapped to a single point by the Legendre transformation. We lose the information about the relative amount of coexisting phases by the Legendre transformation. *However*, it should be noted that from the right graph in Fig. 30.8, we can completely reconstruct internal energy as a function of thermodynamic coordinates by the inverse Legendre transformation $E = \max_T[ST - (-A)]$ (i.e., $E^{**} = E$). This is the implication of the ensemble equivalence.

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