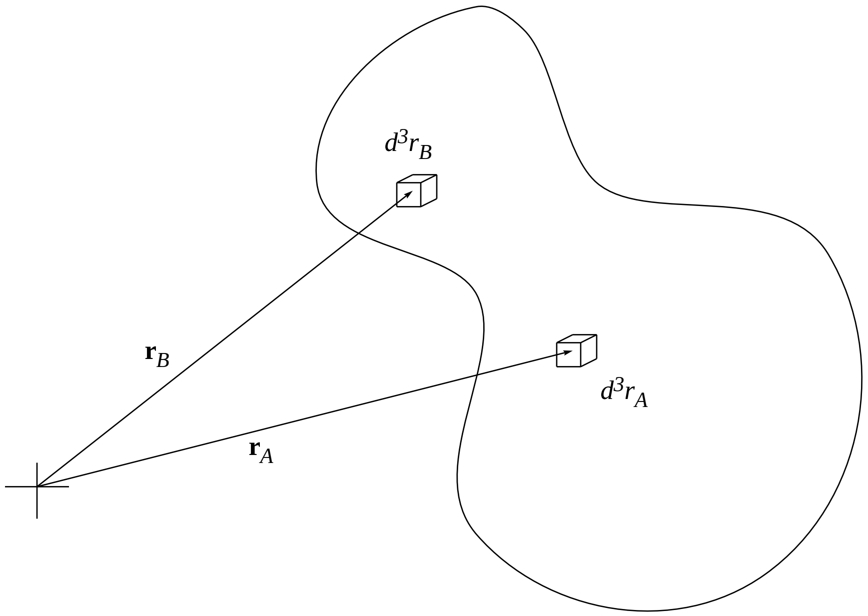

Statistical
Mechanics

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> *Although, as a matter of history, statistical mechanics owes its origin to investigations in thermodynamics, it seems eminently worthy of an independent development, both on account of the elegance and simplicity of its principles, and because it yields new results and places old truths in a new light.*
>
> — J. Willard Gibbs
> *Elementary Principles in Statistical Mechanics*

Contents

Chapter 0

Preface

This is a book about statistical mechanics at the advanced undergraduate level. It assumes a background in classical mechanics through the concept of phase space, in quantum mechanics through the Pauli exclusion principle, and in mathematics through multivariate calculus. (Section 9.2 also assumes that you can can diagonalize a 2×2 matrix.)

The book is in draft form and I would appreciate your comments and suggestions for improvement. In particular, if you have an idea for a new problem, or for a new class of problems, I would appreciate hearing about it. If you are studying statistical mechanics and find that you are asking yourself "Why is. . . true" or "What would happen if. . . were changed?" or "I wish I were more familiar with. . . ", then you have the germ of a new problem. . . so please tell me!

The specific goals of this treatment include:

- To demonstrate the extraordinary range of applicability of the ideas of statistical mechanics. These ideas are applicable to crystals and magnets, superconductors and solutions, surfaces and even bottles of light. I am always irritated by books that apply statistical mechanics only to fluids, or worse, only to the ideal gas.
- To introduce some modern concepts and tools such as correlation functions and computer simulation. While a full treatment awaits the final two chapters, the need for these tools is presented throughout the book.
- To develop qualitative insight as well as analytic and technical skills. Serving this goal are particular sections of text (e.g. section 2.6) and particular problems (e.g. problem 2.4) as well as overall attention to conceptual issues. Also in support of this goal is an attempt to eliminate misconceptions as well as present correct ideas (see appendix I, "Catalog of Misconceptions"). I particularly aim to foster a qualitative understanding of those central concepts, entropy and chemical potential, emphasizing that the latter is no more difficult to understand (and no less!) than temperature.

- To review classical and quantum mechanics, and mathematics, with a special emphasis on difficult points. It is my experience that some topics are so subtle that they are never learned on first exposure, no matter how well they are taught. A good example is the interchange rule for identical particles in quantum mechanics. The rule is so simple and easy to state, yet its consequences are so dramatic and far reaching, that any student will profit from seeing it treated independently in both a quantum mechanics course and a statistical mechanics course.
- To develop problem solving skills. In the sample problems I attempt to teach both strategy and tactics—rather than just show *how* to solve a problem I point out *why* the steps I use are profitable. (See the index entry on "problem solving tips".) Throughout I emphasize that doing a problem involves more than simply reaching an algebraic result: it also involves trying to understand that result and appreciate its significance.

The problems are a central part of this book. (Indeed, I wrote the problems first and designed the book around them.) In any physics course, the problems play a number of roles: they check to make sure you understand the material, they force you to be an active (and thus more effective) participant in your own learning, they expose you to new topics and applications. For this reason, the problems spread over a wide range of difficulty, and I have identified them as such.

- Easy problems (marked with an E) might better be called "questions". You should be able to answer them after just a few moment's thought, usually without the aid of pencil and paper. Their main purpose is to check your understanding or to reinforce conceptual points already made in the text. You should do all the easy problems as you come to them, but they are not usually appropriate for assigned problem sets. The level of these problems is similar to that of problems found on the Graduate Record Examination in physics. . . some of them are even set up in multiple-choice format.
- Intermediate problems (marked with an I) are straightforward applications of the text material. They might better be called "exercises" because they exercise the skills you learned in the text without calling them into stress. They are useful both for checking your understanding and for forcing your participation. Sometimes the detailed derivation of results described in the text is left for such an exercise, with appropriate direction and clues.
- Difficult problems (marked with one to three D's, to indicate the level of difficulty) are more ambitious and usually require the student to pull together knowledge and skills from several different pieces of this book, and from other physics courses as well. Sometimes these problems introduce and develop topics that are not mentioned in the text at all.
- In addition, some easy or intermediate problems are marked with a star (e.g. I*) to indicate that they are "essential problems". These problems are so important to the development of the course material that you *must* do them to have any hope of being able to understand the course material. Essential problems are either relied upon in later text material (e.g. problem 1.2) or else cover important topics that are not covered in the text itself (e.g. problem 3.6). In the latter case, I covered that important

topic through a problem rather than trough text material because I thought it was easier to understand in that form.

I have attempted to make all of the problems at all of the levels interesting in their own right, rather than burdens to complete out of necessity. For that reason, I recommend that you read all of the problems, even the ones that you don't do.

The bibliographies at the end of each chapter are titled "Resources" rather than "Additional Reading" because they include references to computer programs and world wide web pages as well as to books and articles. The former will no doubt go out of date quickly, but to ignore them would be criminal.

Ideas. Perhaps book should come with disk of some public domain programs... or maybe I should set up a web page for the book.

Appendices J and K should appear as rear and front endpapers, respectively.

Chapter 1

The Properties of Matter in Bulk

1.1 What is Statistical Mechanics About?

Statistical mechanics treats matter in bulk. While most branches of physics. . . classical mechanics, atomic physics, quantum mechanics, nuclear physics. . . deal with one or two or a few dozen particles, statistical mechanics deals with, typically, about a mole of particles at one time. A mole is 6.02×10^{23}, considerably larger than a few dozen. Let's compare this to a number often considered large, namely the U.S. national debt. This debt is (2018) about 21 trillion dollars, so the national debt is less than 40 trillionth of a mole of dollars.[1] Even so, a mole of water molecules occupies only 18 ml or about half a fluid ounce. . . it's just a sip.

The huge number of particles present in the systems studied by statistical mechanics means that the traditional questions of physics are impossible to answer. For example, the traditional question of classical mechanics is the time-development problem: Given the positions and velocities of all the particles now, find out what they will be at some future time. This problem has has not been completely solved for three gravitating bodies. . . clearly we will get nowhere asking the same question for 6.02×10^{23} bodies! But in fact, a solution of the time-development problem for a mole of water molecules would be useless even if it could be obtained. Who cares where each molecule is located? No experiment will ever be able to find out. To make progress, we have to ask different questions, question like "How does the pressure change with volume?", "How does the temperature change upon adding particles?", "What is the mean distance between atoms?", or "What is the probability for finding two atoms separated by a given distance?". Thus the challenge of statistical mechanics is two-fold: first find the questions, and only then find the answers.

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[1] In contrast, the Milky Way galaxy contains about 0.3 or 0.6 trillionth of a mole of stars. The entire universe probably contains fewer than a mole of stars.

1.2 Outline of Book

This book begins with a chapter, *the properties of matter in bulk*, that introduces statistical mechanics and shows why it is so fascinating.

It proceeds to discuss the *principles of statistical mechanics*. The goal of this chapter is to motivate and then produce a conceptual definition for that quantity of central importance: entropy. In contrast to, say, quantum mechanics, it is not useful to cast the foundations of statistical mechanics into a mathematically rigorous "postulate, theorem, proof" mold. Our arguments in this chapter are often heuristic and suggestive; "plausibility arguments" rather than proofs.

Once we have defined entropy and know a few of its properties, what can we do with it? The subject of thermodynamics asks what can be discovered about substance by just knowing that entropy exists, without knowing a formula for it. It is one of the most fascinating fields in all of science, because it produces a large number of dramatic and unexpected results based on this single modest assumption. This book's chapter on *thermodynamics* begins begins by developing a concrete operational definition for entropy, in terms of heat and work, to complement the conceptual definition produced in the previous chapter. It goes on to apply entropy to situations as diverse as fluids, phase transitions, and light.

The chapter on *ensembles* returns to issues of principle, and it produces formulas for the entropy that are considerably easier to apply than the one produced in chapter 2. Armed with these easier formulas, the rest of the book uses them in various applications.

The first three applications are to the classic topics of *classical ideal gases*, *quantal ideal gases*, including Fermi-Dirac and Bose-Einstein statistics, and *harmonic lattice vibrations* or phonons.

The subject of ideal gases (i.e. gases of non-interacting particles) is interesting and often useful, but it clearly does not tell the full story. . . for example, the classical ideal gas can never condense into a liquid, so it cannot show any of the fascinating and practical phenomena of phase transitions. The next chapter treats *weakly interacting fluids*, using the tools of perturbation theory and the variational method. The correlation function is introduced as a valuable tool. This is the first time in the book that we ask questions more detailed than the questions of thermodynamics.

Finally we treat *strongly interacting systems and phase transitions.* Here our emphasis is on magnetic systems. Tools include mean field theory, transfer matrices, correlation functions, and computer simulations. Under this heading fall some of the most interesting questions in all of science. . . some answered, many still open.

The first five chapters (up to and including the chapter on *classical ideal gases*) are essential background to the rest of the book, and they must be treated in the sequence presented. The last four chapters are independent and can be treated in any order.

1.3 Fluid Statics

I mentioned above that statistical mechanics asks questions like "How does the pressure change with volume?". But what is pressure? Most people will answer by saying that pressure is force per area:

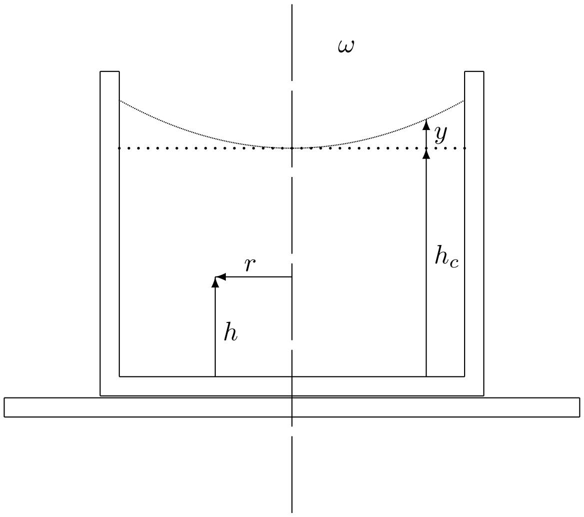
$$\text{pressure} = \frac{\text{force}}{\text{area}}. \tag{1.1}$$

But force is a vector and pressure is a scalar, so how can this formula be correct? The aim of this section is to investigate what this formula means and find out when it is correct.[2]

1.3.1 Problems

1.1 (I) **The rotating water glass**

A cylinder containing a fluid of mass density ρ is placed on the center of a phonograph turntable and rotated with constant angular velocity ω. After some initial sloshing of the fluid, everything calms down to a steady state.



a. The pressure is a function of height h and distance from the axis r. Show that the variation of pressure with radial distance is

$$\frac{\partial p(r,h)}{\partial r} = \rho\omega^2 r, \tag{1.2}$$

while the variation with vertical distance is

$$\frac{\partial p(r,h)}{\partial h} = -\rho g. \tag{1.3}$$

(Where g is the acceleration of gravity.)

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[2] As such, the aim of this section is quite modest. If you want to learn more about the interesting subject of fluid flow, see the "Resources" section of this chapter.

b. The pressure at the surface of the fluid at the center of the cylinder ($r = 0$, $h = h_c$) is of course atmospheric pressure p_a. Integrate the differential equations of part (a.) to show that, at any point in the fluid,

$$p(r, h) = p_a + \tfrac{1}{2}\rho\omega^2 r^2 - \rho g(h - h_c). \tag{1.4}$$

c. Show that the profile of the fluid surface is given by

$$y(r) = \frac{\omega^2}{2g} r^2. \tag{1.5}$$

1.4 Phase Diagrams

Too often, books such as this one degenerate into a study of gases... or even into a study of the ideal gas! Statistical mechanics in fact applies to all sorts of materials: fluids, crystals, magnets, metals, polymers, starstuff, even light. I want to show you some of the enormous variety of behaviors exhibited by matter in bulk, and that can (at least in principle) be explained through statistical mechanics.

Because the axes of a phase diagram are pressure and temperature, the misconception arises that phase diagrams plot pressure as a function of temperature. No. Pressure and temperature are independent variables. For example, volume is a function of pressure and temperature, $V(T, p)$. Instead, the lines on a phase diagram mark the places where there are cliffs in the function $V(T, p)$.

End with the high Tc phase diagram of Amnon Aharony discussed by MEF at Gibbs Symposium. Birgeneau.

Resources

The problems of fluid flow are neglected in the typical American undergraduate physics curriculum. An introduction to these fascinating problems can be found in the chapters on elasticity and fluids in any introductory physics book, such as

F.W. Sears, M.W. Zemansky, and H.D. Young, *University Physics*, fifth edition (Addison-Wesley, Reading, Massachusetts, 1976), chapters 10, 12, and 13, or

D. Halliday, R. Resnick, and J. Walker, *Fundamentals of Physics*, fourth edition (John Wiley, New York, 1993), sections 16–1 to 16–7.

More idiosyncratic treatments are given by

R.P. Feynman, R.B. Leighton, and M. Sands, *The Feynman Lectures on Physics* (Addison-Wesley, Reading, Massachusetts, 1964), chapters II-40 and II-41, and

Jearl Walker *The Flying Circus of Physics* (John Wiley, New York, 1975), chapter 4.

Hansen and McDonald

An excellent description of various states of matter (including liquid crystals, antiferromagnets, superfluids, spatially modulated phases, and more) extending our section on "Phase Diagrams" is

> Michael E. Fisher, "The States of Matter—A Theoretical Perspective" in W.O. Milligan, ed., *Modern Structural Methods* (The Robert A. Welch Foundation, Houston, Texas, 1980) pp. 74–175.

1.5 Additional Problems

1.2 (I*) **Compressibility, expansion coefficient**

The "isothermal compressibility" of a substance is defined as

$$\kappa_T(p,T) = -\frac{1}{V(p,T)}\frac{\partial V(p,T)}{\partial p}, \tag{1.6}$$

where the volume $V(p,T)$ is treated as a function of pressure and temperature.

a. Justify the name "compressibility". If a substance has a large κ_T is it hard or soft? Since "squeeze" is a synonym for "compress", is "squeezeabilty" a synonym for "compressibility"? Why were the negative sign and the factor of $1/V$ included in the definition?

b. The "expansion coefficient" is

$$\beta(p,T) = \frac{1}{V(p,T)}\frac{\partial V(p,T)}{\partial T}. \tag{1.7}$$

In most situations β is positive, but it can be negative. Give one such circumstance.

c. What are κ_T and β in a region of two-phase coexistence (for example, a liquid in equilibrium with its vapor)?

d. Find κ_T and β for an ideal gas, $V(p,T) = Nk_BT/p$.

e. Show that

$$\frac{\partial \kappa_T(p,T)}{\partial T} = -\frac{\partial \beta(p,T)}{\partial p} \tag{1.8}$$

for all substances.

f. Verify this relation for the ideal gas. (Clue: The two expressions are *not* both equal to $-Nk_B/p^2V$.)

1.3 (I*) **Heat capacity as a susceptibility**

Later in this book we will find that the "heat capacity" of a fluid[3] is

$$C_V(T,V,N) = \frac{\partial E(T,V,N)}{\partial T}, \tag{1.9}$$

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[3] Technically, the "heat capacity at constant volume".

where the energy $E(T, V, N)$ is considered as a function of temperature, volume, and number of particles. The heat capacity is easy to measure experimentally and is often the first quantity observed when new regimes of temperature or pressure are explored. (For example, the first sign of superfluid He^3 was an anomalous dip in the measured heat capacity of that substance.)

a. Explain how to measure the heat capacity of a gas given a strong, insulated bottle, a thermometer, a resistor, a voltmeter, an ammeter, and a clock.

b. Near the superfluid transition temperature T_c, the heat capacity of Helium is given by

$$C_V(T) = -A \ln(|T - T_c|/T_c). \tag{1.10}$$

Sketch the heat capacity and the energy as a function of temperature in this region.

c. The heat capacity is one member of a class of thermodynamic quantities called "susceptibilities". Why does it have that name? (Clues: A change in temperature causes a change in energy, but how much of a change? If the heat capacity is relatively high, is the system relatively sensitive or insensitive (i.e. susceptible or insusceptible) to such temperature changes?)

d. Interpret the isothermal compressibility (1.6) as a susceptibility. (Clue: A change in pressure causes a change in volume.)

1.4 (I) **The meaning of "never"**

(This problem is modified from Kittel and Kroemer, *Thermal Physics*, second edition, page 53.)

It has been said[4] that "six monkeys, set to strum unintelligently on typewriters for millions of years, would be bound in time to write all the books in the British Museum". This assertion gives a misleading impression concerning very large numbers.[5] Consider the following situation:

- The quote considers six monkeys. Let's be generous and allow 10^{10} monkeys to work. (About twice the present human population.)
- The quote vaguely mentions "millions of years". The age of the universe is about 14 billion years, so let's allow all of that time, about 10^{18} seconds.
- The quote wants to write out all the books in a very large library. Let's be modest and demand only the production of Shakespeare's *Hamlet*, a work of about 10^5 characters.
- Finally, assume that a monkey can type ten characters per second, and for definiteness, assume a keyboard of 29 characters (letters, comma, period, space... ignore caPitALIzaTion).

a. Show that the probability that a given sequence of 10^5 characters comes out through a random striking of 10^5 keys is

$$\frac{1}{29^{100\,000}} \approx 10^{-146\,240}. \tag{1.11}$$

How did you perform the arithmetic?

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[4] J. Jeans, *Mysterious Universe* (Cambridge University Press, Cambridge, 1930) p. 4.

[5] An insightful discussion of the "monkeys at typewriters" problem, and its implications for biological evolution, is given by Richard Dawkins in his book *The Blind Watchmaker* (Norton, New York, 1987) pp. 43–49.

b. Show that the probability of producing *Hamlet* through the “unintelligent strumming” of 10^{10} monkeys over 10^{18} seconds is about $10^{-146\,211}$, which is small enough to be considered zero for most purposes.

1.5 **Human genetics**

There are about 21,000 genes in the human genome. Suppose that each gene could have any of three possible states (called “alleles”). (For example, if there were a single gene for hair color, the three alleles might be black, brown, and blond.) Then how many genetically distinct possible people would there be? Compare to the current worldwide human population. Estimate how long it would take for every possible genetically distinct individual to be realized. Compare to the age of the universe. Comment on the phrase: “If you’re one in a million, there are 7000 people just like you.”

Chapter 2

Principles of Statistical Mechanics

In a book on classical or quantum mechanics, the chapter corresponding to this one would be titled "Foundations of Classical (or Quantum) Mechanics". Here, I am careful to use the term "principles" rather than "foundations". The term "foundations" suggests rock solid, logically rigorous, hard and fast rules, such as the experimental evidence that undergirds quantum theory. Statistical mechanics lacks such a rigorous undergirding. Remember that our first job in statistical mechanics is to find the questions. Of course, we can ask any question we wish, but we need to find profitable questions. Such a task is not and cannot be one of rigor.

Our treatment here is based on classical mechanics, not quantum mechanics. This approach is easier and more straightforward than the approach through quantum mechanics, and—as you will soon see—there are quite enough difficulties and subtleties in the classical approach! After we investigate the principles of statistical mechanics from a classical perspective, we will outline (in section 4.10) the generalization to quantum mechanics.

2.1 Microscopic Description of a Classical System

This section deals with classical mechanics, not statistical mechanics. But any work that attempts to build macroscopic knowledge from microscopic knowledge—as statistical mechanics does—must begin with a clear and precise statement of what that microscopic knowledge is.

The microscopic description of a physical system has two components: First, "What are the parts of the system? How do they affect each other?", second, "How are those parts arranged?". The first question is answered by giving the *mechanical parameters*[1] of the system. The second is answered by giving its *dynamical variables*. Rather than give formal definitions of these terms, we give two examples.

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[1] The mechanical parameters are sometimes called "parameters in the Hamiltonian", or "external parameters", or "fields".

The earth-moon system. In this system, the mechanical parameters are the mass of the earth, the mass of the moon, and (because the earth and moon interact gravitationally), the gravitational constant G. The dynamical variables are the position and velocity (or momentum) of each body. (Alternative dynamical variables are the position of the center of mass and the separation between the bodies, plus the total momentum of the system and the angular momentum of the two bodies about the center of mass.) You can see from this example that the mechanical parameters give you the knowledge to write down the Hamiltonian for the system, while the dynamical variables are the quantities that change according to the laws governed through that Hamiltonian. The mechanical parameters do not depend upon the initial condition of the system—the dynamical variables do. Often (although not always) the mechanical parameters are time-constant while the dynamical variables are time-varying.

Helium atoms in a box. It is natural to begin the description by saying that there are N atoms, each of mass m. But this innocent beginning is neither obvious nor precisely correct. By saying that the only thing we need to know about each atom is its mass, we are modeling the atoms as point particles. A more precise model would describe the system as N nuclei and $2N$ electrons, but then our treatment would necessarily involve quantum mechanics rather than classical mechanics. Furthermore we would not gain anything by this more precise and more difficult description... we know from experience that under ordinary conditions the nuclei and electrons *do* bind themselves together as atoms. Even the more precise description would not result in unassailable rigor, because the nuclei themselves are made up of nucleons and the nucleons of quarks. In fact, a model-building process similar to this one went on unmentioned even in our treatment of the earth-moon system: When we said that we needed to know only the masses of the two bodies, we were assuming (a good but not perfect assumption) that the distribution of matter through the earth and moon was irrelevant to their motion. We will adopt the model that replaces helium atoms by point particles, but you should keep in mind that it *is* a model.

To continue in our microscopic description, we need to know how the atoms interact with each other. A common model is that atoms interact in a pairwise fashion through some sort of atom-atom interaction potential such as the "Lennard-Jones 6–12 potential":

$$\text{atom-atom potential energy } = -\frac{a}{r^6} + \frac{b}{r^{12}}. \tag{2.1}$$

Here the quantities a and b are mechanical parameters.

An important part of the microscopic description of helium atoms in a box is a description of the box. We must know where the walls are located and how the walls interact with the atoms. There are many different models for the wall-atom interaction: common models include the "hard wall" and "soft wall" potential energy functions sketched in figure 2.1. But even by assuming that the walls and atoms interact through a potential at all we are making a dramatic and easily overlooked assumption: the assumption of a smooth, non-atomic wall. Real box walls are themselves made up of atoms, which can of course move, so there is no fixed "zero-distance" point as implied by the graphs in the figure. The assumption of fixed, smooth walls implies that when an atom collides with the wall its energy is unchanged, while it is quite possible for the atom to gain or loose some energy while colliding with a real, atomic wall. The assumption of a smooth wall is particularly suspicious, and we will find in chapter 4 that it can be relaxed very profitably.

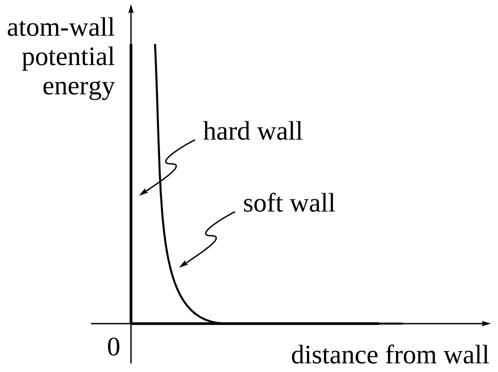

Figure 2.1:

The final step is to recognize that there might be externally electric, magnetic, or gravitational fields that affect the system. If these external fields are present and relevant they will have to be added to the list of mechanical parameters.

At last we are ready to turn to the dynamical variables for the helium-atoms-in-a-box system. These are (mercifully) easy to describe: they are just the position and momentum of each particle, a total of $2N$ 3-dimensional vectors. A shorthand name for this information is "point in phase space". Phase space is an abstract space with one coordinate corresponding to each dynamical variable. Thus in our example the coordinates are the positions and momenta for particle number 1, number 2,… number 9,… and number N:

$$(x_1, y_1, z_1, p_{x,1}, p_{y,1}, p_{z,1}, x_2, y_2, z_2, p_{x,2}, p_{y,2}, p_{z,2}, \ldots x_9, y_9, z_9, p_{x,9}, p_{y,9}, p_{z,9}, \ldots x_N, y_N, z_N, p_{x,N}, p_{y,N}, p_{z,N}). \tag{2.2}$$

For a system of N particles, phase space is $6N$-dimensional. A single point in phase space gives the position *and* momentum of *every* particle in the system.

2.1.1 Time development of a classical system

Given a microscopic description such as either of the two above, what can we do with it? The time development of the system is represented by the motion of a point in phase space. That point will snake through many points in the phase space but all of the points visited will have the same energy.[2] Because *many* points of the given energy will be visited, it is natural to ask whether, in fact, *all* phase space points corresponding to a given energy will eventually be visited by a system started at any one of those points.

It is easy to find systems for which this statement is false, but all such examples seem to be in one way or another atypical. For example, consider two or three or even many millions of non-interacting particles in a

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[2] For the earth-moon model, all the points visited will also have the same total momentum and angular momentum, but this is *not* the case for the helium-in-a-smooth-box model.

hard-walled box, and start them all traveling straight up and down. They will travel straight up and down forever. The points in phase space with identical energy, but with the particles traveling left and right, will never be visited. This example is atypical because if the particles interacted, even slightly, then they would fall out of the "straight up and down" regions of phase space.

Problems

2.1 (Q) **Three-body interactions: microscopic**
Make up a problem involving two charged point particles and a polarizable atom.

2.2 **Mechanical parameters and dynamical variables**
Here is a classical mechanics problem: "A pendulum bob of mass m swings at the end of a cord which runs through a small hole in the ceiling. The cord is being pulled up through the hole so that its length is $\ell(t) = \ell_0 - \alpha t$. At time $t = 0$ the bob is at rest and at angle θ_0. Find the subsequent motion of the bob." *Do not* solve this problem. Instead, list the mechanical parameters and the dynamical variables that appear in it.

2.3 **A Hamiltonian**
Write down the total Hamiltonian of a neutral plasma of N protons and N electrons moving in a rectangular box with interior dimensions of $L_x \times L_y \times L_z$, assuming that i) any proton or electron interacts with the wall material through a potential energy function

$$W(d) = \begin{cases} W_0\left(\dfrac{1}{d^2} - \dfrac{1}{a^2}\right) & \text{for } d < a \\ 0 & \text{otherwise,} \end{cases} \tag{2.3}$$

where d is the (perpendicular) distance of the particle in question from the wall, and ii) the system is subject to a uniform electric field in the $\hat{\mathbf{x}}$ direction of magnitude E. List the mechanical parameters that appear in this Hamiltonian, and distinguish them from the dynamical variables.

2.4 (Q) **For discussion: Mechanical parameters, dynamical variables, and modeling**
List the mechanical parameters and dynamical variables of these systems:

a. Hydrogen molecules enclosed in a sphere.
b. Water molecules in a box.
c. A mixture of hydrogen molecules and helium atoms in a box.

To what extent are you making models as you generate descriptions? To what extent are you making assumptions? (For example, by using non-relativistic classical mechanics.)

2.2 Macroscopic Description of a Large Equilibrium System

The title of this section introduces two new terms… large and equilibrium. A system is large if it contains many particles, but just how large is "large enough"? A few decades ago, physicists dealt with systems of one or two or a dozen particles, or else they dealt with systems with about 10^{23} particles, and the distinction was clear enough. Now that computer chips have such small lines, systems of intermediate size are coming under investigation. (This field carries the romantic name of "mesoscopic physics".) In practical terms, it is usually easy enough to see when the term "large" applies, but there is no rigorous criterion and there have been some surprises in this regard.

A similar situation holds for the term equilibrium. A system is said to be in equilibrium if its macroscopic properties are not changing with time. Thus a cup of tea, recently stirred and with churning, swirling flow, is not at equilibrium, whereas some time later the same cup, sedate and calm, is at equilibrium. But some of the properties of the latter cup *are* changing with time: for example, the height of water molecule number 173 changes rapidly. Of course this is not a macroscopic property, but then there is no rigorous definition of macroscopic *vs.* microscopic properties. Once again there is little difficulty in practice, but a rigorous criterion is wanting and some excellent physicists have been fooled. (For example, a mixture of hydrogen gas and oxygen gas can behave like a gas in equilibrium. But if a spark is introduced, these chemicals will react to form water. The gas mixture is in equilibrium as far as its physical properties are concerned, but not as far as its chemical properties are concerned.)

With these warnings past, we move on to the macroscopic description. As with the microscopic description, it has two parts: the first saying what the system is and the second saying what condition the system is in. For definiteness, we consider the helium-in-a-smooth-box model already introduced.

To say what this system is, we again list mechanical parameters. At first these are the same as for the microscopic description: the number of particles N, the mass of each particle m, and a description of the atom-atom interaction potential (e.g. the Lennard-Jones parameters a and b). But we usually don't need to specify the atom-wall interaction or even the location of the walls… instead we specify only the volume of the container V. The reason for this is not hard to see. If we deal with a large system with typical wall-atom interactions (short range) and typical walls (without intricate projections and recesses) then very few particles will be interacting with the walls at any one instant, so we expect that the details of wall-atom interaction and container shape will be affect only a tiny minority of atoms and hence be irrelevant to macroscopic properties. There are of course exceptions: for example, in a layered substance such as graphite or mica, or one of the high-temperature superconductors, the shape of the container might well be relevant. But in this book we will not often deal with such materials.

Finally, what condition is the system in? (In other words, what corresponds to the dynamical variables in a microscopic description?) Clearly the "point in phase space", giving the positions and momenta of each and every particle in the system, is far too precise to be an acceptable *macroscopic* description. But at the same time it is not acceptable to say we don't care anything about microscopic quantities, because the energy of this system is conserved, so energy will be a feature of both the microscopic and macroscopic descriptions. In fact, for the helium-in-a-smooth-box model, energy is the *only* quantity that is conserved,[3] so it is the only item in the list of macroscopic descriptors. (Other systems, such as the earth-moon system, will have additional conserved quantities, and hence additional items in that list.)

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[3] The momentum and angular momentum of the helium atoms is not conserved, because there are external forces due to the box.

What equilibrium is not

There's a common misconception that at equilibrium, the sample is uniform. This might not be true: A mixture of ice and water at atmospheric pressure and temperature 0 C is at equilibrium but is not uniform. Or, consider a container of air 50 kilometers tall with its base on Earth at sea level: most of the molecules huddle at the bottom of the container, and the top is near-vacuum.

2.5 (Q) **Three-body interactions: macroscopic**
Even though three-body interactions do exist, they can usually be ignored in a macroscopic description. (Just as the wall-atom interaction does exist, but it can usually be ignored in a macroscopic description.) Why?

2.6 (Q,E) **Lost in space**
A collection of N asteroids floats in space far from other gravitating bodies. Model each asteroid as a hard sphere of radius R and mass m. What quantities are required for a microscopic description of this system? For a macroscopic description?

2.3 Fundamental Assumption

Define microstate and macrostate.

There are many microstates corresponding to any given macrostate. The collection of all such microstates is called an "ensemble". (Just as a musical ensemble is a collection of performers.)

Note: An ensemble is a (conceptual) collection of macroscopic systems. It is *not* the collection of atoms that makes up a macroscopic system.

(Terminology: A microstate is also called a "configuration" or a "complexion"... both poor terms. A macrostate is also called a "thermodynamic state". A "corresponding" microstate is sometimes called an "accessible" or a "consistent" microstate.)

A system is said to be "isolated" if no energy goes in or out, and if the mechanical parameters (N, V, etc.) are also fixed. Most of the systems you deal with in classical mechanics classes, for example, are isolated.

The fundamental assumption of statistical mechanics is:

> An isolated system in an equilibrium macrostate has equal probability of being in any of the microstates corresponding to that macrostate.

Conceptual difficulties:

1. What is equilibrium?

2. What is probability? (Any experiment is done on *one* system.)
3. May be false! (Can be motivated by the ergodic hypothesis, but this is just suggestive, and the ergodic hypothesis itself has not been proven and may be false. Cellular automata may violate this assumption. . . but do physical/biological systems? See for example Andrew I. Adamatzky, *Identification of Cellular Automata* (Taylor and Francis, 1995) and the essay review by Normand Mousseau, in *Contemporary Physics*, **37** (1996) 321–323; Stephen Wolfram, *A New Kind of Science* (Wolfram Media, 2002).)

Practical difficulties.

1. Gives way to find average values of microscopic quantities, such as

   $$\langle\text{kinetic energy}\rangle, \langle\text{potential energy}\rangle, \langle\text{height}\rangle,$$

   but not things like temperature and pressure.
2. Based on model. (In particular, infinitely hard smooth walls.)
3. For point particle model, requires infinitely thin sheet in phase space. Work instead with the volume of phase space corresponding to energies from E to $E + \Delta E$, and at the end of the calculation take the limit $\Delta E \to 0$.

To examine these practical difficulties in more detail, consider again the helium-in-a-smooth-box model. Suppose we want to find the number of microstates with energy ranging from E to $E + \Delta E$, in a system with N identical particles in a box of volume V.

Your first answer might be that there are an infinite number of points in phase space satisfying this criterion. This is true but it misses the point: A thimble and a Mack truck both contain an infinite number of points, but the Mack truck carries more because it has more volume. Clearly the microstate count we desire is some sort of measure of phase-space volume. I'll call the region of phase space with energy ranging from E to $E + \Delta E$ by the name $\sigma(E, \Delta E)$, and call its volume

$$\int_{\sigma(E,\Delta E)} d\Gamma. \qquad \text{(Volume in phase space.)} \tag{2.4}$$

However, this volume isn't precisely what we want. Permutation argument for N identical particles. (For a system with N identical particles, there are $N!$ points in phase space corresponding to the same microstate.) A better measure of the microstate count is thus

$$\frac{1}{N!}\int_{\sigma(E,\Delta E)} d\Gamma. \qquad \text{(Delabeled volume in phase space.)} \tag{2.5}$$

There remains one more problem. We desire a count, which is dimensionless, and the above expression gives a phase-space volume, which has the dimensions of

$$(\text{angular momentum})^{3N}.$$

The solution to this problem is straightforward if clunky. Pick a quantity with the dimensions of angular momentum. Any quantity will do, so make an arbitrary choice. Call the quantity h_0. (Clearly, by the time we produce a measurable physical result at the end of a calculation, it had better be independent of our choice of h_0, just as the value of any measurable result in a classical mechanics problem has to be independent of choice of the potential energy zero.) Then define the microstate count as the dimensionless quantity

$$\Omega(E, \Delta E, V, N) = \frac{1}{h_0^{3N}} \frac{1}{N!} \int_{\sigma(E,\Delta E)} d\Gamma. \qquad \text{(Dimensionless, delabeled volume in phase space.)} \tag{2.6}$$

In poker, there are 52 cards in a deck, so the probability of drawing any given card from a shuffled deck is 1/52. The number 52 plays a fundamental role in answering any question concerning probability in poker.

In statistical mechanics, there are Ω microstates corresponding to a macrostate, so the probability of encountering any given microstate is (if the fundamental assumption is correct) $1/\Omega$. The number Ω plays the same fundamental role in statistical mechanics that 52 does in poker.

2.7 **Microstate count for a mixture**
What expression corresponds to (2.6) for a collection of N_{He} Helium atoms and N_{Ar} Argon atoms?

2.4 Statistical Definition of Entropy

Logarithms and dimensions
You cannot take the logarithm of a number with dimensions.
Perhaps you have heard this rule phrased as "you can't take the logarithm of 3.5 meters" or "you can't take the logarithm of five oranges". Why not? A simple argument is "Well, what would be the units of ln(3.5 meters)?" A more elaborate argument follows.
The logarithm function is the inverse of the exponential function:

$$y = \ln(x) \quad \text{means the same as} \quad x = e^y.$$

But remember that

$$x = e^y = 1 + y + \frac{1}{2!}y^2 + \frac{1}{3!}y^3 + \cdots .$$

If y had the dimensions of length, then the expression above would be a meaningless sum of 1 plus a length plus an area plus a volume plus so forth.
You cannot exponentiate a number with dimensions, and you cannot take the logarithm of a number with dimensions.

Additivity (see problem 2.10) . . . don't physically mix.

$$S(E, \Delta E, V, N) = k_B \ln \Omega(E, \Delta E, V, N) \tag{2.7}$$

The constant k_B in this definition is called the "Boltzmann constant". It is clear from the argument that the Boltzmann constant could have been chosen to have any value: 1, π, whatever. For historical reasons, it was chosen to have the value

$$k_B = 1.38 \times 10^{-23} \text{ joule/kelvin.} \tag{2.8}$$

There is no particular physical significance to this number: its logical role is analogous to 2.54 cm/inch or 4.186 joule/calorie. In other words, the origin of this number is not to be sought in nature, but in the history of the definition of the joule and the kelvin. It is a conversion factor.

Problems

2.8 (E) **Accessible regions of phase space**

Suppose that N non-interacting particles, each of mass m, move freely in a one-dimensional box (i.e. an infinite square well). Denote the position coordinates by $x_1, x_2, \ldots, x_N$ and the momentum coordinates by $p_1, p_2, \ldots, p_N$. The box restricts all the positions to fall between $x_i = 0$ and $x_i = L$. The energy of the system lies between E and $E + \Delta E$.

a. If only one particle is present, draw the system's phase space and shade the regions of phase space that are accessible.

b. If two particles are present then phase space is four dimensional, which makes it difficult to draw. Draw separately the part of phase space involving positions and the part involving momenta. Shade the accessible regions of phase space.

c. Suppose two particles are present, and consider the slice of phase space for which $x_1 = (2/3)L$ and p_2 equals some constant called $\tilde{p}_2$. Draw a (carefully labeled) sketch of this slice with the accessible regions shaded.

d. Describe the accessible regions of phase space if N particles are present.

2.9 **Accessible configurations of a spin system**

Consider an isolated system of N spin-$\frac{1}{2}$ atoms in a magnetic field H. The atoms are fixed at their lattice sites and the spins do not interact. Each atom has a magnetic moment m that can point either "up" (parallel to the field H) or "down" (antiparallel to H). A microstate (or configuration) of this system is specified by giving the direction of every spin. An up spin has energy $-mH$, a down spin has energy $+mH$, so a configuration with $n_\uparrow$ up spins and $n_\downarrow$ down spins has energy

$$E = -(n_\uparrow - n_\downarrow)mH. \tag{2.9}$$

This system is called the "ideal paramagnet".

a. Not every energy is possible for this model. What is the maximum possible energy? The minimum? What is the minimum possible non-zero energy difference between configurations?

b. Suppose we know that the system has $n_\uparrow$ up spins and $n_\downarrow$ down spins, but we do not know how these spins are arranged. How many microstates are consistent with this knowledge?

c. The variables $n_\uparrow$ and $n_\downarrow$ cannot be determined directly from macroscopic measurements. Find expressions for $n_\uparrow$ and $n_\downarrow$ in terms of N, E, and H. (Hand a paramagnet sample to an experimentalist and ask her to find the number of up spins. She will just look at you quizzically. But ask her to find the number, the energy, and the magnetic field and she'll be happy to.)

d. Consider the energy range from E to $E + \Delta E$ where ΔE is small compared to NmH but large compared to mH. What is the approximate number of states $\Omega(E, \Delta E, H, N)$ lying in this energy range? Express your answer in a form that does not include the quantities $n_\uparrow$ or $n_\downarrow$.

2.10 **Microstates for a combined system**
System #1 is in a macrostate with three corresponding microstates, labeled A, B, and C. System #2 is in a macrostate with four corresponding microstates, labeled α, β, γ, and δ. How many microstates are accessible to the combined system consisting of system #1 and system #2? List all such microstates.

2.11 (E) **The logarithm**
Suppose that a differentiable function satisfies

$$f(xy) = f(x) + f(y) \tag{2.10}$$

for all positive x and y. Show that

$$f(x) = k \ln(x). \tag{2.11}$$

[Clues: 1) Take derivative with respect to x, then set $x = 1$. 2) Set $y = 1$ in equation (2.10).]

2.5 Entropy of a Monatomic Ideal Gas

So far in this chapter, we have been dealing very abstractly with a very general class of physical systems. We have made a number of assumptions that are reasonable but that we have not tested in practice. It is time to put some flesh on these formal bones. We do so by using our statistical definition of entropy to calculate the entropy of a monatomic ideal gas. (Here "monatomic" means that we approximate the atoms by point particles, and "ideal" means that those particles do not interact with each other. In addition, we assume that the gas contains only one chemical species and that classical mechanics provides an adequate description. Thus a more precise name for our system would be the "pure classical monatomic idea gas", but in this case we wisely prefer brevity to precision.) Working with this concrete example will show us that what we have said is sensible (at least for this system), and guide us in further general developments.

The previous pages have been remarkably free of equations for a physics book. Now is the time to remedy that situation. Before studying this section, you need to know that the volume of a d-dimensional sphere is

$$V_d(r) = \frac{\pi^{d/2}}{(d/2)!} r^d. \tag{2.12}$$

If you don't already know this, then read appendix D, "Volume of a Sphere in d Dimensions", before reading this section. And if you don't know the meaning of $x!$, where x is a half-integer, then you should read appendix C, "Clinic on the Gamma Function", before reading appendix D. Finally, if you don't know Stirling's approximation for the factorial function, namely

$$\ln n! \approx n \ln n - n \qquad \text{for } n \gg 1, \tag{2.13}$$

then you should also read appendix E, "Stirling's Approximation", before reading further. (Do not be discouraged by this long list of prerequisites. This mathematical material is quite interesting in its own right and will be valuable throughout this book.)

We consider a system of N identical, classical, non-interacting point particles, each of mass m. The kinetic energy of this system is

$$\frac{1}{2m}(p_1^2 + p_2^2 + \cdots + p_N^2), \tag{2.14}$$

and the potential energy is

$$\begin{cases} 0 & \text{if all particles are inside container} \\ \infty & \text{otherwise.} \end{cases} \tag{2.15}$$

(One sometimes hears that the ideal gas has "no potential energy". It is true that there is no potential energy due to atom-atom interaction, but, as the above expression makes clear, there is indeed a potential energy term due to atom-wall interaction. Because of the character we assume for that term, however, the numerical value of the potential energy is always zero. Note also that the ideal gas is not the same as the "hard-sphere gas". In the hard-sphere model two atoms have infinite potential energy if they are separated by a distance of twice the hard-sphere radius or less. In the ideal gas model two atoms do not interact. It is permissible even for two atoms to occupy the same location. . . only in the model, of course!)

Now that the system is completely specified, it is time to begin the problem. We wish to calculate the entropy

$$S(E, \Delta E, V, N) = k_B \ln \frac{W(E, \Delta E, V, N)}{N! h_0^{3N}}, \tag{2.16}$$

where the function W represents the volume in phase space corresponding to energies from E to $E + \Delta E$ (i.e. the volume of the region $\sigma(E, \Delta E)$). Before jumping into this (or any other) problem, it is a good idea to list a few properties that we expect the solution will have. . . this list might guide us in performing the calculation; it will certainly allow us to check the answer against the list to see if either our mathematics or our expectations need revision. We expect that:

- We will be able to take the limit as $\Delta E \to 0$ and get sensible results.
- The entropy S will depend on only the volume of the container and not on its shape.
- If we double the size of the system, by doubling E, V, and N, then we will double S. (Additivity.)
- S will depend on h_0 in a trivial, "sea-level" fashion.

The formal expression for the volume of the accessible region of phase space is

$$\begin{aligned} W(E, \Delta E, V, N) &= \text{accessible volume in phase space} && (2.17)\\ &= \int_{\sigma(E,\Delta E)} d\Gamma && (2.18)\\ &= \int dx_1 \int dy_1 \int dz_1 \cdots \int dx_N \int dy_N \int dz_N \cdots \\ &\qquad \int dp_{x,1} \int dp_{y,1} \int dp_{z,1} \cdots \int dp_{x,N} \int dp_{y,N} \int dp_{z,N}. \end{aligned}$$

The complexity of this integral rests entirely in the complexity of the shape of $\sigma(E, \Delta E)$ rather than in the complexity of the integrand, which is just 1. Fortunately the integral factorizes easily into a position part and a momentum part, and the position part factorizes into a product of integrals for each particle (see problem 2.8). For, say, particle number 5, if the particle is inside the container it contributes 0 to the energy, so the total energy might fall between E and $E + \Delta E$ (depending on other factors). But if it is outside the container, then it contributes ∞ to the energy, which *always* exceeds the limit $E + \Delta E$. Thus the integral is just the volume of the container:

$$\int dx_5 \int dy_5 \int dz_5 = V. \tag{2.19}$$

This integral depends on the volume V but is independent of the shape of the container. We will soon see that, as a consequence, the entropy depends on volume but not shape (which is in accord with our expectations).

The integrals over momentum space do not factorize, so we must consider the entire $3N$-dimensional momentum space rather than N separate 3-dimensional spaces. We know that the total potential energy is zero (unless it is infinite), so the energy restriction is taken up entirely by the kinetic energy. Equation (2.14) tells us that the momentum space points with energy E fall on the surface of a sphere of radius $\sqrt{2mE}$. Thus the accessible region in momentum space is a shell with inner radius $\sqrt{2mE}$ and with outer radius $\sqrt{2m(E + \Delta E)}$. (Notice that we are counting *all* the microstates within the accessible region of phase space, not just "typical" microstates there. For example, one microstate to be counted has all of the particles at rest, except for one particle that has all the energy of the system and is heading due west. This is to be counted just as seriously as is the microstate in which the energy is divided up with precise equality among the several particles, and they are traveling in diverse specified directions. Indeed, the system has exactly the same probability of being in either of these two microstates.) Using equation (2.12) for the volume of a $3N$-dimensional sphere, the volume of that shell is

$$\frac{\pi^{3N/2}}{(3N/2)!}\left[(2m(E + \Delta E))^{3N/2} - (2mE)^{3N/2}\right]. \tag{2.20}$$

I prefer to write this result in a form with all the dimensionfull quantities lumped together, namely as

$$\frac{\pi^{3N/2}}{(3N/2)!}(2mE)^{3N/2}\left[\left(1 + \frac{\Delta E}{E}\right)^{3N/2} - 1\right]. \tag{2.21}$$

The quantity in square brackets is dimensionless.

To find the accessible volume of the entire phase space, we multiply the above result by V^N, the result of performing N separate position integrals. Thus

$$W(E,\Delta E,V,N)=\frac{(2\pi mEV^{2/3})^{3N/2}}{(3N/2)!}\left[\left(1+\frac{\Delta E}{E}\right)^{3N/2}-1\right]. \tag{2.22}$$

As promised, W depends upon the variables E, ΔE, V, and N. It also depends upon the "unmentioned" mechanical parameter m. The arguments on page 15 have been vindicated…the phase space volume W depends only upon V and not upon the detailed shape of the container.

At last we can find the entropy! It is

$$S=k_B\ln\frac{W}{N!h_0^{3N}}=k_B\ln\left\{\left(\frac{2\pi mEV^{2/3}}{h_0^2}\right)^{3N/2}\frac{1}{N!(3N/2)!}\left[\left(1+\frac{\Delta E}{E}\right)^{3N/2}-1\right]\right\} \tag{2.23}$$

or

$$\frac{S}{k_B}=\tfrac{3}{2}N\ln\left(\frac{2\pi mEV^{2/3}}{h_0^2}\right)-\ln N!-\ln(\tfrac{3}{2}N)!+\ln\left[\left(1+\frac{\Delta E}{E}\right)^{3N/2}-1\right]. \tag{2.24}$$

How does this expression compare to our list of expectations on page 21?

- If we take the limit $\Delta E\to 0$, the entropy approaches $-\infty$, contrary to expectations.
- The entropy S depends on the volume of the container but not on its shape, in accord with expectations.
- If we double E, V, and N, then S will not exactly double, contrary to expectations.
- The entropy S does depend on h_0 in a "sea-level" fashion, in accord with expectations.

Only two of our four expectations have been satisfied. (And it was obvious even from equation (2.16) that the fourth expectation would be correct.) How could we have gone so far wrong?

The trouble with expression (2.24) for the entropy of a monatomic ideal gas is that it attempts to hold for systems of any size. In justifying the definition of entropy (2.7) (and in writing the list of expectations on page 21) we relied upon the assumption of a "large" system, but in deriving expression (2.24) we never made use of that assumption. On the strength of this revised analysis we realize that our expectations will hold only approximately for finite systems: they will hold to higher and higher accuracy for larger and larger systems, but they will hold exactly only for infinite systems.

There is, of course, a real problem in examining an infinite system. The number of particles is infinite, as is the volume, the energy, and of course the entropy too. Why do we need an equation for the entropy when we already know that it's infinite? Once the problem is stated, the solution is clear: We need an expression not for the total entropy S, but for the entropy per particle $s=S/N$. More formally, we want to examine the system in the "thermodynamic limit", in which

$$N\to\infty \quad \text{in such a way that} \quad \frac{E}{N}\to e,\ \frac{V}{N}\to v,\ \text{and}\ \frac{\Delta E}{N}\to\delta e. \tag{2.25}$$

In this limit we expect that the entropy will grow linearly with system size, i.e. that

$$S(E, \Delta E, V, N) \to N s(e, v, \delta e). \tag{2.26}$$

The quantities written in lower case, such as e, the energy per particle, and v, the volume per particle, play the same role in statistical mechanics as "per capita" quantities do in demographics. (The gross national product of the United States is much larger than the gross national product of Kuwait, but that is just because the United States is much larger than Kuwait. The GNP per capita is higher in Kuwait than in the United States.)

Let's take the thermodynamic limit of expression (2.24) (the entropy of a *finite* system) to find the entropy per particle of an *infinite* monatomic ideal gas. The first thing to do, in preparing to take the thermodynamic limit, is to write V as vN, E as eN, and ΔE as $\delta e\, N$ so that the only size-dependent variable is N. This results in

$$\frac{S}{k_B} = \tfrac{3}{2} N \ln\left(\frac{2\pi m e v^{2/3} N^{5/3}}{h_0^2}\right) - \ln N! - \ln(\tfrac{3}{2}N)! + \ln\left[\left(1 + \frac{\delta e}{e}\right)^{3N/2} - 1\right]. \tag{2.27}$$

Next we use Stirling's approximation,

$$\ln n! \approx n \ln n - n \quad \text{for } n \gg 1, \tag{2.28}$$

to simplify the expressions like $\ln(\frac{3}{2}N)!$ above. Thus for large values of N we have approximately (an approximation that becomes exact as $N \to \infty$)

$$\begin{aligned}
\frac{S}{k_B} &\approx \tfrac{3}{2} N \ln\left(\frac{2\pi m e v^{2/3} N^{5/3}}{h_0^2}\right) - N\ln N + N - (\tfrac{3}{2}N)\ln(\tfrac{3}{2}N) + \tfrac{3}{2}N + \ln\left[\left(1 + \frac{\delta e}{e}\right)^{3N/2} - 1\right] \\
&= \tfrac{3}{2} N \ln\left(\frac{2\pi m e v^{2/3}}{h_0^2}\right) + \tfrac{3}{2}N \ln N^{5/3} - N\ln N + N - \tfrac{3}{2}N\ln(\tfrac{3}{2}N) + \tfrac{3}{2}N + \ln\left[\left(1 + \frac{\delta e}{e}\right)^{3N/2} - 1\right].
\end{aligned}$$

The first term on the right increases linearly with N. The next bunch of terms is

$$\begin{aligned}
& \tfrac{3}{2}N \ln N^{5/3} - N\ln N + N - \tfrac{3}{2}N\ln(\tfrac{3}{2}N) + \tfrac{3}{2}N \\
= \; & \tfrac{5}{2}N\ln N - N\ln N + N - \tfrac{3}{2}N\ln(\tfrac{3}{2}) - \tfrac{3}{2}N\ln(N) + \tfrac{3}{2}N \\
= \; & N\left[\tfrac{5}{2} - \tfrac{3}{2}\ln(\tfrac{3}{2})\right],
\end{aligned}$$

which again increases linearly with N. The final term is, as N grows,

$$\ln\left[\left(1 + \frac{\delta e}{e}\right)^{3N/2} - 1\right] \approx \ln\left(1 + \frac{\delta e}{e}\right)^{3N/2} \tag{2.29}$$

$$= \tfrac{3}{2}N\ln\left(1 + \frac{\delta e}{e}\right). \tag{2.30}$$

This term not only increases linearly with N in the thermodynamic limit, it also vanishes as $\delta e \to 0$! (This is a general principle: One must first take the thermodynamic limit $N \to \infty$, and only then take the "thin phase space limit" $\delta e \equiv \Delta E/N \to 0$.)

Our expectation (2.26) that in the thermodynamic limit the entropy would be proportional to the system size N has been fully vindicated. So has the expectation that we could let $\Delta E \to 0$, although we have seen that we must do so carefully. The end result is that the entropy per particle of the pure classical monatomic ideal gas is

$$s(e, v) = k_B \left[\tfrac{3}{2} \ln \left(\frac{4\pi m e v^{2/3}}{3h_0^2} \right) + \tfrac{5}{2} \right]. \tag{2.31}$$

This is called the “Sackur-Tetrode formula”.[4] It is often written as

$$S(E, V, N) = k_B N \left[\tfrac{3}{2} \ln \left(\frac{4\pi m E V^{2/3}}{3h_0^2 N^{5/3}} \right) + \tfrac{5}{2} \right], \tag{2.32}$$

with the understanding that it should be applied only to very large systems, i.e. to systems effectively at the thermodynamic limit.

Problems

2.12 Entropy of a spin system

Consider again the ideal paramagnet of problem 2.9.

a. Write down an expression for $\ln \Omega(E, \Delta E, H, N)$ as a function of E. Simplify it using Stirling’s approximation for large values of N. (Clue: Be careful to never take the logarithm of a number with dimensions.)

b. Find an expression for the entropy per spin $s(e, H)$ as a function of the energy per spin e and magnetic field H in the thermodynamic limit.

c. Sketch the resulting entropy as a function of the dimensionless quantity $u \equiv e/mH$. Does it take on the proper limits as $e \to \pm mH$? (In your sketch pay special attention to endpoints of the domain, and to any places where the function or its derivative suffers a discontinuity, or a kink, or goes to zero or infinity. In general, it is important that the sketch convey a correct impression of the qualitative character of the function, and less important that it be quantitatively accurate.)

2.13 The approach to the thermodynamic limit

For the classical monatomic ideal gas, plot entropy as a function of particle number using both the “finite size” form (2.24) and the Sackur-Tetrode form (2.32). We will see in problem 4.11 that for a gas at room temperature and atmospheric pressure, it is appropriate to use

$$E V^{2/3}/h_0^2 = (1.66 \times 10^{29}\ \mathrm{kg}^{-1}) N^{5/3}. \tag{2.33}$$

Use the masses of argon and krypton. All other things being equal, is the thermodynamic limit approached more rapidly for atoms of high mass or for atoms of low mass?

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[4] Otto Sackur (1880–1914) was a German physical chemist. Hugo Tetrode (1895–1931) was a Dutch theoretical physicist. Each independently uncovered this equation in 1912.

2.14 **Other energy conventions**

In the text we found the entropy of a monatomic ideal gas by assuming that the potential energy of an atom was zero if the atom were inside the box and infinite if it were outside the box. What happens if we choose a different conventional zero of potential energy so that the potential energy is U for an atom inside the box and infinite for an atom outside the box?

2.15 **Other worlds**

Find the entropy as a function of E, V, and N in the thermodynamic limit for a monatomic ideal gas in a world with arbitrary[5] spatial dimensionality d.

2.16 **Ideal gas mixtures**

Consider a large sample of classical monatomic ideal gas that is a mixture of two components: N_A particles of mass m_A and N_B particles of mass m_B. If $N \equiv N_A + N_B$, show that the entropy is

$$\begin{aligned} S(E,V,N_A,N_B) \quad = \quad & +k_B N_A\left[\tfrac{3}{2}\ln\left(\frac{4\pi m_A E V^{2/3}}{3h_0^2 N^{5/3}}\right)+\tfrac{5}{2}\right] \\ & +k_B N_B\left[\tfrac{3}{2}\ln\left(\frac{4\pi m_B E V^{2/3}}{3h_0^2 N^{5/3}}\right)+\tfrac{5}{2}\right] \\ & -k_B N\left[\left(\frac{N_A}{N}\right)\ln\left(\frac{N_A}{N}\right)+\left(\frac{N_B}{N}\right)\ln\left(\frac{N_B}{N}\right)\right]. \end{aligned} \tag{2.34}$$

(Clue: Use the result of problem D.2.)

2.6 Qualitative Features of Entropy

The concept of entropy is notoriously difficult to grasp. Even the consummate mathematician and physicist Johnny von Neumann claimed that "nobody really knows what entropy is anyway." Although we have an exact and remarkably simple formula for the entropy of a macrostate in terms of the number of corresponding microstates, this simplicity merely hides the subtle characterization needed for a real understanding of the entropy concept. To gain that understanding, we must examine the truly wonderful (in the original meaning of that overused word) surprises that this simple formula presents when applied to real physical systems.

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[5] Why, you wonder, should anyone care about a world that is not three-dimensional? For three reasons: (1) There are important physical approximations of two-dimensional worlds (namely surfaces) and of one-dimensional worlds (namely polymers). (2) The more general formulation might help you in unexpected ways. For example, Ken Wilson and Michael Fisher were trying to understand an important problem concerning critical points. They found that their technique could not solve the problem in three dimensions, but it *could* solve the problem in four dimensions. Then they figured out how to use perturbation theory to slide carefully from four dimensions to three dimensions, thus making their solution relevant to real physical problems. Wilson was awarded the Nobel Prize for this work. This illustrates the third reason, namely you never can tell what will be important and hence: (3) Knowledge is better than ignorance.

2.6.1 Surprises

The monatomic ideal gas

Let us examine the Sackur-Tetrode formula (2.32) qualitatively to see whether it agrees with our understanding of entropy as proportional to the number of microstates corresponding to a given macrostate. If the volume V is increased, then the formula states that the entropy S increases, which certainly seems reasonable: If the volume goes up, then each particle has more places where it can be, so the entropy ought to increase. If the energy E is increased, then S increases, which again seems reasonable: If there is more energy around, then there will be more different ways to split it up and share it among the particles, so we expect the entropy to increase. (Just as there are many more ways to distribute a large booty among a certain number of pirates than there are to distribute a small booty.) But what if the mass m of each particle increases? (Experimentally, one could compare the entropy of, say, argon and krypton under identical conditions. See problem 2.27.) Our formula shows that entropy increases with mass, but is there any way to understand this qualitatively?

In fact, I can produce not just one but two qualitative arguments concerning the dependence of S on m. Unfortunately the two arguments give opposite results! The first relies upon the fact that

$$E = \frac{1}{2m}\sum_i p_i^2, \tag{2.35}$$

so for a given energy E, any individual particle may have a momentum ranging from 0 to $\sqrt{2mE}$. A larger mass implies a wider range of possible momenta, which suggests more microstates and a greater entropy. The second argument relies upon the fact that

$$E = \frac{m}{2}\sum_i v_i^2, \tag{2.36}$$

so for a given energy E, any individual particle may have a speed ranging from 0 to $\sqrt{2E/m}$. A larger mass implies a narrowed range of possible speeds, which suggests fewer microstates and a smaller entropy. The moral is simple: Qualitative arguments can backfire!

> That's the *moral* of the paradox. The *resolution* of the paradox is both deeper and more subtle: It hinges on the fact that the proper home of statistical mechanics is phase space, not configuration space, because Liouville's theorem implies conservation of volume in phase space, not in configuration space. This issue deeply worried the founders of statistical mechanics. See Ludwig Boltzmann, *Vorlesungen über Gastheorie* (J.A. Barth, Leipzig, 1896–98), part II, chapters III and VII [translated into English by Stephen G. Brush: *Lectures on Gas Theory* (University of California Press, Berkeley, 1964)]; J. Willard Gibbs, *Elementary Principles in Statistical Mechanics* (C. Scribner's Sons, New York, 1902), page 3; and Richard C. Tolman, *The Principles of Statistical Mechanics* (Oxford University Press, Oxford, U.K., 1938), pages 45, 51–52.

Freezing water

It is common to hear entropy associated with “disorder,” “smoothness,” or “homogeneity.” How do these associations stand up to the simple situation of a bowl of liquid water placed into a freezer? Initially the water is smooth and homogeneous. As its temperature falls, the sample remains homogeneous until the freezing point is reached. At the freezing temperature the sample is an inhomogeneous mixture of ice and liquid water until all the liquid freezes. Then the sample is homogeneous again as the temperature continues to fall. Thus the sample has passed from homogeneous to inhomogeneous to homogeneous, yet all the while its entropy has decreased. (We will see later that the entropy of a sample always decreases as its temperature falls.)

Suppose the ice is then cracked out of its bowl to make slivers, which are placed back into the bowl and allowed to rest at room temperature until they melt. The jumble of irregular ice slivers certainly seems disordered relative to the homogeneous bowl of meltwater, yet it is the ice slivers that have the lower entropy. The moral here is that the huge number of microscopic degrees of freedom in the meltwater completely overshadow the minute number of macroscopic degrees of freedom in the jumbled ice slivers. But the analogies of entropy to “disorder” or “smoothness” invite us to ignore this moral and concentrate on the system’s gross appearance and nearly irrelevant macroscopic features.

Reentrant phases

When the temperature falls at constant pressure, most pure materials pass from gas to liquid to solid. But the unusual materials called “liquid crystals,” which consist of rod-like molecules, display a larger number of phases. For typical liquid crystals, the high-temperature liquid phase is isotropic, meaning that the positions and the orientations of the molecules are scattered about nearly at random. At lower temperatures, the substance undergoes a transition into the so-called “nematic” phase, in which the molecules tend to orient in the same direction but in which positions are still scattered. At still lower temperatures it passes into the “smectic” phase, in which the molecules orient in the same direction and their positions tend to fall into planes. Finally, at even lower temperatures, the molecules freeze into a conventional solid. The story told so far reinforces the picture of “entropy as disorder,” with lower-temperature (hence lower entropy) phases showing more and more qualitative order.

But not all liquid crystals behave in exactly this fashion. One material called “hexyloxy-cyanobiphenyl” or “6OCB” passes from isotropic liquid to nematic to smectic *and then back to nematic again* as the temperature is lowered. The first transition suggests that the nematic phase is “less orderly” than the smectic phase, while the second transition suggests the opposite!

One might argue that the lower-temperature nematic phase — the so-called “reentrant nematic” — is somehow qualitatively different in character from the higher-temperature nematic, but the experiments summarized in figure 2.2 demonstrate that this is not the case. These experiments involve a similar liquid crystal material called “octyloxy-cyanobiphenyl” or “8OCB” which has no smectic phase at all. Adding a bit of 8OCB into a sample of 6OCB reduces the temperature range over which the smectic phase exists.

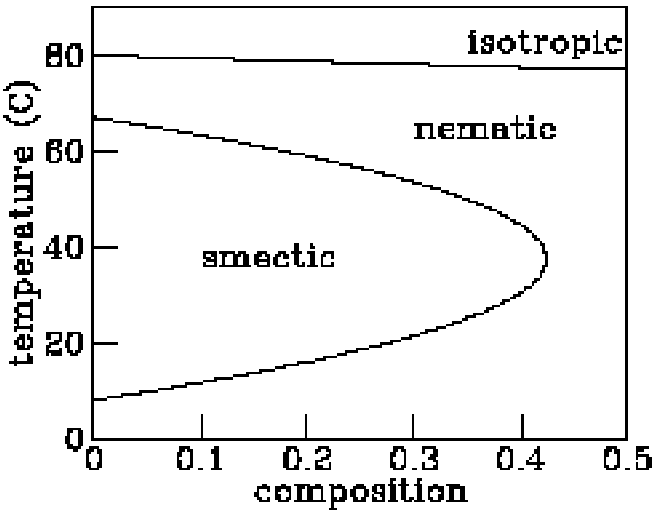

Figure 2.2: Phase diagram of a liquid crystal mixture. The variable "composition" refers to the molecular weight ratio of 6OCB to 8OCB.

Adding a bit more reduces that range further. Finally, addition of enough 8OCB makes the smectic phase disappear altogether. The implication of figure 2.2 is clear: there is no qualitative difference between the usual nematic and the reentrant nematic phases — you can move continuously from one to the other in the temperature–composition phase diagram.

The implication of reentrant phases for entropy is profound: Under some conditions the nematic phase has more entropy than the smectic phase and under other conditions less, while in all cases the nematic is qualitatively less ordered.

Another example of reentrant behavior appears in the phase diagram of the mixture of water and nicotine (see figure 2.3). For a wide range of mixing ratios, this mixture is a homogeneous solution at high temperatures, segregates into water-rich and nicotine-rich phases at moderate temperatures, yet becomes homogeneous again at low temperatures. At mixing ratios closer to pure water or pure nicotine, the mixture is homogeneous at all temperatures. Thus the high-temperature and reentrant homogeneous phases are in fact the same phase. (Reentrant phases are also encountered in type-II superconductors.)

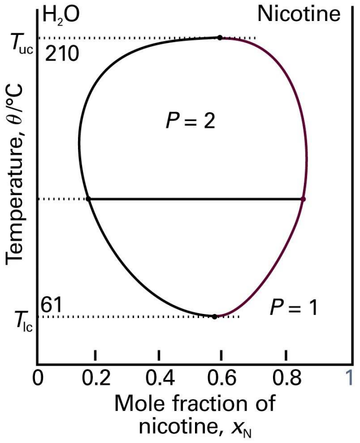

Figure 6-25
Atkins Physical Chemistry, Eighth Edition
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Figure 2.3: Phase diagram for a mixture of water and nicotine.

Rust

According to a common misconception, "The entropy law describes the tendency for all objects to rust, break, fall apart, wear out, and otherwise move to a less ordered state."[6] Or "Entropy tends to make our eyes grow weaker as we age . . . entropy causes iron and other metals to rust."[7] Or "Entropy imposes itself in the form of limitation and in the natural tendency toward confusion and chaos, toward decay and destruction. Entropy is why ice cream melts and people die. It is why cars rust and forests burn. Preponderantly, the second law describes effects that we don't want to see."[8]

At least one error is held in common by these three quotes. Does rusting lead to increased entropy?

The rust reaction is

$$4\,\mathrm{Fe} + 3\,\mathrm{O}_2 \to 2\,\mathrm{Fe}_2\mathrm{O}_3.$$

According to standard tables[9] the entropy (at room temperature 298.15 K and at pressure 10^5 Pa) of one mole of Fe is 27.280 J/K, of one mole of O_2 is 205.147 J/K, and of one mole of $\mathrm{Fe}_2\mathrm{O}_3$ is 87.404 J/K. The entropy of the reactants is 724.561 J/K, the entropy of the products is 174.808 J/K, so the reaction results in an entropy *decrease* of 549.753 J/K.

It is easy to understand why this should be so: gases typically have much greater entropies that solids. And of course this doesn't mean that during rusting, the entropy of the universe decreases: although the en-

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[6] Cutler J. Cleveland and Robert Kaufmann "Fundamental principles of energy," in *Encyclopedia of Earth*, last updated 29 August 2008, http://www.eoearth.org/article/Fundamental_principles_of_energy.

[7] Louis M. Savary, *Teilhard de Chardin: The Divine Milieu Explained* (Paulist Press, Mahwah, NJ, 2007) page 163.

[8] Gilbert L. Wedekind, *Spiritual Entropy* (Xulon Press, Fairfax, VA, 2003) page 68.

[9] Ihsan Barin, *Thermochemical Data of Pure Substances* (VCH Publishers, Weinheim, Germany, 1995) pages 675, 1239, and 702.

tropy of the iron plus oxygen decreases, the entropy of the surroundings increases by even more. Nevertheless, it is clear that rusting itself involves a decrease in entropy, not an increase.

2.6.2 Entropy and the lattice gas

The four examples above should caution us about relying on qualitative arguments concerning entropy. Here is another situation[10] to challenge your intuition: The next page shows two configurations of $13^2 = 169$ squares tossed down on an area that has $35 \times 35 = 1225$ empty spaces, each of which could hold a square. (This system is called the "lattice gas model.") The two configurations were produced by two different computer programs (*Toss1* and *Toss2*) that used different rules to position the squares. (The rules will be presented in due course; for the moment I shall reveal only that both rules employ random numbers.) Which configuration do you think has the greater entropy? Be sure look at the configurations, ponder, and make a guess (no matter how ill-informed) before reading on.

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[10] The argument of this section was invented by Edward M. Purcell and is summarized in Stephen Jay Gould, *Bully for Brontosaurus* (W.W. Norton, New York, 1991), pages 265–268, 260–261. The computer programs mentioned, which work under MS-DOS, are available for free downloading through http://www.oberlin.edu/physics/dstyer/.

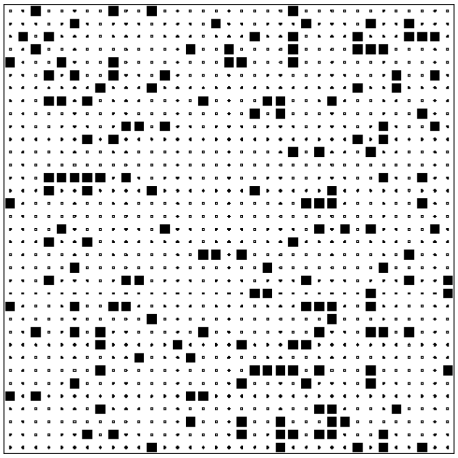

Figure 2.4: A lattice gas configuration generated by the program *Toss1*.

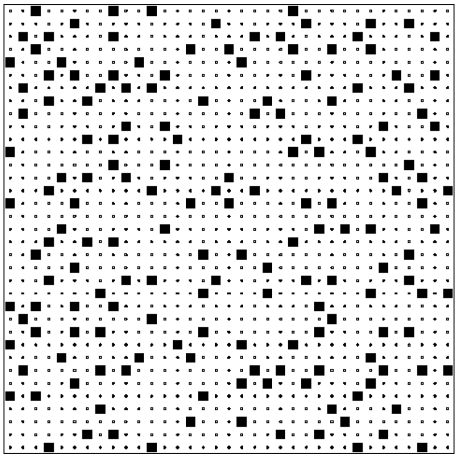

Figure 2.5: A lattice gas configuration generated by the program *Toss2*.

Before analyzing these pictures, I must first confess that my question was very misleading. I asked “Which configuration has the greater entropy?”, but entropy is not defined in terms of a single configuration (a single microstate). Instead, entropy is defined for a macrostate, and is related to the number of microstates that the system can take on and still be classified in that same macrostate. Instead of asking the question I did, I should have pointed out that I had two classes, two pools, of microstates, and that I used my two computer programs to select one member from each of those two pools. The selection was done at random, so the selected configuration should be considered typical. Thus my question should have been “Which configuration was drawn from the larger pool?”, or “Which configuration is typical of the larger class?”. Given this corrected question, you might want to go back and look at the configurations again.

I have asked these questions of a number of people (both students and professionals) and most of them guess that the lower configuration (the output of program *Toss2*), is typical of the class with larger entropy. The lower configuration is smoother, less clumpy. They look at the upper configuration and see patterns, which suggests some orderly process for producing that configuration, while the smoothness of the lower configuration suggests a random, disorderly construction process.

Let me end the suspense and tell you how my computer programs produced the two configurations. The top configuration was produced by tossing $169 = (13)^2$ squares down at random onto an area with $35 \times 35 = 1225$ locations, subject only to the rule that two squares could not fall on the same location. The bottom configuration was produced in exactly the same manner except that there was an additional rule, namely that two squares could not fall on adjacent locations either. Thus the top configuration was drawn from the pool of *all* patterns with 169 squares, while the bottom configuration was drawn from the much smaller pool of patterns with 169 squares *and with no two squares adjacent*. The top configuration is typical of the class with more configurations and hence greater entropy.

Look again at the bottom configuration. You will notice that there are no squares immediately adjacent to any given square. This "nearest neighbor exclusion" rule acts to spread out the squares, giving rise to the smooth appearance that tricks so many into guessing that the bottom configuration is typical of a class with high entropy.

Now look again at the top configuration. You will notice holes and clumps of squares, the inhomogeneities that lead many to guess that it is typical of a small class. But in fact one should *expect* a random configuration to have holes — only a very exceptional configuration is perfectly smooth.[11] This involves the distinction between a *typical* configuration and an *average* configuration. Typical configurations have holes: some have holes in the upper right, some in the middle left, some in the very center. Because the holes fall in various locations, the average configuration — the one produced by adding all the configurations and dividing by the number of configurations — is smooth. The average configuration is actually atypical. (Analogy: A typical person is not of average height. A typical person is somewhat taller or somewhat shorter than average, and very few people are exactly of average height. Any clothing manufacturer that produced only shirts of average size would quickly go bankrupt.) The presence of holes or clumps, therefore, need not be an indication of a pattern or of a design. However, we humans tend to find patterns wherever we look, even when no design is present.[12] In just this way the ancient Greeks looked into the nighttime sky, with stars

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[11] The book *The Second Law* by P.W. Atkins (Scientific American Books, New York, 1984) promotes the idea that entropy is a measure of homogeneity. (This despite the everyday observation of two-phase coexistence.) To buttress this claim, the book presents five illustrations (on pages 72, 74, 75, and 77) of "equilibrium lattice gas configurations." Each configuration has 100 occupied sites on a 40×40 grid. If the occupied sites had been selected at random, then the probability of any site being occupied would be 100/1600, and the probability of any given pair of sites both being occupied would be $1/(16)^2$. The array contains $2 \times 40 \times 39$ adjacent site pairs, so the mean number of occupied adjacent pairs would be $2 \times 40 \times 39 \times (1/16)^2 = 12.19$. The actual numbers of occupied nearest-neighbor pairs in the five illustrations are 7, 3, 7, 4, and 3. A similar calculation shows that the mean number of empty rows or columns in a randomly occupied array is $2 \times 40 \times (15/16)^{40} = 6.05$. The actual numbers for the five illustrations are 5, 5, 4, 4, and 0. I am confident that the sites in these illustrations were not occupied at random, but rather to give the impression of uniformity.

[12] Look again at figure 2.4. Do you see the dog catching a ball in the middle left? Do you see the starship *Enterprise* in the bottom right?

sprinkled about at random, and saw the animals, gods, and heroes that became our constellations.

2.6.3 Entropy and poker

An excellent illustration of the nature of entropy is given by the card game poker. There are many possible hands in poker, some valuable and most less so. For example, the hand

$$A\heartsuit, K\heartsuit, Q\heartsuit, J\heartsuit, 10\heartsuit \tag{2.37}$$

is an example of a royal flush, the most powerful hand in poker. There are only four royal flushes (the royal flush of hearts, of diamonds, of spades, and of clubs) and any poker player who has ever been dealt a royal flush will remember it for the rest of his life.

By contrast, no one can remember whether he has been dealt the hand

$$4\diamondsuit, 3\diamondsuit, J\heartsuit, 2\spadesuit, 7\diamondsuit \tag{2.38}$$

because this hand is a member of an enormous class of not-particularly-valuable poker hands. But the probability of being dealt this hand is *exactly* the same as the probability of being dealt the royal flush of hearts. The reason that one hand is memorable and the other is not has nothing to do with the rarity of that particular hand, it has everything to do with the size of the class of which the hand is a member.

This illustration of the importance of class rather than individual configuration is so powerful and so graphic that I shall call that distinction "the poker paradox".

2.6.4 Conclusion

It is often said that entropy is a measure of the disorder of a system. This qualitative concept has at least three failings: First, it is vague. There is no precise definition of disorder. Some find the abstract paintings of Jackson Pollock to be disorderly; others find them pregnant with structure. Second, it uses an emotionally charged word. Most of us have feelings about disorder (either for it or against it), and the analogy encourages us to transfer that like or dislike from disorder, where our feelings are appropriate, to entropy, where they are not. The most important failing, however, is that the analogy between entropy and disorder invites us to think about a single configuration rather than a class of configurations. In the lattice gas model there are many "orderly" configurations (such as the checkerboard pattern of figure 2.6) that are members of both classes. There are many other "orderly" configurations (such as the solid block pattern of figure 2.7) that are members only of the larger (higher entropy!) class.[13] The poker hand

$$2\clubsuit, 4\diamondsuit, 6\heartsuit, 8\spadesuit, 10\clubsuit$$

is very orderly, but a member of a very large class of nearly worthless poker hands.

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[13] Someone might raise the objection: "Yes, but how many configurations would you have to draw from the pool, on average, before you obtained exactly the special configuration of figure 2.7?" The answer is, "Precisely the same number that you would need to draw, on average, before you obtained exactly the special configuration of figure 2.4." These two configurations are equally special and equally rare.

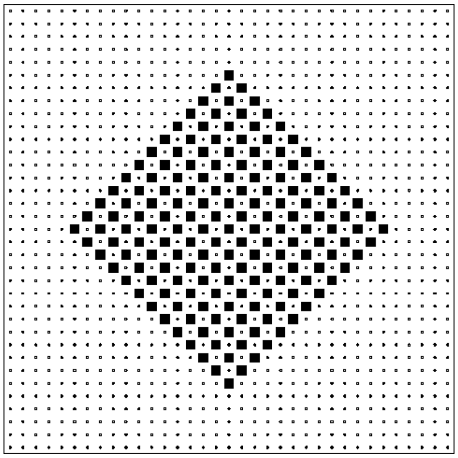

Figure 2.6: An orderly lattice gas configuration that is a member of both the large class and the small class of configurations.

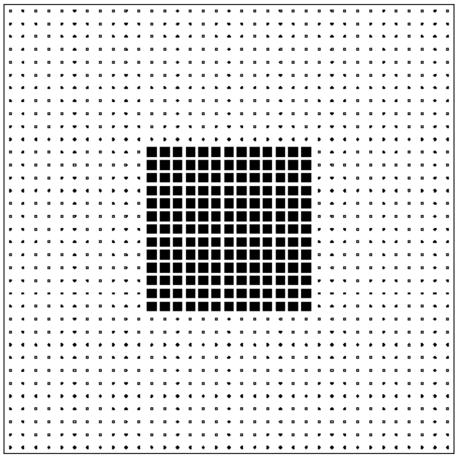

Figure 2.7: An orderly lattice gas configuration that is a member of only the large (high entropy!) class of configurations.

Given the clear need for an intuition concerning entropy, and the appealing but unsatisfactory character of the simile "entropy as disorder," what is to be done? I suggest an additional simile, namely "entropy as freedom," which should be used not by itself but in conjunction with "entropy as disorder."

"Freedom" means a range of possible actions, while "entropy" means a range of possible microstates. If only one microstate corresponds to a certain macrostate, then the system has no freedom to choose its microstate — and it has zero entropy. If you are free to manage your own bedroom, then you may keep it either neat or messy, just as high entropy macrostates encompass both orderly and disorderly microstates. The entropy gives the number of ways that the constituents of a system can be arranged and still be a member of the club (or class). If the class entropy is high, then there are a number of different ways to satisfy the class membership criteria. If the class entropy is low, then that class is very demanding — very restrictive — about which microstates it will admit as members. In short, the advantage of the "entropy as freedom" analogy is that it focuses attention on the variety of microstates corresponding to a macrostate whereas the "entropy as disorder" analogy invites focus on a single microstate.

While "entropy as freedom" has these benefits, it also has two of the drawbacks of "entropy as disorder." First, the term "freedom" is laden with even more emotional baggage than the term "disorder." Second, it is even more vague: political movements from the far right through the center to the extreme left all characterize themselves as "freedom fighters." Is there any way to reap the benefits of this analogy without sinking into the mire of drawbacks?

For maximum advantage, I suggest using *both* of these analogies. The emotions and vaguenesses attached to "freedom" are very different from those attached to "disorder," so using them together tends to cancel out the emotion. A simple sentence like "For macrostates of high entropy, the system has the freedom to chose one of a large number of microstates, and the bulk of such microstates are microscopically disordered" directs attention *away* from glib emotional baggage and *toward* the perspective of "more entropy means more microstates."

But perhaps it is even better to avoid analogies all together. Just think of entropy as describing the number of microstates consistent with the prescribed macrostate. And then you will remember always that entropy applies to a macrostate, i.e. a class of microstates, rather than to an individual microstate.

Problems

2.17 **Entropy of the classical monatomic ideal gas: limits**

a. Every macrostate has at least one corresponding microstate. Use this to show that in all cases $S \geq 0$.

b. Use the Sackur-Tetrode formula (2.31) to find the entropy of the classical monatomic ideal gas in the limit of high density (i.e. volume per particle approaches zero). [This absurd result indicates a breakdown in the approximation of "ideal" non-interacting particles. At high densities, as the particles crowd together, it is no longer possible to ignore the repulsive interactions which are responsible for the "size" of each atom.]

c. What is the entropy of the classical monatomic ideal gas when the energy equals the ground-state energy (i.e. $E \to 0$)? [This absurd result indicates a breakdown in the "classical" approximation. As we will see in chapter 6, quantum mechanics becomes a significant effect at low energies. Historically, this absurdity was one of the first indications that classical mechanics could not be universally true.]

2.18 (Q,E) **The coin toss**

If you flip a coin ten times, you expect on average to get five heads and five tails.

a. The pattern `HHHHHHHHHH` violates this expectation dramatically. What is the probability of obtaining this pattern?

b. The pattern `HTHTHTHTHT` matches this expectation exactly. What is the probability of obtaining this pattern?

c. What is the probability of obtaining the pattern `HTTTHHTTHT`?

d. What is the probability of obtaining a pattern with one tail and nine heads?

2.19 (Q) **Random walks**

You are presented with two pictures that supposedly sketch the progress of a random walker as it moves through space. One was drawn by a computer using a random number generator, the other by a human being. One picture is more or less uniform, the other has some spaces dark with lines and other spaces hardly touched. Which picture was drawn in which way?

2.20 **Poker**

In the game of poker, a hand consists of five cards drawn from a deck of 52 cards. The cards are evenly divided into four suits (hearts, diamonds, clubs, spades).

a. How many hands are there in poker? Explain your reasoning.

b. How many hands are flushes? (That is, all five cards of the same suit.)

c. Harry plays poker every evening, and each evening he is dealt 100 hands. How long must Harry play, on average, before being dealt the hand

$$4\diamondsuit, 3\diamondsuit, J\heartsuit, 2\spadesuit, 7\diamondsuit \tag{2.39}$$

2.7 Using Entropy to Find (Define) Temperature and Pressure

References: Schroeder sections 3.1, 3.4, and 3.5. Reif section 3.3. Kittel and Kroemer pages 30–41.

You will remember that one of the problems with our ensemble approach to statistical mechanics is that, while one readily sees how to calculate ensemble average values of microscopic (mechanical) quantities like the kinetic energy, the potential energy, or the mean particle height, it is hard to see how to calculate the sort of macroscopic (thermodynamic) quantity that we're really more interested in anyway, such as the temperature or pressure. In fact, it is not even clear how we should define these important quantities. Our task in this lecture is to motivate such definitions. Because our arguments are motivations rather than deductions, they will be suggestive rather than definitive. The arguments can be made substantially more solid, but only at the cost of dramatic increase in mathematical complexity. (See David Ruelle's *Statistical Mechanics: Rigorous Results* [Physics QC174.8.R84 1989].) At this stage in your education, you should just accept the arguments and the definitions, realizing that they are not definitive, and go on to learn how to use them. If you're still worried about them a year from now, then that would be a good time to read the more complex arguments in Ruelle's book.

An analogy will help explain the mathematical level of this lecture. Why is the period of the simple harmonic oscillator independent of amplitude? I can give two answers: 1) At larger amplitudes, the particle has more distance to move, but it also moves faster, and these two effects exactly cancel. 2) Solve the problem mathematically, and you'll see that $\omega = \sqrt{k/m}$ which is clearly unaffected by amplitude. The first answer gives more insight into what is going on physically, but it is not definitive. (It does not explain why the two effects cancel exactly rather that have one dominate the other, which is the case for non-parabolic oscillators.) The second argument is bulletproof, but it gives little insight. It is best to use both types of argument in tandem. Unfortunately, the bulletproof arguments for this section are really too elaborate and formal to present here. (In a few weeks I will give you a sample of a rigorous statistical mechanical argument: "The Grand Canonical Ensemble in the Thermodynamic Limit", section 4.8. It is the easiest such argument that I know of, and you will see that it's not very easy at all!)

2.7.1 Rapidly increasing character of the $\Omega(E)$ function

For a monatomic ideal gas ("in the thermodynamic limit") the entropy is

$$S(E,V,N) \equiv k_B \ln \Omega(E,V,N) = k_B N \left[\frac{3}{2} \ln \left(\frac{4\pi m E V^{2/3}}{3h_0^2 N^{5/3}} \right) + \frac{5}{2} \right]. \tag{2.40}$$

Thus $\Omega(E,V,N)$, the number of microstates consistent with the macrostate (or thermodynamic state) specified by E, V, and N, is

$$\Omega(E,V,N) = e^{(5/2)N} \left(\frac{4\pi m E V^{2/3}}{3h_0^2 N^{5/3}} \right)^{(3/2)N}. \tag{2.41}$$

In particular, as a function of energy,

$$\Omega(E) = (\text{constant}) E^{(3/2)N}. \tag{2.42}$$

This is a very rapidly increasing function of E. (The function $f(x) = x^2$ increases more rapidly than $f(x) = x$. The function $f(x) = x^3$ increases more rapidly than $f(x) = x^2$. The function $f(x) = x^{10^{23}}$ increases very rapidly indeed!) Although we have proven this result only for the ideal gas, it is plausible[14] for interacting systems as well: If you throw more energy into a system, there are more ways for the energy to be arranged. (There is an argument to this effect in Reif's section 2.5. The result is not, however, *always* true. . . check out the ideal paramagnet.)

As the particle number N grows larger and larger (approaching the "thermodynamic limit") this increase of Ω with E becomes more and more rapid.

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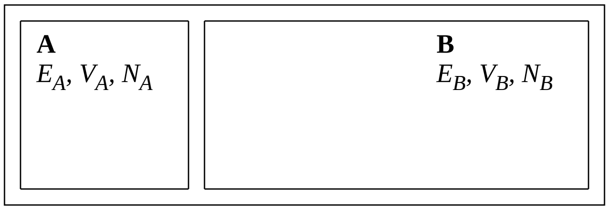
[14] Through the booty argument of page 27.

2.7.2 Two isolated systems

Consider two systems, A and B, enclosed in our perfectly reflecting no-skid walls. System A has energy E_A, volume V_A, and particle number N_A; similarly for system B.



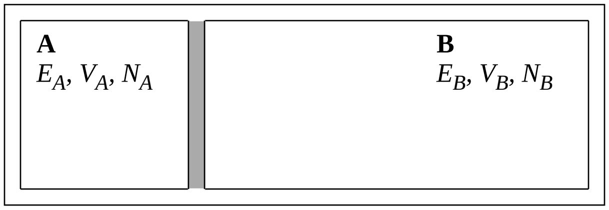
I have drawn the two systems adjacent, but they might as well be miles apart because they can't affect each other through the no-skid walls. No energy can flow from one system to the other because no energy can move from the atoms in the system into the walls. The formal name for such walls is "insulating" or "adiabatic". As we have discussed previously, such perfectly insulating walls do not exist in nature (if nothing else, system A affects system B through the gravitational interaction), but good experimental realizations exist and they are certainly handy conceptually.

The total system consisting of A plus B is characterized by the macroscopic quantities E_A, E_B, V_A, V_B, N_A, and N_B. The number of microstates corresponding to this macrostate is

$$\Omega_T(E_A, E_B, V_A, V_B, N_A, N_B) = \Omega_A(E_A, V_A, N_A)\Omega_B(E_B, V_B, N_B). \tag{2.43}$$

2.7.3 Two systems in thermal contact

Consider the same two systems, A and B, as before, but now allow the wall between them to be an ordinary, energy-permeable wall. Such a wall is called "diathermal". (The walls between the systems and the outside world are still insulating.)



Now the mechanical parameters V_A, V_B, N_A, and N_B still remain constant when the two systems are brought together, but the energies E_A and E_B change. (Of course the total energy $E_T \equiv E_A + E_B$ remains constant as individual energies change.) Such contact between two systems, where energy can flow between the systems but where the mechanical parameters don't change, is called "thermal contact". Once they are in contact, I don't *know* what the distribution of energy between A and B is: It could be that A is in its ground state and all the excess energy is in B, or vice versa, and it could change rapidly from one such extreme to the other. But while I no longer have *knowledge* of the distribution, I do have an *expectation*. My expectation, drawn from daily experience, is that energy will flow from one system to another until E_A and E_B take on some pretty well-defined final equilibrium values. The exact energies will then fluctuate about those equilibrium values, but those fluctuations will be small. And what characterizes this final equilibrium situation? Your first guess might be that the energy on each side should be equal. But no, if a big system were in contact with a small system, then you'd expect more energy to end up in the big system. Then you might think that the energy per particle on each side should be equal, but that's not right either. (Ice and liquid water are in equilibrium at the freezing point, despite the fact that the energy per particle of liquid water is much greater than than of ice.) The correct expectation (known to any cook) is that:

> When two systems A and B are brought into thermal contact, E_A and E_B will change until they reach equilibrium values $E_A^{(e)}$ and $E_B^{(e)}$, with negligible fluctuations, and at equilibrium both systems A and B will have the same "temperature".

This is the qualitative property of temperature that will allow us, in a few moments, to produce a rigorous, quantitative definition. To do so we now look at the process microscopically instead of through our macroscopic expectations.

Once the two systems are in thermal contact the energy of system A could be anything from 0 to the total energy E_T.[15] For any given E_A, the number of accessible microstates of the combined system, A plus B, is $\Omega_A(E_A)\Omega_B(E_T - E_A)$. Thus the total number of microstates of the combined system is

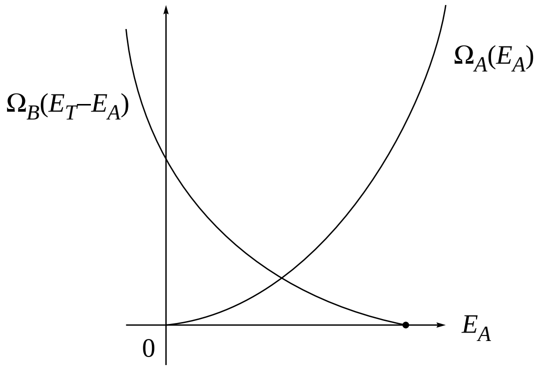
$$\Omega_T(E_T) = \sum_{E_A=0}^{E_T} \Omega_A(E_A)\Omega_B(E_T - E_A). \tag{2.44}$$

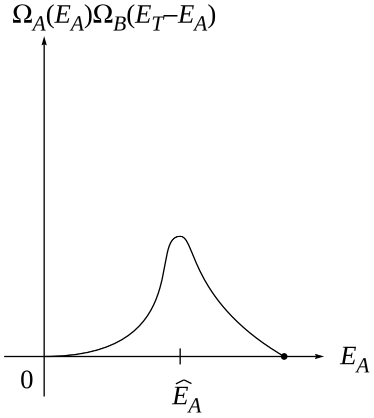
(Please don't tell me the obvious. . . that E_A is a continuous quantity so you have to integrate rather than sum. This is a seat-of-the-pants argument. If you want attention to fine points, look them up in Ruelle's book.)

Let us examine the character of the summand, $\Omega_A(E_A)\Omega_B(E_T - E_A)$, as a function of E_A. The functions $\Omega_A(E_A)$ and $\Omega_B(E_B)$ are both rapidly increasing functions of their arguments, so $\Omega_B(E_T - E_A)$ is a rapidly *decreasing* function of E_A. Thus the product $\Omega_A(E_A)\Omega_B(E_T - E_A)$ will start out near zero, then jump up for a narrow range of E_A values and then fall quickly to near zero again.

---

[15] Here and in the rest of this section, we assume that the ground state energy of both system A and system B has been set by convention to zero.





In conclusion, for most values of E_A the summand nearly vanishes, so most of the contribution to the sum comes from its largest term, which is located at an energy we will call $\hat{E}_A$:

$$\Omega_T(E_T) = \Omega_A(\hat{E}_A)\Omega_B(E_T - \hat{E}_A) + \text{ small change.} \tag{2.45}$$

The sharply peaked character of the product $\Omega_A(E_A)\Omega_B(E_T - E_A)$ becomes more and more pronounced as the thermodynamic limit is approached, so in this limit the "small change" can be ignored. You can see that for macroscopic systems the "microscopically most probable value" $\hat{E}_A$ should be interpreted as the thermodynamic equilibrium value $E_A^{(e)}$.

We locate this value by maximizing

$$\Omega_A(E_A)\Omega_B(E_T - E_A). \tag{2.46}$$

To make life somewhat easier, we will not maximize this function directly but, what is the same thing, maximize its logarithm

$$\begin{aligned} f(E_A) &\equiv \ln[\Omega_A(E_A)\Omega_B(E_T - E_A)] & (2.47)\\ &= \ln\Omega_A(E_A) + \ln\Omega_B(E_T - E_A). & (2.48)\end{aligned}$$

Recognizing the entropy terms we have

$$k_B f(E_A) = S_A(E_A) + S_B(E_T - E_A), \tag{2.49}$$

and differentiation produces

$$\frac{\partial(k_B f(E_A))}{\partial E_A} = \frac{\partial S_A}{\partial E_A} + \frac{\partial S_B}{\partial E_B}\underbrace{\frac{\partial E_B}{\partial E_A}}_{-1}. \tag{2.50}$$

We locate the maximum by setting the above derivative to zero, which tells us that at equilibrium

$$\frac{\partial S_A}{\partial E_A} = \frac{\partial S_B}{\partial E_B}. \tag{2.51}$$

Our expectation is that the temperature will be the same for system A and system B at equilibrium, while our microscopic argument shows that $\partial S/\partial E$ will be the same for system A and system B at equilibrium. May we conclude from this that

$$\frac{\partial S}{\partial E} = \text{Temperature ?} \tag{2.52}$$

No we cannot! All we can conclude is that

$$\frac{\partial S}{\partial E} = \text{invertible function (Temperature)}. \tag{2.53}$$

To find out which invertible function to choose, let us test these ideas for the ideal gas. Using

$$S(E) = k_B \ln C + \tfrac{3}{2} k_B N \ln E + \tfrac{5}{2} k_B N \tag{2.54}$$

we find

$$\frac{\partial S}{\partial E} = \frac{3}{2} k_B \frac{N}{E}, \tag{2.55}$$

so a large value of E results in a small value of $\partial S/\partial E$. Because we are used to thinking of high temperature as related to high energy, it makes sense to *define (absolute) temperature* through

$$\frac{1}{T(E,V,N)} \equiv \frac{\partial S(E,V,N)}{\partial E}. \tag{2.56}$$

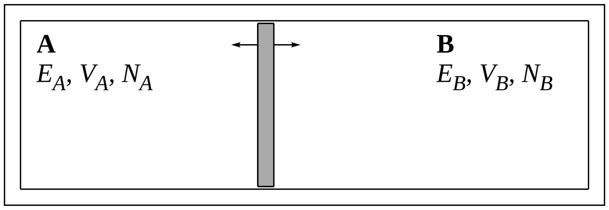
Applying this definition to the ideal gas gives the famous result

$$\frac{E}{N} = \frac{3}{2} k_B T. \tag{2.57}$$

In fact, this result is *too* famous, because people often forget that it applies only to a classical monatomic ideal gas. It is a common misconception that temperature is defined through equation (2.57) rather than through equation (2.56), so that temperature is always proportional to the average energy per particle or to the average kinetic energy per particle. If this misconception were correct, then when ice and water were in equilibrium, the molecules in the ice and the molecules in the water would have the same average energy per particle! In truth, these proportionalities hold exactly only for noninteracting classical point particles.

2.7.4 Two systems in thermal and mechanical contact

Consider the same two systems, A and B, as before, but now allow them to exchange both energy and volume. (The wall between A and B is a sliding, diathermal wall. The walls between the systems and the outside world remains insulating and rigid.)



Now the numbers N_A and N_B remain constant, but the energies E_A and E_B, and the volumes V_A and V_B, do change. Both the total energy $E_T \equiv E_A + E_B$ and the total volume $V_T \equiv V_A + V_B$ remain constant as the individual energies and volumes change. Because of the type of contact, I don't *know* the distribution of energy between A and B, nor do I *know* the distribution of volume between A and B. But just as with energy, I do have an *expectation.*

> When two systems A and B are brought into thermal and mechanical contact, E_A, E_B, V_A, and V_B will change until they reach equilibrium values $E_A^{(e)}$, $E_B^{(e)}$, $V_A^{(e)}$, and $V_B^{(e)}$, with negligible fluctuations, and at equilibrium systems A and B will have the same temperature and the same "pressure".

Just as with energy and temperature, this qualitative expectation will lead us, after a microscopic argument, to a rigorous, quantitative definition of pressure.

> In most cases the system will first reach a preliminary mechanical equilibrium as the wall slides quickly to make the pressure equal on both sides. Then more slowly, as energy seeps from one side to the other, the two temperatures will equilibrate. As the temperatures change the pressure on each side changes, and the wall again slides, more slowly now, to reflect these changes. The argument that follows could be carried out using a sliding insulated wall, instead of a sliding diathermal wall, but in this case energy is still transferred from A to B through mechanical work, so the argument is in fact more complicated that way.

The total number of microstates of the combined system is

$$\Omega_T(E_T, V_T) = \sum_{E_A}\sum_{V_A} \Omega_A(E_A, V_A)\Omega_B(E_T - E_A, V_T - V_A). \tag{2.58}$$

For an ideal gas, $\Omega(V) = CV^N$, but in general we expect $\Omega(V)$ to be a rapidly increasing function of V. (In analogy to the "pirate booty argument", we might call this the "sardine argument.") Just as before, this leads us to expect that the product $\Omega_A(E_A, V_A)\Omega_B(E_T - E_A, V_T - V_A)$ will nearly vanish except in the vicinity of the equilibrium values $E_A = E_A^{(e)}$ and $V_A = V_A^{(e)}$, and that the sum can be approximated by its largest value

$$\Omega_T(E_T, V_T) \approx \Omega_A(E_A^{(e)}, V_A^{(e)})\Omega_B(E_T - E_A^{(e)}, V_T - V_A^{(e)}). \tag{2.59}$$

We locate the equilibrium values by maximizing the product $\Omega_A(E_A, V_A)\Omega_B(E_T - E_A, V_T - V_A)$ with respect to both E_A and V_A. This leads directly to the requirements

$$\frac{\partial S_A}{\partial E_A} = \frac{\partial S_B}{\partial E_B}, \tag{2.60}$$

as before, and

$$\frac{\partial S_A}{\partial V_A} = \frac{\partial S_B}{\partial V_B}. \tag{2.61}$$

We conclude that

$$\frac{\partial S}{\partial V} = \text{invertible function (Pressure, Temperature)}. \tag{2.62}$$

The dimensions of $\partial S/\partial V$ are

$$\left[\frac{\partial S}{\partial V}\right] = \frac{\mathrm{J/K}}{\mathrm{m}^3} \tag{2.63}$$

while those for pressure are

$$[p] = \frac{\mathrm{J}}{\mathrm{m}^3}. \tag{2.64}$$

This motivates us to *define pressure* through

$$\frac{p(E,V,N)}{T(E,V,N)} \equiv \frac{\partial S(E,V,N)}{\partial V}. \tag{2.65}$$

For an ideal gas,

$$S(V) = k_B N[C + \ln V]. \tag{2.66}$$

so

$$\frac{\partial S}{\partial V} = \frac{k_B N}{V} = \frac{p}{T}, \tag{2.67}$$

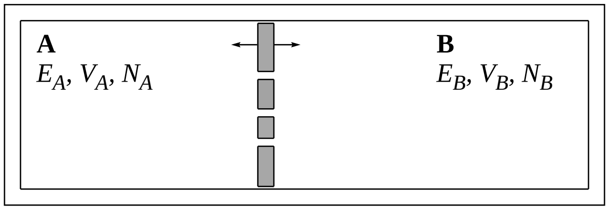
leading to

$$pV = Nk_B T, \tag{2.68}$$

the ideal gas equation of state! (Which is again too famous for its own good. Too many statistical mechanics courses degenerate into "an intensive study of the ideal gas", and it is a shame to waste such a beautiful, powerful, and diverse subject on the study of only one substance, especially since that substance doesn't even exist in nature!)

2.7.5 Two systems that can exchange energy, volume, and particles

We return to the same situation as before, but now the wall between A and B is not only diathermal and sliding, but also allows particles to flow. (Imagine piercing a few tiny holes in the wall.)



The reasoning in this case exactly parallels the reasoning already given two above, so I will not belabor it. I will merely point out that we can now define a new quantity, the *chemical potential* μ, which governs the flow of particles just as temperature governs the flow of energy or pressure governs the flow of volume. It is

$$-\frac{\mu(E,V,N)}{T(E,V,N)} \equiv \frac{\partial S(E,V,N)}{\partial N}. \tag{2.69}$$

2.7.6 The meaning of chemical potential

The upshot of all our definitions is that

$$dS = \frac{1}{T}\,dE + \frac{p}{T}\,dV - \frac{\mu}{T}\,dN. \tag{2.70}$$

What do these definitions mean physically? The first term says that if two systems are brought together so that they can exchange energy but not volume or particle number, then in the system with high temperature the energy will decrease while in the system with low temperature the energy will increase. The second term says that if two systems with the same temperature are brought together so that they can exchange volume but not particle number, then in the system with high pressure the volume will increase while in the system with low pressure the volume will decrease. The third term says that if two systems with the same temperature and pressure are brought together so that they can exchange particles, then in the system with high chemical potential the number will decrease while in the system with low chemical potential the number will increase. In summary:

Exchange of energy?	Exchange of volume?	Exchange of particles?	Result:
Yes.	Prohibited.	Prohibited.	System with high T decreases in E.
Permitted, but $\Delta T = 0$.	Yes.	Prohibited.	System with high p increases in V.
Permitted, but $\Delta T = 0$.	Permitted, but $\Delta p = 0$.	Yes.	System with high μ decreases in N.

Chemists have a great name for chemical potential... they call it "escaping tendency", because particles tend to move from a region of high μ to a region of low μ just as energy tend to move from a region of high T to a region of low T. (G.W. Castellan, *Physical Chemistry*, 2nd edition, Addison-Wesley, Reading, Mass., 1971, section 11–2.) You can see that chemical potential is closely related to density, and indeed for an ideal gas

$$\mu = k_B T \ln(\lambda^3(T)\rho), \tag{2.71}$$

where $\rho = N/V$ is the number density and $\lambda(T)$ is a certain length, dependent upon the temperature, that we will see again (in equation (5.4)).

> Once again, remember that this relation holds *only* for the ideal gas. At the freezing point of water, when ice and liquid water are in equilibrium, the chemical potential is the same for both the solid and the liquid, but the densities clearly are not!

Problems

2.21 (Q) **The location of $E_A^{(e)}$**

In the figure on page 41, does the equilibrium value $E_A^{(e)}$ fall where the two curves $\Omega_A(E_A)$ and $\Omega_B(E_T - E_A)$ cross? If not, is there a geometrical interpretation, in terms of that figure, that does characterize the crossing?

2.22 (Q) **Meaning of temperature and chemical potential**

The energy of a microscopic system can be dissected into its components: the energy due to motion, the energy due to gravitational interaction, the energy due to electromagnetic interaction. Can the temperature be dissected into components in this way? The chemical potential? (Clue: Because the temperature and chemical potential are derivatives of the entropy, ask yourself first whether the entropy can be dissected into components.)

2.23 (E) **Chemical potential of an ideal gas**

a. Show that the chemical potential of a pure classical monatomic ideal gas is

$$\begin{aligned} \mu &= -\frac{3}{2}k_BT\ln\left(\frac{4\pi mEV^{2/3}}{3h_0^2N^{5/3}}\right) && (2.72)\\ &= -k_BT\ln\left[\left(\frac{2\pi mk_BT}{h_0^2}\right)^{3/2}\frac{V}{N}\right]. && (2.73)\end{aligned}$$

b. Show that when the temperature is sufficiently high and the density sufficiently low (and these are, after all, the conditions under which the ideal gas approximation is valid) the chemical potential is negative.

c. Show that

$$\frac{\partial\mu(T,V,N)}{\partial T} = \frac{\mu(T,V,N)}{T} - \frac{3}{2}k_B. \qquad (2.74)$$

At a fixed, low density, does μ increase or decrease with temperature?

2.24 **Ideal paramagnet, take three**

Find the chemical potential $\mu(E,H,N)$ of the ideal paramagnet. (Your answer must *not* be a function of T.) (To work this problem you must have already worked problems 2.9 and 2.12.)

Resources

Percival as CM for chaos and SM. Hilborn on chaos.

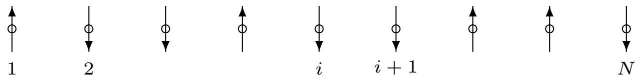
PAS chaos programs, public domain stadium and wedge. CUPS stadium.

Tolman, Ruelle.

2.8 Additional Problems

2.25 **Accessible configurations in another spin system**

The *Ising model* for a ferromagnetic material such as nickel is different from the "ideal paramagnet" discussed in problem 2.9. In this model the spins reside at lattice sites and may point either up or down, but in contrast to the ideal paramagnet model, two adjacent spins *do* interact. Specifically, if two adjacent spins point in the same direction, the pair has energy $-J$. If they point in different directions, the pair has energy $+J$. (In the ferromagnetic situation considered here, $J > 0$.) We consider here a one-dimensional Ising model of N sites with zero external magnetic field.



a. Not every energy is possible for this model. What is the maximum possible energy? The minimum? What is the smallest possible energy spacing between configurations?

b. Consider the energy range from E to $E + \Delta E$ where ΔE is small compared to NJ but large compared to J. What is the approximate number of states $\Omega(E, \Delta E, J, N)$ lying within this energy range?

c. Write down an expression for the entropy $S(E, \Delta E, J, N)$ as a function of E. (Clue: Be careful to never take the logarithm of a number with dimensions.)

d. Take the thermodynamic limit to find the entropy per atom as a function of the energy per atom: $s(e, J)$. (Clue: Use Stirling's approximation.)

e. Check your work by comparing the Ising entropy per spin $s(e, J)$ when the interactions vanish ($J = 0$) to the ideal paramagnet entropy per spin $s(e, H)$ in zero field. (See problem 2.12. Clue: If $J = 0$, then $e = 0$ also. Why?)

General clues: It helps to concentrate not on the status of the *spins* (up or down) but on the status of the *pairs* (alike or different). How many nearest neighbor pairs are there? For each given configuration of pairs, how many corresponding configurations of spins are there?

2.26 **Shake and spin**

Make up a problem involving an ideal paramagnet with atoms free to move around.

2.27 **Entropy as a function of mass**

Use the Sackur-Tetrode formula to find the difference between the entropy of a sample of argon gas and a sample krypton gas under identical conditions. Use the data in Ihsan Barin, *Thermochemical Data of Pure Substances*, third edition (VCH Publishers, New York, 1995) to test this prediction at the temperatures 300 K and 2000 K.

2.28 (Q,D) **For discussion: "The icy cold of outer space"**
Is outer space at a high temperature or a low temperature? Before answering, consider these points:

a. The environment of outer space consists of protons and photons streaming away from the sun. The two systems are virtually uncoupled (do not interact with each other). I'm asking for the temperature of the protons.

b. It was implicitly (perhaps illicitly) assumed in section 2.7.3 that the centers of mass of the two systems in thermal contact were in the same reference frame. This is a general principle: When referring to the temperature of a moving body, we mean the temperature as measured by a thermometer moving along with that body.

c. Remember that in the arguments of section 2.7.3 the two systems could exchange energy *but not particles.*

d. What if we approximated the protons by an ideal gas?

e. Look at the *Handbook of Chemistry and Physics* under index entry "Temperature, Earth's atmosphere".

2.29 (Q,D) **Errors in Reif**
Scan Reif pages 47–61, but don't read them in detail as they are rife with errors. Point out the major error in quantum mechanics made in each of the following passages. (Use a maximum of three sentences per passage.)

a. The examples on pages 48 and 49.

b. The second paragraph on page 57.

c. The first paragraph on page 60.

2.30 **Polymers**
I'd like to think up some problem concerning polymers of fixed length *vs.* polymers of fixed "activity for length". The activity is analogous to chemical potential in that it is a control knob for polymer length. It might render the whole concept more concrete.

Chapter 3

Thermodynamics

3.1 Heat and Work

We've seen how to calculate—at least in principle, although our techniques were primitive and difficult to use—the entropy $S(E, V, N)$. We've also argued ("the booty argument", section 2.7.1) that for most systems entropy will increase monotonically with energy when V and N are fixed. Thus we (can)/(will always be able to) invert the function to find energy as a function of entropy, volume, and number:

$$E(S, V, N). \tag{3.1}$$

Recall that V and N are just stand-ins as representative mechanical parameters.

But how can we measure entropy? Walk into any laboratory and the experimentalist there will say "I have thermometers for measuring temperature. I have resistors, ammeters, and voltmeters, and a I have a procedure for using these instruments to measure the heat flowing into a sample. I have calibers for measuring volume and manometers for measuring pressure. But I have no instrument to measure the number of microstates consistent with a given macrostate." Although we have produced a *conceptual definition* of entropy, we need also an *operational definition* of entropy.

An "operational definition" defines the target word, not in terms of other words, but in terms of a procedure that produces a decision or a numerical value concerning that target word. For example, an operational definition for the word *tuberculosis* is "a disease marked by wasting, cough, fever, and formation of small cheesy lumps in the lungs". In contrast, a conceptual definition is "a disease caused by the bacillus bacterium *Mycobacterium tuberculosis*". The operational definition tells you how to diagnose the disease; the conceptual definition tells you what's going on and suggests a cure. We need to produce an operational definition to go along with our conceptual definition of entropy, and that's the starting point of this chapter.

Heat:

Change in energy with no change in mechanical parameters =
Change in energy due to temperature difference between system and surroundings =
Heat (absorbed by system / brought to system) = Q

Configuration work:

Change in energy due to change in mechanical parameters =
Change in energy when system is wrapped in insulating ("no-skid") walls =
Configuration work (done on system / performed on system) = W_{conf}

Dissipative work:

Change in energy due to non-equilibrium effects =
Change in energy due to, e.g., shaking, stirring, or running current through the system =
Dissipative work (done on system / performed on system) = W_{diss}

It is an empirical fact (sometimes called "the second law of thermodynamics"), that dissipative work always increases the energy of the system. $W_{\text{diss}} \geq 0 \ldots$ equality for "quasistatic changes".

Joule the brewer; story about honeymoon at Cascade de Sallanches.

Caution 1: Many books, especially older ones, use W_{conf} to represent, not the worn done *on* the system, but the work done *by* the system. If we were to say "$W_{\text{conf}} = 7.3$ J", such books would instead say "$W_{\text{conf}} = -7.3$ J".

Caution 2: Heat and work refer to mechanisms for energy *change*, not to types of energy. Do not think that heat goes into a change of kinetic energy (or into "mixed up energy") whereas work goes into a change of potential energy (or into "ordered energy").

Any change due to heating could also be done via dissipative work, and there's no way you could tell the difference. Joule called this "the conversion of work to heat", although that's not correct using the modern definitions of "work" and "heat".

Analogy: You can put money into your bank account through depositing cash or checks, or through an electronic funds transfer. You can take money out of your bank account through these three mechanisms too. But once the money is inside your bank account, you cannot say "This dollar was deposited through cash, while that dollar was deposited through electronic funds transfer." Once they're in your account, you can't distinguish the dollars through the mechanism of entrance. Similarly with energy. You can increase the temperature and energy of a cup of water by putting it near a flame, or by putting it near a high-temperature resistor, or by stirring it rigorously. Given a high-temperature cup of water, there's no way to tell which of these mechanisms was used.

$$\Delta E = Q + W_{\text{conf}} + W_{\text{diss}} \tag{3.2}$$

Problems

3.1 **What is heat?**

Below is an excerpt from a sixth-grade science textbook. Find at least six errors in the excerpt.

> *What is heat?*
>
> You have learned that all matter is made up of atoms. Most of these atoms combine to form molecules. These molecules are always moving—they have kinetic energy. *Heat* is the energy of motion (kinetic energy) of the particles that make up any piece of matter.
>
> The amount of heat a material has depends on how many molecules it has and how fast the molecules are moving. The greater the number of molecules and the faster they move, the greater the number of collisions between them. These collisions produce a large amount of heat.
>
> How is heat measured? Scientists measure heat by using a unit called a *calorie.* A calorie is the amount of heat needed to raise the temperature of 1 gram of 1 water 1 degree centigrade (Celsius).
>
> A gram is a unit used for measuring mass. There are about 454 grams in 1 pound.
>
> *What is temperature?*
>
> The amount of hotness in an object is called its temperature. A thermometer is used to measure temperature in units called degrees. Most thermometers contain a liquid.

3.2 Entropy

$$\begin{aligned} dE &= T\,dS - p\,dV + \mu\,dN \\ &= đQ + đW_{\text{conf}} + đW_{\text{diss}} \\ &\geq đQ + đW_{\text{conf}} \end{aligned}$$

but

$$đW_{\text{conf}} = -p\,dV + \mu\,dN$$

so

$$T\,dS \geq đQ$$

where the equality holds for quasistatic changes.

The operational definition of entropy is that, for a quasistatic change,

$$dS = \frac{đQ}{T}. \tag{3.3}$$

If we walk into a laboratory with *this* definition of entropy, the experimentalist will say "Sure I can find this quantity. I've got thermometers; and I've got resistors, ammeters, and voltmeters, plus a procedure for using them to calculate heat flow."

For any change (perhaps quasistatic, perhaps not)

$$dS \geq \frac{đQ}{T}. \tag{3.4}$$

(The entropy change might be due to heat, might be due to dissipative work, might be due to a combination of the two.)

Configurational entropy vs. thermal entropy

The operational, thermodynamic definition for entropy, equation (3.3), was in fact discovered before the more fundamental, conceptual, statistical definition (2.7) was. Because of this dual definition some people get the misconception that there are two kinds of entropy: the statistical kind ("configurational entropy") and the operational kind ("thermal entropy"). That's false. These are two different ways of looking at the same thing.

3.2 (I) **Ideal gas with variables S and V.**

a. Use equation (2.32) to show that for a sample of monatomic ideal gas with a fixed number of particles, the energy function is

$$E(S,V) = E_0 \left(\frac{V_0}{V}\right)^{2/3} e^{S/S_0}, \tag{3.5}$$

where E_0, V_0, and S_0 are constants with the dimensions of energy, volume, and entropy.

b. Use the formulas

$$T(S,V) = \frac{\partial E(S,V)}{\partial S} \quad \text{and} \quad p(S,V) = -\frac{\partial E(S,V)}{\partial V} \tag{3.6}$$

to find the temperature and pressure functions for this sample.

3.3 (I) **Dependence of heat and work on path**

Suppose the ideal gas sample mentioned in the previous problem undergoes a change from an initial state with volume V_0 and entropy S_0 to a final state with volume $8V_0$ and entropy $(1+5\ln 2)S_0$. There are an infinite number of quasistatic paths that execute this change. For example:

A First increase the entropy from $S = S_0$ to $S = (1+5\ln 2)S_0$, keeping the volume fixed at $V = V_0$, then expand from $V = V_0$ to $V = 8V_0$, keeping the entropy fixed at $S = (1+5\ln 2)S_0$.

B Increase the volume and entropy simultaneously along the path

$$S(V) = S_0\left[\frac{5}{3}\ln\left(\frac{V}{V_0}\right)+1\right]. \tag{3.7}$$

C First expand from $V = V_0$ to $V = 8V_0$, keeping the entropy fixed at $S = S_0$, then increase the entropy from $S = S_0$ to $S = (1+5\ln 2)S_0$, keeping the volume fixed at $V = 8V_0$.

Each path has the same change in volume, entropy, and energy, but each will have a different heat and work. (Remember that each path is quasistatic.)

a. Calculate the heat absorbed by the sample and the work done on the sample for each of these three paths.

b. Find the sum $Q+W$ for each of these three paths.

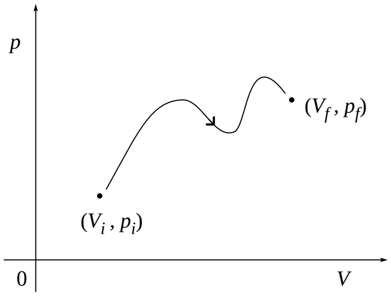
c. A fourth path from the initial to the final state involves a non-quasistatic change and the absorption of heat $Q = 3E_0$. What work is done on the sample during this change?

(In making up this problem I choose somewhat peculiar initial and final states, and connecting paths, so that the above quantities could be calculated analytically. Despite these peculiarities the principle illustrated by the problem should be clear: heat and work depend upon path, but their difference the energy change does not.)

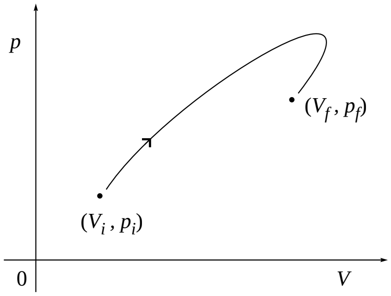
3.4 (I*) **Work in terms of p and V**

We have so far considered work and heat in a fluid system specified by the variables S, V, and N, and have often assumed that N is constant. Another way of specifying such a system is through the variables p (pressure) and V. This problem considers quasistatic processes described as paths in the (p, V) plane.

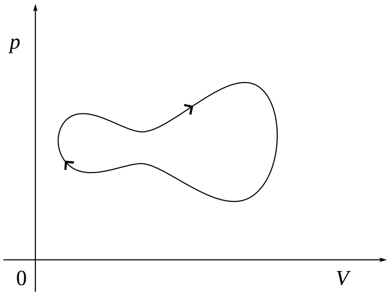
a. Show that the work done on the system in changing quasistatically from the initial state (V_i, p_i) to the final state (V_f, p_f) along the path shown in the figure below is the negative of the area under the curve. What is the work done if the path is traversed in the opposite direction?



b. What is the work done on the system through the same change along the path below?



c. Finally, what is the work done on the system if it comes back to its starting point as in the cycle shown below? What if the cycle is instead executed in a counterclockwise fashion?



3.5 (I) **Fluid work**

In a quasistatic, adiabatic process, a sample of gas expands from $V_i = 1\text{ m}^3$ to $V_f = 8\text{ m}^3$, while the pressure drops from $p_i = 32$ Pa to $p_f = 1$ Pa. It is observed that during this process the pressure and volume are related by

$$pV^\gamma = \text{ constant}, \tag{3.8}$$

where the constant γ is $\frac{5}{3}$. Of course, this is not the only process leading from this particular initial state to that particular final state. Find the total work done on the system and heat absorbed by the system in each of the following quasistatic processes, all of which connect the same two thermodynamic states.

a. The adiabatic process described above.
b. At constant pressure, the gas expands from V_i to V_f. (Heat must be added to the system during this expansion in order to keep the pressure constant.) Then at constant volume, the the pressure is reduced from p_i to p_f. (Heat must be extracted from the system during this stage of the process.)
c. The volume is increased and heat is supplied at just the right rate to make the pressure decrease linearly with volume.
d. As in part (b.) but with the two steps performed in opposite order.

3.3 Heat Engines

The emphasis of this course is on the properties of matter. This section is independent of the properties of matter! It is included because:

1. historically important
2. expected coverage (e.g. for GRE)
3. important from an applications and engineering standpoint (See, for example, "Hurricane heat engines" by H.E. Willoughby, *Nature* **401** (14 October 1999) 649–650. Or "A thermoacoustic Stirling heat engine" by S. Backhaus and G.W. Swift, *Nature* **399** (27 May 1999) 335–338, and "Traveling-wave thermoacoustic electric generator," by S. Backhaus, E. Tward, and M. Petach, *Applied Physics Letters* **85** (9 August 2004) 1085–1087, concerning an engine that might replace nuclear thermal power sources in deep space missions.)
4. fascinating

This section follows Reif sections 3.1 and 5.11.

Heat engines do not include electrical and chemical engines (such as muscles). The Carnot theorems don't apply to them. The name Carnot is French, so it is pronounced "Car-no" rather than "Car-not".

Problems

3.6 (I*) **The Carnot cycle**

Describe the Carnot cycle. Always means quasistatic. Take this order:

1. Expand at constant $T = T_1$ from A to B, decreasing pressure. Absorb heat q_1 from high-temperature heat bath.
2. Expand even more, adibatically, from B to C, decreasing pressure still more.
3. Contract at constant $T = T_2$ from C to D, increasing pressure. Expel heat q_2 into low-temperature heat bath.
4. Contract even more, adibatically, increasing pressure still more, until system comes back to original state A.

3.7 (E) **The Carnot cycle**

(This problem is stolen from a GRE Physics test.)

The p-V diagram for a quasistatic Carnot cycle is shown in Reif page 189. Legs bc and da represent isotherms, while ab and cd represent adiabats. A system is carried through the cycle abcd, taking in heat q_1 from the hot reservoir at temperature T_1 and releasing heat q_2 to the cold reservoir at temperature T_2. Which of the following statements is false?

a. $q_1/T_1 = q_2/T_2$.

b. The entropy of the hot reservoir decreases.

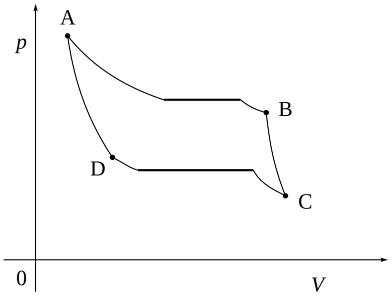
c. The entropy of the system increases.

d. The work w is equal to the net heat absorbed, $q_1 - q_2$.

e. The efficiency of the cycle is independent of the working substance.

3.8 (D) **The liquifying Carnot cycle**

Suppose a quasistatic Carnot cycle is executed with a working substance of steam rather than ideal gas. Furthermore, suppose that the cycle straddles the liquid-vapor coexistence curve, so that when the working substance is at a high volume and low pressure it is steam, but when it is at a low volume and high pressure it is liquid water. Then the (p, V) diagram of the cycle resembles the following:



a. Explain the significance of the flat portions of the isotherms.

b. Of the four points A, B, C, and D, which represent liquid and which represent gas?

c. Below is a list of properties of the Carnot cycle executed with an ideal gas. Which of these properties remain true for our liquifying Carnot cycle?
   i. The efficiency is $1 - T_1/T_2$.
   ii. The adiabats BC and DA are described by $pV^\gamma =$ constant.
   iii. The work done is the area enclosed by the cycle.
   iv. More.

3.4 Multivariate Calculus

What is a section on multivariate calculus doing in a physics book. . . particularly a physics book which assumes that you already know multivariate calculus? The answer is that you went through your multivariate calculus course learning one topic after another, and there are some subtle topics that you covered early in the course that really couldn't be properly understood until you had covered other topics that came later in the course. (This is *not* the fault of your teacher in multivariate calculus, because the later topics could not be understood *at all* without an exposure to the earlier topics.) This section goes back and investigates five subtle points from multivariate calculus to make sure they don't trip you when they are applied to thermodynamics.

3.4.1 What is a partial derivative?

Given a function $f(x, y, z)$, what is the meaning of $\partial f/\partial y$? Many will answer that

$$\frac{\partial f}{\partial y} \text{ is the change of } f \text{ with } y \text{ while everything else is held constant.} \tag{3.9}$$

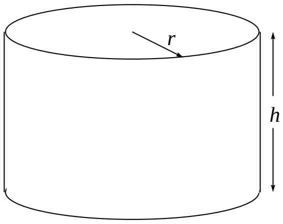
This answer is WRONG! If f changes, then f^2 changes, and $\sin(f)$ changes, and so forth, so it can't be that "everything else" is held constant. The proper answer is that

$$\frac{\partial f}{\partial y} \text{ is the change of } f \text{ with } y \text{ while all other variables are held constant.} \tag{3.10}$$

Thus it becomes essential to keep clear which quantities are variables and which are functions. This is not usually hard in the context of mathematics: the functions are f, g, and h while the variables are x, y, and z. But in the context of physics we use symbols like E, V, p, T, and N which suggest the quantities they represent, and it is easy to mix up the functions and the variables.

An illustration from geometry makes this point very well. Consider the set of all right circular cylinders. Each cylinder can be specified uniquely by the variables r, radius, and h, height. If you know r and h for a cylinder you can readily calculate any quantity of interest—such as the area of the top, $T(r, h)$, the area of the side $S(r, h)$, and the volume $V(r, h)$—as shown on the left side of the table below. But this is not the only way to specify each cylinder uniquely. For example, if you know the height and the side area of the cylinder, you may readily calculate the radius and hence find our previous specification. Indeed, the specification through the variables S and h is just as good as the one through the variables r and h, as is shown on the right side of the table below. [There are many other possible specifications (e.g. r and S, or T and V) but these two sets will be sufficient to make our point.]

Describing a Cylinder



variables:		**variables:**	
radius	r	side area	S
height	h	height	h
functions:		**functions:**	
top area	$T(r, h) = \pi r^2$	radius	$r(S, h) = S/2\pi h$
side area	$S(r, h) = 2\pi r h$	top area	$T(S, h) = S^2/4\pi h^2$
volume	$V(r, h) = \pi r^2 h$	volume	$V(S, h) = S^2/4\pi h$

All of this is quite straightforward and ordinary. But now we ask one more question concerning the geometry of cylinders, namely "How does the volume change with height?" The last line of the table presents two formulas for volume, so taking appropriate derivative gives us either

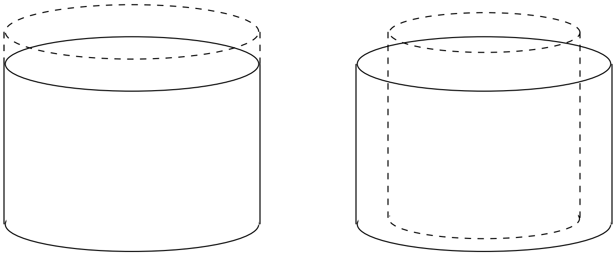
$$\frac{\partial V}{\partial h} = \pi r^2 = T \quad \text{or} \quad \frac{\partial V}{\partial h} = -S^2/4\pi h^2 = -T. \tag{3.11}$$

What? Is $\partial V/\partial h$ equal to T or to $-T$? It can't be equal to both!

The problem with equation (3.11) is that we were careless about specifying the variables. The two expressions for volume,

$$V(r, h) = \pi r^2 h \quad \text{and} \quad V(S, h) = S^2/4\pi h, \tag{3.12}$$

are in fact two completely different functions, with completely different variables, so we should *expect* completely different derivatives. If we increase the height h keeping the radius r fixed, the figure on the left below makes it clear that the volume increases. But if we increase the height and keep the side area S fixed, the radius will have to decrease as shown on the right below. The change on the right adds to the volume at the top of the cylinder but subtracts from the volume all along the sides. It would be most remarkable if the two volume changes were equal and, as our derivatives have shown, they are not.



A mathematician would say that we got ourselves in trouble in equation (3.11) because we gave two different functions the same name. A physicist would reply that they both represent the volume, so they deserve the same name. Rather than get into an argument, it is best to write out the variables of all functions explicitly, thus rewriting (3.11) as

$$\frac{\partial V(r,h)}{\partial h} = \pi r^2 = T(r,h) \quad \text{or} \quad \frac{\partial V(S,h)}{\partial h} = -S^2/4\pi h^2 = -T(S,h). \tag{3.13}$$

(Physicists often neglect to write out the full list of variables, which saves some time and some ink but which invites error. R.H. Price and J.D. Romano (*Am. J. Phys.* **66** (1998) 114) expose a situation in which a physicist published a deep error, which he made by neglecting to write out an explicit variable list.)

It becomes tiresome to write out the entire argument list for every function, so a shorthand notation has been developed. A right hand parenthesis is written after the partial derivative, and the functional arguments that are not being differentiated are listed as subscripts to that parenthesis. Thus the derivatives above are written as

$$\frac{\partial V(r,h)}{\partial h} = \left.\frac{\partial V}{\partial h}\right)_r \quad \text{and} \quad \frac{\partial V(S,h)}{\partial h} = \left.\frac{\partial V}{\partial h}\right)_S. \tag{3.14}$$

The expression on the left is read "the partial derivative of V with respect to h while r is held constant".

3.4.2 The Legendre transformation

Let us return to a description of cylinders in terms of the variables r and h. Clearly, one of the functions of interest is the volume

$$V(r,h). \tag{3.15}$$

A glance at the table on page 58 (or a moment's thought about geometry) shows that the total differential of V as a function of r and h is

$$dV = S(r,h)\,dr + T(r,h)\,dh, \tag{3.16}$$

whence

$$S(r,h) = \left.\frac{\partial V}{\partial r}\right)_h \quad \text{and} \quad T(r,h) = \left.\frac{\partial V}{\partial h}\right)_r. \tag{3.17}$$

Thus knowledge of the function $V(r,h)$ gives us a bonus…if we know $V(r,h)$, then we can take simple derivatives to find the other quantities of interest concerning cylinders, namely $S(r,h)$ and $T(r,h)$. Because of the central importance of $V(r,h)$, it is called a "master function" and the total differential (3.16) is called a "master equation".

Is there any way to find a similarly convenient "master description" in terms of the variables S and h? Indeed there is, and it is given by the "Legendre transformation". In the Legendre transformation from the variables r and h to the variables S and h, we change the focus of our attention from the master function $V(r,h)$ to the function

$$\Phi(S,h) = V(r(S,h),h) - Sr(S,h). \tag{3.18}$$

(The above equation is written out in full with all arguments shown. It is more usually seen as

$$\Phi = V - Sr, \tag{3.19}$$

although this form raises the possibility that variables and functions will become mixed up.) The total differential of Φ is

$$\begin{aligned} d\Phi &= dV - S\,dr - r\,dS & (3.20)\\ &= S\,dr + T\,dh - S\,dr - r\,dS & (3.21)\\ &= -r\,dS + T\,dh. & (3.22) \end{aligned}$$

We have found a new master function! It is

$$\Phi(S,h), \tag{3.23}$$

and the new master equation is

$$d\Phi = -r(S,h)\,dS + T(S,h)\,dh, \tag{3.24}$$

giving rise immediately to

$$r(S,h) = -\left.\frac{\partial \Phi}{\partial S}\right)_h \quad \text{and} \quad T(S,h) = \left.\frac{\partial \Phi}{\partial h}\right)_S. \tag{3.25}$$

This description has all the characteristics of a master description: once the master function is known, all the other interesting functions can be found by taking straightforward derivatives.

3.4.3 Maxwell relations

Suppose

$$df = A(x,y)\,dx + B(x,y)\,dy. \tag{3.26}$$

Then

$$A(x,y) = \left.\frac{\partial f}{\partial x}\right)_y \quad \text{and} \quad B(x,y) = \left.\frac{\partial f}{\partial y}\right)_x.$$

But because

$$\frac{\partial^2 f(x,y)}{\partial x \partial y} = \frac{\partial^2 f(x,y)}{\partial y \partial x}$$

it follows that

$$\left.\frac{\partial A}{\partial y}\right)_x = \left.\frac{\partial B}{\partial x}\right)_y. \tag{3.27}$$

This is called a "Maxwell relation".

Applied to equation (3.16), this tells us at a glance that

$$\left.\frac{\partial S}{\partial h}\right)_r = \left.\frac{\partial T}{\partial r}\right)_h. \tag{3.28}$$

We know that these two derivatives are equal without needing to find either one of them! Applied to equation (3.24), it tells us with equal ease that

$$\left.\frac{\partial r}{\partial h}\right)_S = -\left.\frac{\partial T}{\partial S}\right)_h. \tag{3.29}$$

3.4.4 Implicit function theorem

Suppose $f(x, y)$ is a function of the variables x and y. What is

$$\left.\frac{\partial y}{\partial x}\right)_f, \tag{3.30}$$

the slope of a contour of constant f?

Start with

$$df = \left.\frac{\partial f}{\partial x}\right)_y dx + \left.\frac{\partial f}{\partial y}\right)_x dy. \tag{3.31}$$

which holds for any differential change dx and dy. But we're not interested in *any* differential change: to evaluate the slope (3.30), we need a change in which $df = 0$ so

$$0 = \left.\frac{\partial f}{\partial x}\right)_y dx + \left.\frac{\partial f}{\partial y}\right)_x dy \qquad \text{with } dx,\ dy \text{ on contour of } f.$$

Thus

$$\frac{dy}{dx} = -\frac{\left.\frac{\partial f}{\partial x}\right)_y}{\left.\frac{\partial f}{\partial y}\right)_x} \qquad \text{with } dx,\ dy \text{ on contour of } f$$

and, writing the restriction "with dx, dy on contour of f" into the symbols of the equation,

$$\left.\frac{\partial y}{\partial x}\right)_f = -\frac{\left.\frac{\partial f}{\partial x}\right)_y}{\left.\frac{\partial f}{\partial y}\right)_x}. \tag{3.32}$$

Note that you get the wrong answer if you "cancel the small quantity ∂f from numerator and denominator of the ratio." That's because "the small quantity ∂f with constant y" is *different* from "the small quantity ∂f with constant x". I need to write a few words and a figure concerning why.

3.4.5 Multivariate chain rule

Suppose $f(x,y)$ and $g(x,y)$ are two function of the variables x and y. Then again we have

$$df = \left.\frac{\partial f}{\partial x}\right)_y dx + \left.\frac{\partial f}{\partial y}\right)_x dy \tag{3.33}$$

for any differential change dx and dy.

What if we are interested, not in any change, but in a change along a contour of constant g? Specifically, what if we need to find the change of f with x while moving on a contour of constant g? Then just take the exact differential above and apply it to a change dx, dy along the contour with constant g. Divide by the differential quantity dx:

$$\frac{df}{dx} = \left.\frac{\partial f}{\partial x}\right)_y \frac{dx}{dx} + \left.\frac{\partial f}{\partial y}\right)_x \frac{dy}{dx} = \left.\frac{\partial f}{\partial x}\right)_y + \left.\frac{\partial f}{\partial y}\right)_x \frac{dy}{dx} \qquad \text{with } dx,\, dy \text{ on contour of } g.$$

Now write the restriction "with dx, dy on contour of g" into the symbols of the equation to find

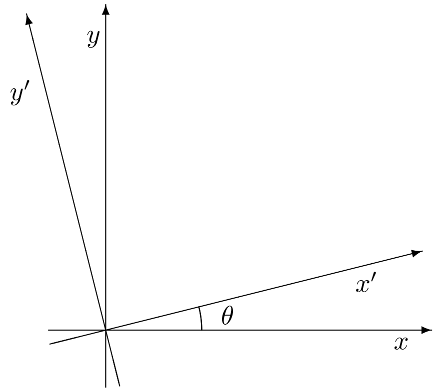
$$\left.\frac{\partial f}{\partial x}\right)_g = \left.\frac{\partial f}{\partial x}\right)_y + \left.\frac{\partial f}{\partial y}\right)_x \left.\frac{\partial y}{\partial x}\right)_g, \tag{3.34}$$

the multivariate chain rule.

Problems

3.9 **Partial derivatives in space**

A point on the plane can be specified either by the variables (x,y) or by the variables (x',y') where



$$\begin{aligned} x' &= +\cos(\theta)\,x + \sin(\theta)\,y, \\ y' &= -\sin(\theta)\,x + \cos(\theta)\,y. \end{aligned} \tag{3.35}$$

If $f(x, y)$ is some function of location on the plane, then write expressions for

$$\left.\frac{\partial f}{\partial x'}\right)_{y'}, \quad \left.\frac{\partial f}{\partial y'}\right)_{x'}, \quad \text{and} \quad \left.\frac{\partial f}{\partial x}\right)_{y'} \tag{3.36}$$

in terms of

$$\left.\frac{\partial f}{\partial x}\right)_{y} \quad \text{and} \quad \left.\frac{\partial f}{\partial y}\right)_{x}. \tag{3.37}$$

Interpret $\partial f/\partial x)_{y'}$ geometrically as a directional derivative. (That is, $\partial f/\partial x)_{y'}$ is the slope of f along which curve in the plane?) Given this interpretation, does it have the expected limits as $\theta \to 0$ and as $\theta \to \pi/2$?

3.10 Maxwell relations for a three-variable system

Suppose $\Phi(x, y, z)$ satisfies

$$d\Phi = A(x, y, z)\,dx + B(x, y, z)\,dy + C(x, y, z)\,dz. \tag{3.38}$$

State three Maxwell relations relating various first derivatives of $A(x, y, z)$, $B(x, y, z)$, and $C(x, y, z)$, and a fourth Maxwell relation relating various second derivatives of these functions.

3.11 The cylinder model with three variables

In the "three-variable cylinder model" the cylinders are described by height h, radius r, and density ρ. The master function is mass $M(h, r, \rho)$, and the master equation is

$$dM(h, r, \rho) = \rho S(h, r)\,dr + \rho T(r)\,dh + V(h, r)\,d\rho, \tag{3.39}$$

where $S(h, r)$ is the side area, $T(r)$ is the top area, and $V(h, r)$ is the volume. Perform a Legendre transformation to a description in terms of the variables h, S, and ρ using the new master function

$$\Phi(h, S, \rho) = M - \rho S r. \tag{3.40}$$

a. Write down the new master equation.

b. Write down the three first-order Maxwell relations and confirm their correctness using explicit formulas such as $M(h, S, \rho) = \rho S^2/(4\pi h)$.

c. Interpret $\Phi(h, S, \rho)$ physically.

3.12 Multivariate chain rule

Invent a problem going through the chain rule argument of section 3.8.1 with the cylinder model.

3.13 Contours of constant side area

Find contours of constant side area preparing for/using the technique of section 3.8.3.

3.5 Thermodynamic Quantities

By a thermodynamic “quantity” I mean either a variable or a function. We have already seen that for fluids we may regard the entropy as a function of energy, volume, and number, $S(E,V,N)$, or the energy as a function of entropy, volume, and number, $E(S,V,N)$: using the term “quantity” avoids prejudging the issue of whether entropy, for example, is to be treated as a variable or a function.

It is traditional to divide thermodynamic quantities into two classes: “extensive” and “intensive”. Extensive quantities increase linearly with system size while intensive quantities are independent of system size. (You might ask, “Why can’t a quantity depend on system size in some other fashion, such as quadratically?” The answer is that this is not impossible—for example, the radius of a spherical sample increses as the cube root of the system size—but it rarely happens in practice for quantities that concern us—see problem 3.18.) Thus extensive quantities are characteristic of the *sample* while intensive quantities are characteristic of the *substance.*

Examples of extensive quantities are energy, volume, number, entropy, and the magnetization $\mathbf{M}$ (i.e. the magnetic dipole moment of the entire sample):

$$E, \quad V, \quad N, \quad S, \quad \mathbf{M}. \tag{3.41}$$

Examples of intensive quantities are temperature, pressure, chemical potential, and the applied magnetic field $\mathbf{H}$:

$$T, \quad p, \quad \mu, \quad \mathbf{H}. \tag{3.42}$$

If one extensive quantities is divided by another extensive quantity, the quotent is an intensive quantity. The most frequently used quantities of this type are the *number densities*, such as

$$e = \frac{E}{N}, \quad s = \frac{S}{N}, \quad \text{and} \quad v = \frac{V}{N}. \tag{3.43}$$

There are also *volume densities* like

$$u = \frac{E}{V}, \quad \mathcal{S} = \frac{S}{V}, \quad \text{and} \quad \rho = \frac{N}{V}. \tag{3.44}$$

Quantities such as E/S are also intensive, but they are rarely used and don’t have special names.

Note that in defining densities such as above, we are not making any assumptions about how the matter in the sample is arranged. For liquid water in equilibrium with ice (e.g. at atmospheric pressure and a temperature of 273 K) the water has a greater number density (and a greater entropy density) than the ice, but the number density of the system is still just the total number divided by the total volume.

Here is a valuable problem solving tip. You know from previous courses that it is important to keep track of the dimensions of physical quantities: if you derive an equation for which the left side has the dimensions of meters and the right side has the dimensions of meters/second, your derivation must be wrong. In thermodynamics there is the equally important check of extensivity: if the left side is extensive and the right side is intensive, then the equation must be wrong. You should keep a running check of these properties as you solve problems. The first time you produce an equation that is incorrect in its dimensions or its extensivity, go back immediately and correct your error.

Problem 1.2 has already introduced the "isothermal compressibility"

$$\kappa_T(p,T) = -\frac{1}{V}\frac{\partial V(p,T)}{\partial p} \tag{3.45}$$

and the "expansion coefficient"

$$\beta(p,T) = \frac{1}{V}\frac{\partial V(p,T)}{\partial T}. \tag{3.46}$$

Both of these quantities are defined so as to be intensive.

Another quantity of interest is the "heat capacity", defined informally as "the amount of heat required to quasistatically raise the temperature of a sample by one kelvin". (The heat capacity was introduced briefly in problem 1.3.) Because this definition refers to a *sample*, heat capacity is an extensive quantity. The definition is incomplete because it doesn't say what path is taken while the heat is added, and we know that heat is a path-dependent quantity.[1] For fluids, the two most frequently used heat capacities are the heat capacity at constant volume and at constant pressure, denoted by

$$C_V \quad \text{and} \quad C_p. \tag{3.47}$$

Thus C_p (which will in general be a function of temperature, pressure, and number) is the amount of heat required to increase the temperature of a sample by one kelvin while the sample is under a constant pressure (often, in earth-bound laboratories, a pressure of one atmosphere). In contrast C_V (which will in general be a function of temperature, volume, and number) is the amount of heat required to increase the temperature of a sample by one kelvin while holding it in a strong box to prevent it from expanding. Because liquids expand little upon heating, C_V and C_p are nearly equal for liquids. But the two quantities differ dramatically for gases.

For small quasistatic changes, we know that

$$\Delta S = \frac{Q}{T} \tag{3.48}$$

whence

$$C = \lim_{\Delta T\to 0}\frac{T\Delta S}{\Delta T}. \tag{3.49}$$

This gives us the formal definitions of heat capacity,

$$C_V = T\frac{\partial S(T,V,N)}{\partial T} \quad \text{and} \quad C_p = T\frac{\partial S(T,p,N)}{\partial T}, \tag{3.50}$$

and from these equations it is again clear that heat capacity is an extensive quantity.

The intensive quantities analogous to heat capacities are called "specific heats":

$$c_V = \frac{C_V}{N} \quad \text{and} \quad c_p = \frac{C_p}{N}. \tag{3.51}$$

The specific heat is readily measured experimentally and we will come back to it again and again.

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[1] In truth, it's worse than this, because it doesn't even specify the end point of the process. If we are describing the fluid sample by V and T, for example, and the starting point were (V_i, T_i), then the end point must have $T_f = T_i + 1$ K, but as far as our informal definition goes, the final volume could be anything.

Problems

3.14 (E) **Which one was it?**

For a system with a fixed number of particles, the reciprocal of the absolute (kelvin) temperature T is given by which of the following derivatives? Explain your reasoning. Do not look up the answer or, if you have memorized it, don't use that piece of your memory. (Clue: Dimensional analysis will work, but there's an even easier way.)

$$\frac{\partial p(S,V)}{\partial V} \quad \frac{\partial p(S,V)}{\partial S} \quad \frac{\partial S(E,p)}{\partial p} \quad \frac{\partial V(E,p)}{\partial p} \quad \frac{\partial S(E,V)}{\partial E} \tag{3.52}$$

3.15 (I) **Acceptable forms for the entropy**

Below are seven equations purporting to be equations for $S(E,V,N)$ for various thermodynamic systems. However, four of them are not physically acceptable. Find the four inpermissible equations and for each indicate why it cannot be correct. The quantities T_0 and v_0 are in all cases positive, intensive quantities with the dimensions of temperature and volume, respectively.

$$S(E,V,N) = \left(\frac{k_B^2}{v_0 T_0}\right)^{1/3} (EVN)^{1/3} \tag{3.53}$$

$$S(E,V,N) = \left(\frac{k_B v_0^2}{T_0^2}\right)^{1/3} \left(\frac{EN}{V}\right)^{2/3} \tag{3.54}$$

$$S(E,V,N) = \left(\frac{k_B v_0^2}{T_0^2}\right)^{1/3} \frac{EN}{V} \tag{3.55}$$

$$S(E,V,N) = \left(\frac{k_B}{T_0}\right)^{1/2} \left(NE + \frac{k_B T_0 V^2}{v_0^2}\right)^{1/2} \tag{3.56}$$

$$S(E,V,N) = k_B N \ln(EV/N^2 k_B T_0 v_0) \tag{3.57}$$

$$S(E,V,N) = k_B N \exp(-EV/N^2 k_B v_0) \tag{3.58}$$

$$S(E,V,N) = k_B N \exp(-EV^2/N^2 k_B T_0 v_0^2) \tag{3.59}$$

3.16 (I) **Heat capacities for the ideal gas**

Use equation (2.32) to find the heat capacities

$$C_V(T,V,N) = T\left.\frac{\partial S}{\partial T}\right)_{V,N} \qquad \text{and} \qquad C_p(T,p,N) = T\left.\frac{\partial S}{\partial T}\right)_{p,N}$$

for the pure classical monatomic ideal gas.

3.17 (I) **Heat capacity at a phase transition**

What is C_p for a fluid when the liquid and gas coexist?

3.18 (D) **Gravitational potential energy**

Consider a uniform sphere of mass M and radius R.

a. Use dimensional analysis to show that the gravitational potential energy of the sphere is of the form

$$U_G = -cG\frac{M^2}{R}, \tag{3.60}$$

where c is a dimensionless constant independent of M and R.

b. Is U_G intensive, extensive, or neither?

c. Is the total energy E (which is equal to U_G plus contributions from other forms of energy) intensive, extensive, or neither?

d. Estimate the value of U_G for a glass of water.

You should conclude from this problem that the total energy E is in principle non-extensive, but that the deviations from being extensive are negligible for everyday thermodynamic systems.

e. (Optional and quite time consuming.) Use ideas from classical mechanics to show that the dimensionless constant in equation (3.60) is $c = 3/5$.

3.6 The Thermodynamic Dance

A more conventional name for this section would be "Changes of Variable in Thermodynamics", but the changes of variable involved always remind me of an elaborate dance where partners are exchanged and where patterns seem to dissolve and then reappear, but in fact are always present, even if hidden.

3.6.1 Description in terms of variables (S, V, N)

We know that in many circumstances (e.g. pure, non-magnetic fluids) the thermodynamic state of a system is uniquely specified by giving the entropy S, the volume V, and the particle number N. The master function for this description is the energy

$$E(S, V, N) \tag{3.61}$$

whose total differential is

$$dE = T\,dS - p\,dV + \mu\,dN. \tag{3.62}$$

Remember that a "master function" is one from which all functions of interest can be obtained by simple differentiation... the equation above, for example, shows directly that

$$p(S, V, N) = -\left.\frac{\partial E}{\partial V}\right)_{S,N}. \tag{3.63}$$

Remember also that the variables V and N are just representative mechanical parameters. Other mechanical parameters such as particle mass m, particle radius r_{HS}, or the numbers of two different species, N_{H_2} and N_{He}, will be relevant in other circumstances.

3.6.2 Description in terms of variables (T, V, N)

For many purposes the description in terms of S, V, and N is awkward. (Entropy, for example, can be difficult to measure and to understand.) In these situations a more natural set of variables might be temperature T, volume V, and number N. We can change[2] to this set through a Legendre transformation (a process sometimes called "trading in an S for a T") obtaining the new master function

$$F(T, V, N) = E - TS, \tag{3.64}$$

which is called the "Helmholtz potential" (or the "Helmholtz free energy"[3]). and which has the associated master equation

$$dF = -S\,dT - p\,dV + \mu\,dN. \tag{3.65}$$

(In some books, the Helmholtz potential is denoted by A rather than F.)

Lots of information can be read directly from the master equation. For example, the entropy can be found through

$$S(T, V, N) = -\left.\frac{\partial F}{\partial T}\right)_{V,N}. \tag{3.66}$$

It is less obvious how to find the energy, but a little thought shows that

$$E(T, V, N) = F + TS = F - T\left.\frac{\partial F}{\partial T}\right)_{V,N} = \left.\frac{\partial (F/T)}{\partial (1/T)}\right)_{V,N}. \tag{3.67}$$

This equation is frequently used and carries the name "Gibbs-Helmholtz equation".

> One sometimes hears that "energy must be regarded as a function of (S, V, N) while Helmholtz potential must be regarded as a function of (T, V, N)". This is false. The energy $E(T, V, N)$ above is a perfectly good function but it is *not* a master function. The energy is the master function for the description in terms of (S, V, N) but *not* for the description in terms of (T, V, N). Similarly, one could find the Helmholtz potential as a function of (S, V, N), but it would not be a master function.

Another immediate consequence of the master equation is that

$$p(T, V, N) = -\left.\frac{\partial F}{\partial V}\right)_{T,N}. \tag{3.68}$$

This equation is *extremely* well know…it is just the "equation of state", relating pressure, temperature, volume, and number. Examples are the famous ideal gas equation of state

$$p(T, V, N) = \frac{Nk_BT}{V} \tag{3.69}$$

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[2] When we changed variable from (S, V, N) to (E, V, N) (equation 3.1), I argued that this inversion was mathematically legitimate. Here I will not be so formal and just assume that everything will come out all right. (See, however, problem 3.28.) Clifford Truesdell has called this "the principle of thoughtless invertibility".

[3] The term "free" in this name is of only historical significance. Its origin lies in the fact that F is related to the maximum amount of energy that is available ("free") for conversion into work through an isothermal process.

and the only slightly less famous van der Waals equation of state for non-ideal gases

$$p(T,V,N) = \frac{k_B T}{V/N - v_0} - \frac{e_0 v_0}{(V/N)^2}, \tag{3.70}$$

where v_0 and e_0 are positive empirical constants with the dimensions of volume and energy respectively.

> Notice that $S(T,V,N)$, $E(T,V,N)$, and $p(T,V,N)$ are all interesting quantities, but none of them are master functions, that is, none of them contain *all* the thermodynamic information. It is a common misconception that the equation of state contains everything one could want to know about a substance. In fact, for example, helium and nitrogen are both nearly ideal gases at room temperature (so they obey nearly the same equation of state) but the specific heat of nitrogen is about 67% greater than that of helium (so they differ dramatically in some thermodynamic properties).

Yet another immediate consequence of the master equation is the Maxwell relation

$$\left.\frac{\partial S}{\partial V}\right)_{T,N} = \left.\frac{\partial p}{\partial T}\right)_{V,N}. \tag{3.71}$$

Each of the derivatives above is not only a mathematical expression, but also an invitation to perform an experiment. The derivative on the left is measured through an experiment like the following: A sample in a container of variable volume (such as a piston) is placed within a thermostatically controlled bath (so that the temperature doesn't change) and is heated in a slow and carefully monitored way (so that the heat absorbed quasistatically can be divided by the temperature to find the entropy change). As the substance is heated at constant temperature, the volume of the piston must change. Dividing the heat absorbed by the temperature and the volume change gives (for small volume changes) the derivative on the left. This experiment is not impossible, but clearly it is difficult and expensive.

Consider in turn the experiment on the right. The sample is in a "strong box" container of fixed volume and its pressure and temperature are measured as the temperature is changed. The change doesn't need to be controlled carefully and the heat absorbed doesn't need to be monitored: you can just blast your sample with a propane torch. Dividing the measured change in pressure by the measured change in temperature gives (for small temperature changes) the derivative on the right. It is remarkable that the results of these two very different experiments is always the same... and it shows how thermodynamics can save a lot of experimental labor! But it is still more remarkable—nearly unbelievable—that we know these two experiments give the same results because we know that the entropy function $S(E,V,N)$ exists, even though we might not know what that function is.[4] (This Maxwell relation is discussed further in problem 3.24.)

3.6.3 Description in terms of variables (S,p,N)

I don't need to stop with this second description. Both of the descriptions above used volume as a variable. Most experiments executed here on Earth's surface are actually performed with a constant pressure (namely

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[4] If a material existed for which these two experiments *did not* give identical results, then we could use that substance to build a perpetual motion machine.

one atmosphere) rather than with a constant volume, suggesting that pressure should be one of our variables. We may start with the description in terms of (S, V, N) and then trade in a V for a p, obtaining a master function

$$H(S, p, N) = E + pV, \tag{3.72}$$

called the "enthalpy", and the related master equation

$$dH = T\,dS + V\,dp + \mu\,dN. \tag{3.73}$$

We could pause here to write down derivatives of $H(S, p, N)$, Maxwell relations, and so forth, but this would merely be repetitive of what we did in the last section. Instead, we ask for yet another description with the advantages of using both temperature instead of entropy and pressure instead of volume.

3.6.4 Description in terms of variables (T, p, N)

In this description, the master function

$$G(T, p, N) = F + pV \tag{3.74}$$

is called the "Gibbs potential" (or the "Gibbs free energy"[5]) and the master equation is

$$dG = -S\,dT + V\,dp + \mu\,dN. \tag{3.75}$$

(It is most unfortunate that in some books the Gibbs potential is denoted F, the symbol that most books reserve for the Helmholtz potential.)

It is immediately obvious that

$$\mu(T, p, N) = \left.\frac{\partial G}{\partial N}\right)_{T,p}. \tag{3.76}$$

It is also true that G is an extensive quantity, and that it is a function of *only one* extensive quantity, namely N. It follows that G must increase linearly with N, whence

$$\mu(T, p) = \frac{G(T, p, N)}{N}. \tag{3.77}$$

Notice that μ, which appeared from equation (3.76) to depend upon N, is actually independent of N.

The chemical potential has so far been a wallflower in the thermodynamic dance. But there is no reason why we cannot trade in an N for a μ in the same way that we traded in a V for a p.

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[5] I prefer the name "Gibbs potential" because it is like electrostatic potential — the quantity itself is not of intrinsic interest, but one can find many interesting things by taking its derivatives. The name "free energy" is particularly inappropriate: What do you buy from a power company? You've been told "Turn off the lamps to conserve energy", but this is silly: energy is conserved whether the lamps are on or off. There's plenty of thermal energy in any room, but you can't get work out of that energy because the room has uniform temperature. So you don't buy energy from a power company, you in fact buy Gibbs potential. For this reason it should be called "Gibbs expensive energy". I am trying to get the federal government to change the name of the Department of Energy to the Department of Gibbs Potential, but so far I've had no success.

3.6.5 Description in terms of variables (T, V, μ)

Here the master function is

$$\Pi(T, V, \mu) = F - \mu N \tag{3.78}$$

with master equation

$$d\Pi = -S\,dT - p\,dV - N\,d\mu. \tag{3.79}$$

You might wonder why Π doesn't have a name. This is because

$$\Pi = F - \mu N = F - G = -pV \tag{3.80}$$

or, to put it more formally,

$$\Pi(T, V, \mu) = -p(T, \mu)V, \tag{3.81}$$

so Π already has the name of "negative pressure times volume".

3.6.6 Intensive description in terms of variables (T, μ)

Putting equations (3.79) and (3.81) together gives

$$-p\,dV - V\,dp = -S\,dT - p\,dV - N\,d\mu \tag{3.82}$$

whence

$$dp = \frac{S}{V}\,dT + \frac{N}{V}\,d\mu. \tag{3.83}$$

In other words, we have produced a new master function, the pressure

$$p(T, \mu) \tag{3.84}$$

with master equation

$$dp = \mathcal{S}\,dT + \rho\,d\mu \tag{3.85}$$

where we have used the volume densities

$$\mathcal{S} = S/V \quad \text{and} \quad \rho = N/V. \tag{3.86}$$

The master function $p(T, \mu)$ differs in important ways from the others that we have seen. First, it is intensive rather than extensive. Second, it is a function of two rather than three variables, and the two variables are both intensive. It is clear that we cannot get any information about the system size out of $p(T, \mu)$... thus it fails the usual test of a master function, namely that it must provide *all* thermodynamic information. On the other hand, $p(T, \mu)$ provides all the information about intensive quantities. The problems in this chapter demonstrate that $p(T, \mu)$ is a surprisingly useful master function.

This entire section is summarized in appendix J.

Problems

3.19 Stumbling in the thermodynamic dance

a. From the thermodynamic assembly with variables T, p, and N, with master equation

$$dG = -S\,dT + V\,dp + \mu\,dN \tag{3.87}$$

one is tempted to produce an assembly with variables T, p, and μ, using master function

$$\Phi = G - \mu N. \tag{3.88}$$

Why does this fail?

b. Show that what is really desired is an intensive-only description in terms of the variables T and p, for which the master equation is

$$d\mu = -s\,dT + v\,dp, \tag{3.89}$$

where $s = S/N$ and $v = V/N$. (This result is called the "Gibbs-Duhem equation".)

3.20 Falling flat on your face in the thermodynamic dance

We have seen that a fluid can be specified thermodynamically through the variables (T, V, N) or through the variables (T, p, N). Are other sets of variables sufficient?

a. If the fluid in question is the ideal gas, show that the variables (p, V, N) suffice to specify the thermodynamic state.

b. If the fluid in question is water, show that the variables (p, V, N) do *not* suffice.

3.21 Not a master function

The function $E(S, V, N)$ is a master function: all thermodynamic quantities of interest can be obtained by taking suitable derivatives of $E(S, V, N)$. For the variables (T, V, N) the master function is the Helmholtz potential $F(T, V, N)$. While the energy $E(T, V, N)$ of course remains a function, it is no longer a master function. Prove this to yourself by considering two different substances, A and B, with Helmholtz potentials $F_A(T, V, N)$ and $F_B(T, V, N) = F_A(T, V, N) + aTV^2/N$. Show that these two substances have identical energies $E(T, V, N)$ but different equations of state $p(T, V, N)$.

3.22 Thermodynamics of a new substance

The entropy of a newly discovered gas is determined to be

$$S(E, V, N) = \left(\frac{k_B}{T_0}\right)^{1/2}\left(NE + \frac{k_B T_0 V^2}{v_0^2}\right)^{1/2},$$

where the constants T_0 and v_0 are positive, intensive quantities with the dimensions of temperature and volume, respectively.

a. Verify that this equation is acceptable in its dimensions and in its extensivity.

b. Find $T(S, V, N)$ and $p(S, V, N)$ for this gas.

c. Find $C_V(T, V, N)$ for this gas.

3.23 Energy from the Gibbs potential

The text claims that "any thermodynamic function can be obtained from a master function by taking derivatives." To back up this claim, show that

$$\begin{aligned} E(T,p,N) &= G(T,p,N) - T\,\frac{\partial G}{\partial T}\bigg)_{p,N} - p\,\frac{\partial G}{\partial p}\bigg)_{T,N} && (3.90)\\ &= \frac{\partial (G/p)}{\partial (1/p)}\bigg)_{T,N} - T\,\frac{\partial G}{\partial T}\bigg)_{p,N} && (3.91)\\ &= \frac{\partial (G/T)}{\partial (1/T)}\bigg)_{p,N} - p\,\frac{\partial G}{\partial p}\bigg)_{T,N}. && (3.92)\end{aligned}$$

Find an expression for $F(T,p,N)$ in terms of $G(T,p,N)$.

3.24 A Maxwell relation: special cases

a. Apply the Maxwell relation (3.71) to the the special case of an ideal gas (equation of state $pV = Nk_BT$) to show that

$$S(T,V,N) = Nk_B \ln(V/V_0(T)), \tag{3.93}$$

where $V_0(T)$ is an undetermined function of integration that differs from one ideal gas to another. (The remarkable character of our Maxwell relation comes into sharp focus when applied to this special case: The "mechanical-type" experiments which uncover the equation of state enable us to determine much about the entropy function even in the absence of any "heat-type" experiments.)

b. Another special case worth examination is two-phase coexistence of liquid and gas. Verify the Maxwell relation both for "typical" two-phase coexistence—in which the low-temperature phase has higher density than the high-temperature phase—and for the unusual cases—such as the coexistence of water and ice—where the low-temperature phase has a higher density.

3.25 Chemical potential for mixtures

If a system contains a mixture of two chemical substances, say N_A molecules of substance A and N_B molecules of substance B, then the list of mechanical parameters must be expanded, and the entropy is a function

$$S(E,V,N_A,N_B). \tag{3.94}$$

In this case the chemical potential of substance A is

$$\mu_A(E,V,N_A,N_B) = -T(E,V,N_A,N_B)\,\frac{\partial S}{\partial N_A}\bigg)_{E,V,N_B} \tag{3.95}$$

and similarly for B. Notice that the chemical potential of substance A depends upon the number of molecules of B present.

a. Perform the thermodynamic dance down to the function $F(T,V,N_A,N_B)$ to show that

$$\mu_A(T,V,N_A,N_B) = \frac{\partial F}{\partial N_A}\bigg)_{T,V,N_B} \tag{3.96}$$

and similarly for B.

b. Argue that, because μ_A and μ_B are intensive, their functional dependence on V, N_A, and N_B, must be through the number densities $\rho_A = N_A/V$ and $\rho_B = N_B/V$, i.e. that

$$\mu_A(T, V, N_A, N_B) = \mu_A(T, \rho_A, \rho_B). \tag{3.97}$$

c. Consider the Gibbs potential $G(T, p, N_A, N_B)$ and modify the extensivity argument that produced equation (3.77) to show that

$$G(T, p, N_A, N_B) = \mu_A(T, p, N_A/N_B)N_A + \mu_B(T, p, N_A/N_B)N_B, \tag{3.98}$$

where the chemical potentials are independent of the overall numbers N_A and N_B but may depend on their ratio.

3.26 **More parameters**

What is the generalization of

$$dE = T\,dS - p\,dV + \mu\,dN \tag{3.99}$$

for systems that can be lifted and tossed? (That is, for systems in which height h and velocity $\mathbf{v}$ are mechanical parameters.)

3.27 **Another mechanical parameter**

Recall expression (2.32) for the entropy of a monatomic ideal gas, and recall that $E = \frac{3}{2}Nk_BT$. Find expressions for the change in entropy and in volume if the masses of the particles are varied at constant p, T, and N. Suggest experiments that could verify these relations.

3.28 **Which variables to exchange?**

In carrying out the thermodynamic dance, we have exchanged the variable S for the function $T(S, V, N)$, and we have exchanged the variable V for the function $p(T, V, N)$, and more. Why would it never be appropriate to exchange the volume for the temperature? (Clue: Consider the volume of water at temperatures just above and below freezing.)

3.7 Non-fluid Systems

All the results of the previous section relied on the underlying assumption that the system was a pure fluid and thus could be described by specifying, for example, the temperature T, the volume V, and the particle number N. Recall that the latter two were simply examples of many possible mechanical parameters that could be listed, such as the molecular mass, the molecular moment of inertia, or pair interaction parameters such as the hard-sphere radius or the Lennard-Jones parameters.

But of course nature presents us with many materials that are not pure fluids! One obvious example is a fluid mixture, the specification of which requires the number of molecules of each constituent. Another example is a crystal of a layered material such as graphite. To find the energy, for example, it is not sufficient to specify only the volume. You must know the area of the layers and the height to which these layers are stacked.

In this book we will focus instead on a third example, namely magnets. The fundamental thermodynamic relation for magnetic systems is

$$dE = T\,dS - M\,dH, \tag{3.100}$$

where H, the applied magnetic field, is an intensive mechanical parameter and M, the magnetization (total magnetic dipole moment of the sample), is extensive. Just as the thermodynamic equations for fluids presented in the previous section implicitly assume that the magnetic properties of the sample can be ignored (either because the substance is non-magnetic or because the magnetic field does not change), so the equation above implicitly assumes that the volume and number specification of the sample can be ignored.

In another course, you may have learned a mnemonic (the "Max Born square" or the "thermodynamic square") for remembering the thermodynamic differentials and Maxwell relations of a pure fluid systems with a constant particle number. Such mnemonics encourage the very worst problem solving strategy, namely "poke around until you discover an equation that fits". Anyone who uses this strategy finds it impossible to investigate mixtures, crystals, magnets, or any other member of the rich array of materials that nature has so generously spread before us. Instead of memorizing equations and hoping that the right one will present itself, you should think about what sort of equation you will need to solve a problem and then derive it. Appendix J will remind you of the strategy of the thermodynamic dance and will help you keep your signs straight.

3.29 **Magnetic systems**

Show that for magnetic systems (see equation (3.100)),

$$\left.\frac{\partial M}{\partial T}\right)_H = \left.\frac{\partial S}{\partial H}\right)_T \tag{3.101}$$

and

$$\left.\frac{\partial H}{\partial T}\right)_M = -\left.\frac{\partial S}{\partial M}\right)_T . \tag{3.102}$$

3.8 Thermodynamics Applied to Fluids

In the rest of this chapter we apply the general results of section 3.6, "The Thermodynamic Dance", to particular concrete situations. We begin with fluids, that is, systems whose thermodynamic states are adequately described by giving the variables temperature T, volume V, and particle number N. Furthermore, in this section we will not allow particles to enter or leave our system, so only two variables, T and V, are needed.

3.8.1 Heat capacities

Is there any relation between

$$C_p(T,p) = T \left.\frac{\partial S}{\partial T}\right)_p, \tag{3.103}$$

the heat capacity at constant pressure, and

$$C_V(T,V) = T \left.\frac{\partial S}{\partial T}\right)_V, \tag{3.104}$$

the heat capacity at constant volume? Remembering that entirely different experiments are used to measure the two quantities, you might guess that there is not. But mathematically, the difference between C_p and C_V is related to a change in variable from (T,V) to (T,p), so you might begin to suspect a relation. [You might want to prepare for this section by working problem 3.12.]

Begin with the mathematical definition of the total differential of entropy,

$$dS = \left.\frac{\partial S}{\partial T}\right)_V dT + \left.\frac{\partial S}{\partial V}\right)_T dV. \tag{3.105}$$

The above holds for any infinitesimal change. We restrict ourselves to infinitesimal changes at constant pressure, and divide by dT, to find

$$\left.\frac{\partial S}{\partial T}\right)_p = \left.\frac{\partial S}{\partial T}\right)_V + \left.\frac{\partial S}{\partial V}\right)_T \left.\frac{\partial V}{\partial T}\right)_p. \tag{3.106}$$

Multiplying both sides by T gives a heat capacity relation

$$C_p = C_V + T \left.\frac{\partial S}{\partial V}\right)_T \left.\frac{\partial V}{\partial T}\right)_p. \tag{3.107}$$

This relationship is correct but not yet written in its most convenient form. For example, reference books provide tabulations of C_p and C_V, but not of $\partial S/\partial V)_T$ or $\partial V/\partial T)_p$.

The first step in changing the heat capacity relation into “standard form” is an easy one. Recall from problem 1.2 that the expansion coefficient (an intensive tabulated quantity[6]) is defined by

$$\beta(T,p) = \frac{1}{V}\left.\frac{\partial V}{\partial T}\right)_p \tag{3.108}$$

whence

$$C_p = C_V + TV\beta \left.\frac{\partial S}{\partial V}\right)_T. \tag{3.109}$$

The second step is less obvious. At equation (3.71) I discussed the Maxwell relation

$$\left.\frac{\partial S}{\partial V}\right)_T = \left.\frac{\partial p}{\partial T}\right)_V, \tag{3.110}$$

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[6] It is easy to see why $\partial V/\partial T)_p$ itself is not tabulated. Instead of requiring a tabulation for iron, you would need a tabulation for a five gram sample of iron, for a six gram sample of iron, for a seven gram sample of iron, etc.

and mentioned that the right hand side was much easier to measure. Thus we have the preferable expression

$$C_p = C_V + TV\beta \left.\frac{\partial p}{\partial T}\right)_V . \tag{3.111}$$

This expression is still not very convenient, however, because the quantity $\partial p/\partial T)_V$ is neither named nor tabulated. Although easier to measure than $\partial S/\partial V)_T$ is, its measurement still requires a constant-volume strong box. Measurements at constant pressure are easier to perform and hence more frequently tabulated. We now write $\partial p/\partial T)_V$ in terms of such quantities.

The total differential of $V(T, p)$ is

$$dV = \left.\frac{\partial V}{\partial T}\right)_p dT + \left.\frac{\partial V}{\partial p}\right)_T dp \tag{3.112}$$

or, in terms of named quantities,

$$dV = V\beta\, dT - V\kappa_T\, dp. \tag{3.113}$$

(The isothermal compressibility

$$\kappa_T(T, V) \equiv -\frac{1}{V}\left.\frac{\partial V}{\partial p}\right)_T \tag{3.114}$$

was defined in problem 1.2.) Restricting the above total differential to changes at constant V gives

$$V\beta\, dT = V\kappa_T\, dp \tag{3.115}$$

or

$$\frac{\beta}{\kappa_T} = \left.\frac{\partial p}{\partial T}\right)_V . \tag{3.116}$$

This immediately gives us the final form for our relationship between heat capacities,

$$C_p = C_V + TV\frac{\beta^2}{\kappa_T}. \tag{3.117}$$

This is a far from obvious result that is true for all fluids and, I emphasize, was derived assuming only that entropy exists and without the use of any explicit formula for the entropy.

Note that T, V, and κ_T are all positive quantities. The expansion coefficient β may be either positive or negative, but it enters the relationship as β^2. Thus

$$C_p \geq C_V. \tag{3.118}$$

Can we understand these results physically? Heat capacity is the amount of heat required to raise the temperature of a sample by one kelvin. If the sample is heated at constant volume, all of the heat absorbed goes into increasing the temperature. But if the sample is heated at constant pressure, then generally the substance will expand as well as increase its temperature, so some of the heat absorbed goes into increasing the temperature and some is converted into expansion work. Thus we expect that more heat will be needed for a given change of temperature at constant pressure than at constant volume, i.e. that $C_p \geq C_V$. We also expect that the relation between C_p and C_V will depend upon the expansion coefficient β. It is hard, however, to turn these qualitative observations into the precise formula (3.117) without recourse to the formal mathematics that we have used. It is surprising, for example, that β enters into the formula as β^2, so that materials which contract with increasing temperature still have $C_p \geq C_V$.

For solids and liquids, there is little expansion and thus little expansion work, whence $C_p \approx C_V$. But for gases, $C_p \gg C_V$. What happens at two-phase coexistence?

So far we have discussed only the difference between the two heat capacities. It is conventional to also define the "heat capacity ratio"

$$\gamma \equiv \frac{C_p}{C_V}, \tag{3.119}$$

which can be regarded as a function of T and V or as a function of T and p. But the result above shows that for all values of T and V,

$$\gamma(T, V) \geq 1. \tag{3.120}$$

We can apply these results to the ideal gas with equation of state

$$pV = Nk_BT. \tag{3.121}$$

Problem 1.2 used this equation to show that for an ideal gas,

$$\beta = \frac{1}{T} \quad \text{and} \quad \kappa_T = \frac{1}{p}. \tag{3.122}$$

Thus the heat capacity relation (3.117) becomes

$$C_p = C_V + TV\frac{p}{T^2} = C_V + \frac{pV}{T} = C_V + k_BN, \tag{3.123}$$

and we have

$$\gamma = \frac{C_p}{C_V} = 1 + \frac{k_BN}{C_V}. \tag{3.124}$$

3.8.2 Energy as a function of temperature and volume

You know that $E(S, V)$ is a master function with the famous master equation

$$dE = T\,dS - p\,dV. \tag{3.125}$$

For the variables T and V the master function is the Helmholtz potential $F(T, V)$ with master equation

$$dF = -S\,dT - p\,dV. \tag{3.126}$$

Thus in terms of the variables T and V the energy in no longer a master function, but that doesn't mean that it's not a function at all. It is possible to consider the energy as a function of T and V, and in this subsection we will find the total differential of $E(T, V)$.

We begin by finding the total differential of $S(E, V)$ and finish off by substituting that expression for dS into the master equation (3.125). The mathematical expression for that total differential is

$$dS = \left.\frac{\partial S}{\partial T}\right)_V dT + \left.\frac{\partial S}{\partial V}\right)_T dV, \tag{3.127}$$

but we showed in the previous subsection that this is more conveniently written as

$$dS = \frac{C_V}{T}\,dT + \frac{\beta}{\kappa_T}\,dV. \tag{3.128}$$

Thus

$$dE = T\,dS - p\,dV = T\left[\frac{C_V}{T}\,dT + \frac{\beta}{\kappa_T}\,dV\right] - p\,dV \tag{3.129}$$

and, finally,

$$dE = C_V\,dT + \left[T\frac{\beta}{\kappa_T} - p\right]dV. \tag{3.130}$$

The most interesting consequence of this exercise is that the heat capacity C_V, which was defined in terms of an entropy derivative, is also equal to an energy derivative:

$$C_V(T,V) \equiv T\left.\frac{\partial S}{\partial T}\right)_V = \left.\frac{\partial E}{\partial T}\right)_V. \tag{3.131}$$

For an ideal gas

$$\left[T\frac{\beta}{\kappa_T} - p\right] = 0, \tag{3.132}$$

whence

$$dE = C_V\,dT + 0\,dV. \tag{3.133}$$

Thus the energy, which for most fluids depends upon both temperature and volume, depends in the ideal gas only upon temperature:

$$E(T,V) = E(T). \tag{3.134}$$

The same is true of the heat capacity

$$C_V(T,V) = \left.\frac{\partial E}{\partial T}\right)_V = C_V(T), \tag{3.135}$$

and the heat capacity ratio

$$\gamma(T) = 1 + \frac{k_B N}{C_V(T)}. \tag{3.136}$$

Thermodynamics proves that for an ideal gas C_V depends only upon T and not V, but experiment shows that in fact C_V is almost independent of T as well. From the point of view of thermodynamics this is just an unexpected experimental result and nothing deeper. From the point of view of statistical mechanics this is not just a coincidence but is something that can be proved... we will do so in chapter 5.

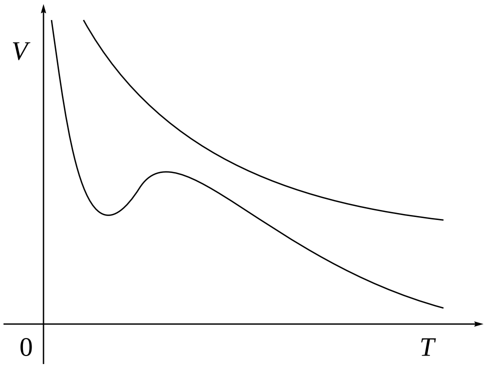
3.8.3 Quasistatic adiabatic processes

This topic, titled by a string of polysyllabic words, sounds like an arcane and abstract one. In fact it has direct applications to the speed of sound, the manufacture of refrigerators, to the inflation of soccer balls, and to the temperature of mountain tops. [You might want to prepare for this section by working problem 3.13.]

If a fluid is changed in a quasistatic, adiabatic manner, its entropy will remain constant during the change. So, for example, if the state of the system is described by the two variables temperature and volume, then during a quasistatic adiabatic process the system will move along contour lines[7] of constant entropy in the (T,V) plane, such as those below.

---

[7] Such contours are sometimes called isoentropic curves or, even worse, adiabats. The latter name is not just a linguistic horror, it also omits the essential qualifier that only *quasistatic* adiabatic processes move along curves of constant entropy.



Our aim in this section is to find an equation V(T) for such constant-entropy contours.

We begin with the now-familiar total differential for the entropy as a function of temperature and volume,

$$dS = \frac{C_V}{T}\,dT + \frac{\beta}{\kappa_T}\,dV. \tag{3.137}$$

This equation holds for any infinitesimal change, but we will apply it now to changes along an entropy contour, i.e. changes for which $dS = 0$. For such changes

$$\frac{\beta}{\kappa_T}\,dV = -\frac{C_V}{T}\,dT \tag{3.138}$$

whence the differential equation for an entropy contour is

$$\frac{dV(T)}{dT} = -\frac{C_V(T,V)\kappa_T(T,V)}{T\beta(T,V)}. \tag{3.139}$$

The quantities on the right are usually (not always) positive, so the entropy contours usually (not always) slope downward. This is as much as we can say for a general fluid.

But for an ideal gas we can fill in the functions on the right to find

$$\frac{dV(T)}{dT} = -\frac{C_V(T)}{p(T,V)} = -\frac{C_V(T)V}{Nk_BT}. \tag{3.140}$$

Using equation (3.136), this result is often written in the form

$$\frac{dV(T)}{dT} = \frac{1}{1-\gamma(T)}\frac{V}{T}. \tag{3.141}$$

This is as far as we can go for an arbitrary ideal gas.

But for an ideal gas with constant heat capacity, and hence with constant γ, this differential equation is readily solved using separation of variables. We write

$$(1-\gamma)\frac{dV}{V} = \frac{dT}{T} \tag{3.142}$$

with the immediate solution

$$(1-\gamma)\ln V = \ln T + \text{ constant}, \tag{3.143}$$

giving

$$V^{1-\gamma} = \text{constant } T \quad \text{or} \quad TV^{\gamma-1} = \text{constant}. \tag{3.144}$$

Remembering that $\gamma \geq 1$, this confirms the downward slope of the entropy contours on the (V, T) plane.

This result is most frequently used with the variables p and T, rather than V and T:

$$pV^\gamma = \text{constant}. \tag{3.145}$$

The above equation holds only for quasistatic, adiabatic processes in ideal gases that have heat capacities independent of temperature. You might think that it is such a restricted result that it holds little interest. This equation is used frequently in applications, in the graduate record examination, and in physics oral examinations! You should memorize it and know how to work with it.

Problems

3.30 Intensive vs. extensive variables

Equation (3.134), $E(T, V) = E(T)$, states that for an ideal gas the energy is a function of temperature alone. How is it possible for E, an extensive quantity, to be a function of only T, an intensive quantity?

3.31 Heat capacity at constant pressure

Equation (3.131) shows that the heat capacity at constant volume, which is defined in terms of an entropy derivative, is also equal to an energy derivative. You might suspect a similar relation between $C_p(T, p, N)$ and

$$\left.\frac{\partial E(T, p, N)}{\partial T}\right)_{p,N}.$$

Show that such a suspicion is *not* correct, and instead find an expression for C_p in terms of a derivative of enthalpy.

3.32 Qualitative heat capacity relations

(This problem is stolen from a GRE Physics test.)

For an ideal gas, C_p is greater than C_V because:

a. The gas does work on its surroundings when its pressure remains constant while its temperature is increased.

b. The heat input per unit increase in temperature is the same for processes at constant pressure and at constant volume.

c. The pressure of the gas remains constant when its temperature remains constant.

d. The increase in the gas's internal energy is greater when the pressure remains constant than when the volume remains constant.

e. The heat needed is greater when the volume remains constant than when the pressure remains constant.

3.33 Heat capacities in a magnetic system

For a magnetic system (see equation (3.100)), show that

$$C_H = T\,\frac{\partial S}{\partial T}\Big)_H, \quad C_M = T\,\frac{\partial S}{\partial T}\Big)_M, \quad \beta = \frac{\partial M}{\partial T}\Big)_H, \quad \text{and} \quad \chi_T = \frac{\partial M}{\partial H}\Big)_T \tag{3.146}$$

are related through

$$C_M = C_H - T\beta^2/\chi_T. \tag{3.147}$$

3.34 Isothermal compressibility

a. Show that the isothermal compressibility, defined in problem 1.2 as

$$\kappa_T = -\frac{1}{V}\,\frac{\partial V}{\partial p}\Big)_{T,N}, \tag{3.148}$$

is also given by

$$\kappa_T = \frac{1}{\rho}\,\frac{\partial \rho}{\partial p}\Big)_T = \frac{1}{\rho^2}\,\frac{\partial \rho}{\partial \mu}\Big)_T = \frac{1}{\rho^2}\,\frac{\partial^2 p}{\partial \mu^2}\Big)_T, \tag{3.149}$$

where ρ is the number density N/V. Clue:

$$\frac{\partial \rho}{\partial p}\Big)_T = \frac{\partial \rho}{\partial \mu}\Big)_T\,\frac{\partial \mu}{\partial p}\Big)_T. \tag{3.150}$$

b. What does this result tell you about the relation between density and chemical potential?

c. In part (a.) we began with a description in terms of the three variables T, p, N and then reduced it to an intensive-only description, which requires just two variables, such as μ and T. Reverse this process to show that

$$\kappa_T = \frac{V}{N^2}\,\frac{\partial N}{\partial \mu}\Big)_{T,V} = -\frac{1}{N}\,\frac{\partial V}{\partial \mu}\Big)_{T,N}. \tag{3.151}$$

3.35 Pressure differential

By regarding pressure as a function of temperature T and number density ρ, show that

$$dp = \frac{\beta}{\kappa_T}\,dT + \frac{1}{\rho\kappa_T}\,d\rho. \tag{3.152}$$

3.36 Isothermal *vs.* adiabatic compressibility

In class we derived a remarkable relation between the heat capacities C_p and C_V. This problem uncovers a similar relation between the isothermal and adiabatic compressibilities,

$$\kappa_T = -\frac{1}{V}\,\frac{\partial V}{\partial p}\Big)_T \quad \text{and} \quad \kappa_S = -\frac{1}{V}\,\frac{\partial V}{\partial p}\Big)_S. \tag{3.153}$$

The adiabatic compressibility κ_S is the compressibility measured when the fluid is thermally insulated. (It is related to the speed of sound: see problem 3.45.)

a. Use

$$dS = \left.\frac{\partial S}{\partial T}\right)_p dT + \left.\frac{\partial S}{\partial p}\right)_T dp \tag{3.154}$$

to show that

$$\left.\frac{\partial T}{\partial p}\right)_S = \frac{\beta T}{C_p/V}. \tag{3.155}$$

Sketch an experiment to measure this quantity directly.

b. From the mathematical relation

$$dV = \left.\frac{\partial V}{\partial p}\right)_T dp + \left.\frac{\partial V}{\partial T}\right)_p dT \tag{3.156}$$

derive the multivariate chain rule

$$\left.\frac{\partial V}{\partial p}\right)_S = \left.\frac{\partial V}{\partial p}\right)_T + \left.\frac{\partial V}{\partial T}\right)_p \left.\frac{\partial T}{\partial p}\right)_S, \tag{3.157}$$

whence

$$\kappa_S = \kappa_T - \frac{\beta^2 T}{C_p/V}. \tag{3.158}$$

c. Finally, show that

$$\gamma \equiv \frac{C_p}{C_V} = \frac{\kappa_T}{\kappa_S}. \tag{3.159}$$

3.37 **Change of chemical potential with temperature**

Prove that

$$\left.\frac{\partial \mu}{\partial T}\right)_{p,N} = -\frac{S}{N}, \tag{3.160}$$

and that

$$\left.\frac{\partial \mu}{\partial T}\right)_{V,N} = -\left.\frac{\partial S}{\partial N}\right)_{T,V} = -\frac{S}{N} + \frac{\beta}{\rho \kappa_T}. \tag{3.161}$$

How's that for weird?

3.9 Thermodynamics Applied to Phase Transitions

At phase coexistence between, say, gas and liquid

$$\mu_G(p,T) = \mu_L(p,T). \tag{3.162}$$

The Clausius-Clapeyron equation relates the slope of a phase coexistence line $p_x(T)$ with the volume and entropy changes when the sample crosses that line:

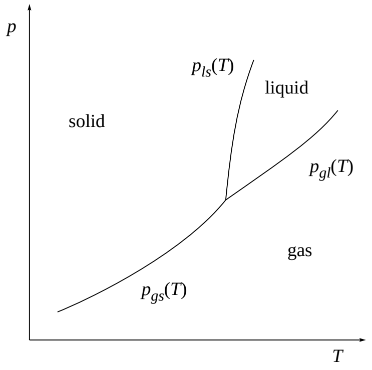
$$\frac{dp_x}{dT} = \frac{\Delta S}{\Delta V}. \tag{3.163}$$

In other words, you can find the slope of the phase coexistence line at one atmosphere by doing experiments only at one atmosphere! You'd think you'd need a pressure apparatus to find this information, but you don't.

Problems

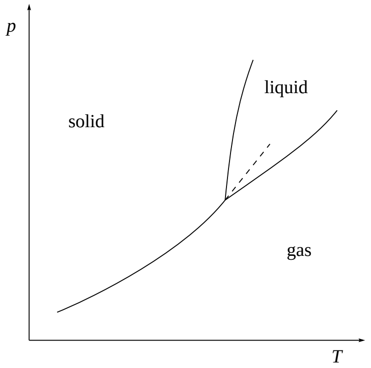
3.38 **Thermodynamics applied to the triple point**

A triple point has the usual arrangement of a rising gas-solid coexistence line splitting into two rising coexistence lines: a liquid-solid line and a gas-liquid line.

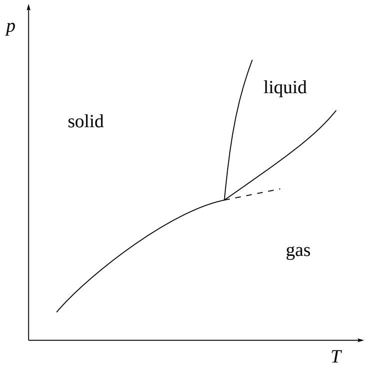


a. Relate the slopes of the three coexistence lines that meet at the triple point to the entropy changes $\Delta S_{gl} = S_{\text{gas}} - S_{\text{liquid}}$ and $\Delta S_{ls} = S_{\text{liquid}} - S_{\text{solid}}$.

b. Show that the gas-solid coexistence line, when extended beyond the triple point, must extend into the liquid phase as show below left. It must *not* extend into the gas phase as shown below right.



Possible

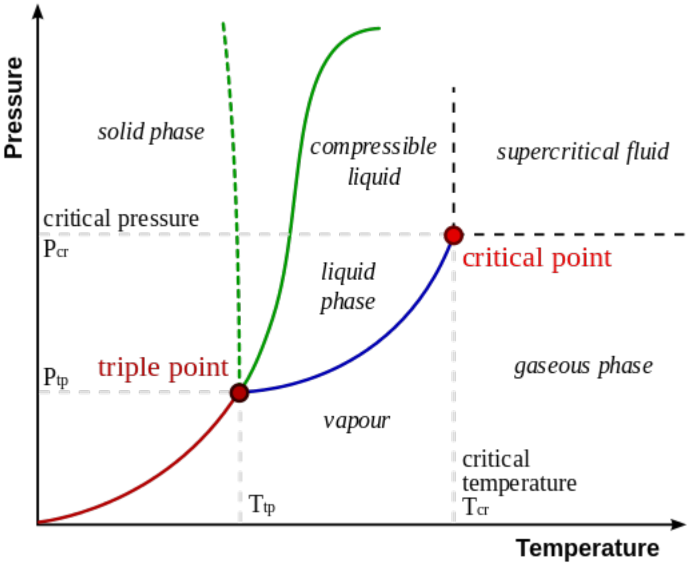


Impossible

[This result is called "the Schreinemakers 180° rule" after Franciscus A. H. Schreinemakers, Dutch chemist, 1864–1945.]

c. Show that in most cases, at the triple point the gas-solid coexistence line has nearly the same slope as the gas-liquid coexistence line.

d. The diagram below illustrates the Wikipedia article "Triple point" (15 December 2014). The caption is "A typical phase diagram. The solid green line applies to most substances; the dotted green line gives the anomalous behaviour of water." Critique this diagram.



3.39 Magnetic phase transitions

The phase diagrams for magnetic systems are usually plotted with temperature on the vertical axis and magnetic field H on the horizontal axis. Show that if such a diagram displays two-phase coexistence along the line $T_x(H)$, then that phase boundary has slope

$$\frac{dT_x}{dH} = -\frac{\Delta M}{\Delta S} \tag{3.164}$$

where ΔM is the magnetization change accompanying the phase transition.

3.40 Curvature of phase coexistence lines

a. Define

$$\beta' = \left.\frac{\partial v}{\partial T}\right)_p = v\beta \quad \text{and} \quad \kappa'_T = -\left.\frac{\partial v}{\partial p}\right)_T = v\kappa_T$$

and show that, for small changes of temperature δT and pressure δp, the resulting change in chemical potential will be

$$\delta\mu = -s\,\delta T + v\,\delta p + \tfrac{1}{2}\left[-\frac{c_p}{T}(\delta T)^2 + 2\beta'(\delta T)(\delta p) - \kappa'_T(\delta p)^2\right] + \cdots.$$

b. Show that for a change along a phase coexistence boundary $p_x(T)$,

$$\delta p = \frac{dp_x}{dT}\delta T + \tfrac{1}{2}\frac{d^2 p_x}{dT^2}(\delta T)^2 + \cdots.$$

c. If $\Delta s = s_A - s_B$, and similarly for Δv, Δc_p, etc., show that for any point on a phase coexistence boundary

$$0 = -\Delta s\,\delta T + \Delta v\,\delta p + \tfrac{1}{2}\left[-\frac{\Delta c_p}{T}(\delta T)^2 + 2\Delta\beta'(\delta T)(\delta p) - \Delta\kappa'_T(\delta p)^2\right] + \cdots.$$

d. Conclude that the slope of the phase coexistence curve is

$$\frac{dp_x}{dT} = \frac{\Delta s}{\Delta v},$$

the usual Clausius-Clapeyron equation, while the second derivative is

$$\frac{d^2 p_x}{dT^2} = \frac{\Delta c_p}{T\Delta v} - 2\frac{\Delta\beta'\Delta s}{(\Delta v)^2} + \frac{\Delta\kappa'_T(\Delta s)^2}{(\Delta v)^3}, \tag{3.165}$$

the "second-order Clausius-Clapeyron equation".

3.10 Thermodynamics Applied to Chemical Reactions

3.10.1 Thermodynamics of mixtures

So far in this book we have considered mostly pure substances. What happens if we have a mixture of several chemical species, say the four substances A, B, C, and D? In this case the mechanical parameters will include the numbers N_A, N_B, N_C, and N_D, and the entropy

$$S(E, V, N_A, N_B, N_C, N_D) \tag{3.166}$$

will have the total differential

$$dS = \frac{1}{T}\,dE + \frac{p}{T}\,dV - \sum_{i=A}^{D} \frac{\mu_i}{T}\,dN_i. \tag{3.167}$$

The differential above defines the quantity

$$\mu_A(E, V, N_A, N_B, N_C, N_D) = -T(E, V, N_A, N_B, N_C, N_D)\left.\frac{\partial S}{\partial N_A}\right)_{E,V,N_B,N_C,N_D}. \tag{3.168}$$

Notice that the chemical potential of substance A can depend upon the number of molecules of B, C, and D present, so it is not necessarily the same as the chemical potential of pure A. (For example, the chemical potential of sugar dissolved in a cup of water is not equal to the chemical potential of pure sugar, unless the solution is saturated and there is undissolved sugar at the bottom of the cup.)

It is convenient to define the total number of molecules

$$N = N_A + N_B + N_C + N_D \tag{3.169}$$

and the (intensive) fractional amounts

$$f_A = \frac{N_A}{N}, \text{ etc.} \tag{3.170}$$

The thermodynamic dance can be followed for mixtures just as well as it can be for pure substances. One noteworthy result is

$$\begin{aligned} G(T, p, N_A, N_B, N_C, N_D) &\equiv E - TS + pV \qquad (3.171)\\ &= \sum_{i=A}^{D} \mu_i(T, p, f_A, f_B, f_C, f_D) N_i \end{aligned}$$

3.10.2 Equilibrium condition for a chemical reaction

Suppose that α molecules of substance A can combine with β molecules of substance B to produce γ molecules of substance C and δ molecules of substance D. If this can happen, then of course the reverse can also occur: γ molecules of substance C may combine with δ molecules of substance D to produce α molecules of substance A and β molecules of substance B. The first action is called a "forward step" of the chemical reaction, and the second is called a "backward step". This chemical reaction is symbolized by

$$\alpha \text{ A} + \beta \text{ B} \Longleftrightarrow \gamma \text{ C} + \delta \text{ D}. \tag{3.172}$$

Thus if we mix together a certain number of molecules each of A, B, C, and D, there can be a reaction and we might not end up with the same distribution of molecules that we started off with. It is possible that there will be more forward than backwards steps, in which case we will end up with more C's and D's and fewer A's and B's than we had at the start, or it could go predominantly the other way. It is allowable for the system to exist in a wide range of conditions, varying from "mostly reactants" to "mostly products", but experience teaches us that the overwhelmingly likely condition is one with some of each are present. In this condition reactions still proceed, in both the forward and backward directions, but steps in both directions proceed at the same rate so there is no net change in the number of molecules of any species. This condition is called "chemical equilibrium".

The above paragraph precisely parallels the discussion in section 2.7, "Using entropy to find (define) temperature and pressure". In that section we saw that if, for example, two systems could exchange volume, it was possible for all the volume to go to one system or for all of it to go to the other system, but that the overwhelmingly likely possibility was the "equilibrium condition" in which the two systems shared volume in such a way that each had the same pressure. The equilibrium condition was the one with a maximum number of microstates (or, equivalently, a maximum entropy) with respect to the distribution of volume.

Precisely the same effect is at work in chemical equilibrium. The equilibrium state is characterized by a maximum in the entropy with respect to the number of number of reaction steps taken. At this equilibrium point the entropy doesn't change when the chemical reaction proceeds by one step in either direction. The change in entropy through a forward step is of course

$$-\alpha\frac{\partial S}{\partial N_A} - \beta\frac{\partial S}{\partial N_B} + \gamma\frac{\partial S}{\partial N_C} + \delta\frac{\partial S}{\partial N_D}, \tag{3.173}$$

and the change in entropy through a backward step is the negative of this. In either case, the equilibrium condition is that this change in entropy vanish, i.e. that

$$\alpha\mu_A + \beta\mu_B = \gamma\mu_C + \delta\mu_D. \tag{3.174}$$

Interpretation in terms of "escaping tendency".

If we specialize to the case of liquid-gas phase equilibrium, this equation is just equation (3.162).

We cannot go further without formulas for the chemical potentials μ. Complete formulas are not available within the realm of thermodynamics, but the next section shows that thermodynamics can put severe constraints on the permissible functional forms for μ.

3.10.3 Chemical potential of an ideal gas

I emphasized on page 69 that the equation of state did not contain full thermodynamic information. Thus, for example, knowledge of the equation of state $V(T,p,N)$ is not sufficient to uncover the master function $G(T,p,N)$. On the other hand, that knowledge is sufficient to restrict the functional form of the Gibbs potential, which in turn restricts the possible functional forms of the chemical potential. In this subsection we uncover that restriction.

Our strategy is to recognize that volume is the derivative of $G(T,p,N)$ with respect to p, and chemical potential is the derivative of $G(T,p,N)$ with respect to N. Given $V(T,p,N)$, we can integrate with respect to p to find $G(T,p,N)$, and then differentiate with respect to N to find $\mu(T,p)$. This process does not completely determine the Gibbs potential or the chemical potential, because a constant of integration is involved. But it does restrict the permissible functional forms of $G(T,p,N)$ and $\mu(T,p)$.

The master thermodynamic equation for variables (T,p,N) is

$$dG = -S\,dT + V\,dp + \mu\,dN, \tag{3.175}$$

whence

$$V(T,p,N) = \left.\frac{\partial G}{\partial p}\right)_{T,N}. \tag{3.176}$$

Thus for a substance obeying the ideal gas equation of state, we have

$$\frac{Nk_BT}{p} = \left.\frac{\partial G}{\partial p}\right)_{T,N}. \tag{3.177}$$

Integrating both sides with respect to p gives

$$Nk_BT \int \frac{dp}{p} = \int \left.\frac{\partial G}{\partial p}\right)_{T,N} dp \tag{3.178}$$

or

$$Nk_BT \ln\left(\frac{p}{\tilde{p}(T,N)}\right) = G(T,p,N). \tag{3.179}$$

The role of “constant of integration” is played by $\tilde{p}(T,N)$, which must be constant with respect to p but which may vary with T and N.

In fact, careful examination of the above equation shows what the dependence of $\tilde{p}(T,N)$ on N must be. The quantities G and N above are extensive, while T and p are intensive, so $\tilde{p}$ must be intensive so that both sides will depend linearly on system size. Thus $\tilde{p}$ is independent of N, and we have

$$G(T,p,N) = Nk_BT \ln\left(\frac{p}{\tilde{p}(T)}\right), \tag{3.180}$$

whence

$$\mu(T,p) = \frac{G(T,p,N)}{N} = k_BT \ln\left(\frac{p}{\tilde{p}(T)}\right). \tag{3.181}$$

This is the form of the Gibbs potential and of the chemical potential for any ideal gas. The function $\tilde{p}(T)$ is undetermined, and it is through differences in $\tilde{p}(T)$ that one ideal gas differs from another. But the dependence on p and on N are completely pinned down by the above results.

This result is frequently written in terms of the number density $\rho = N/V$. For an ideal gas $p = k_BT\rho$, and we can define the function $\tilde{\rho}(T)$ through $\tilde{p}(T) = k_BT\tilde{\rho}(T)$. Then we can write

$$\mu(T, \rho) = k_BT \ln\left(\frac{\rho}{\tilde{\rho}(T)}\right). \tag{3.182}$$

What if the ideal gas is a mixture of, say, the four chemical species A, B, C, and D? Exactly the same result applies for each species:

$$\mu_A(T, \rho_A) = k_BT \ln\left(\frac{\rho_A}{\tilde{\rho}_A(T)}\right) \tag{3.183}$$

where the function $\tilde{\rho}_A(T)$ is the same for a pure ideal gas of A and for an ideal gas mixture. The chemical potential μ_A is independent of the densities ρ_B, ρ_C, and ρ_D. I am looking for a purely thermodynamic argument to proved this result, but until I find it you'll have to accept this statistical argument: In an ideal gas the molecules of A don't interact with the molecules of B, C, and D, so they don't know whether or not such molecules are even present. The behavior of A thus can't depend upon the number of B, C, and D molecules present, and it will be the same even if there are 0 molecules of B, C, and D, that is if the gas is pure.

3.10.4 The equilibrium condition for idea gas reactions

[Before plunging in, I want to point out that there's a contradiction embodied in the term "ideal gas chemical reaction". In an ideal gas, molecules do not interact…when two molecules approach, they just pass right through each other. But a chemical reaction is a form of interaction! Clearly, in this section we are thinking of molecules that interact weakly unless they are very close to each other, but once they approach they interact strongly and react quickly.]

Putting together the general equilibrium condition for chemical reactions

$$\alpha\mu_A + \beta\mu_B = \gamma\mu_C + \delta\mu_D \tag{3.184}$$

with expression (3.183) for the chemical potential of an ideal gas gives the equilibrium condition

$$\alpha k_BT \ln\left(\frac{\rho_A}{\tilde{\rho}_A(T)}\right) + \beta k_BT \ln\left(\frac{\rho_B}{\tilde{\rho}_B(T)}\right) = \gamma k_BT \ln\left(\frac{\rho_C}{\tilde{\rho}_C(T)}\right) + \delta k_BT \ln\left(\frac{\rho_D}{\tilde{\rho}_D(T)}\right). \tag{3.185}$$

Using the properties of logarithms, this can be rewritten as

$$\left(\frac{\rho_A}{\tilde{\rho}_A(T)}\right)^\alpha \left(\frac{\rho_B}{\tilde{\rho}_B(T)}\right)^\beta = \left(\frac{\rho_C}{\tilde{\rho}_C(T)}\right)^\gamma \left(\frac{\rho_D}{\tilde{\rho}_D(T)}\right)^\delta,$$

or, after minor rearrangement, as

$$\frac{\rho_C^\gamma \rho_D^\delta}{\rho_A^\alpha \rho_B^\beta} = \frac{\tilde{\rho}_C^\gamma(T)\tilde{\rho}_D^\delta(T)}{\tilde{\rho}_A^\alpha(T)\tilde{\rho}_B^\beta(T)}. \tag{3.186}$$

Chemists like to write this equation in terms of "the concentration of A", written as [A], namely as

$$\frac{[\mathrm{C}]^\gamma[\mathrm{D}]^\delta}{[\mathrm{A}]^\alpha[\mathrm{B}]^\beta} = K(T), \tag{3.187}$$

where $K(T)$ is called the "equilibrium constant" (despite the fact that it is a function of temperature). This result is called the "law of mass action" despite the fact that it is not a fundamental law (we have just derived it) and even despite the fact that (because it holds only for ideal gases) it's not precisely true for any real substance! (And also, I might add, despite the fact that the "law" has nothing to do with "mass" or with "action".) Even though the result is poorly named, it shows just how valuable thermodynamics is in connecting disparate areas of research. Who would have guessed that the law of mass action follows from only thermodynamics and the ideal gas equation of state? We have proven the result without once doing a chemical experiment!

Problems

3.41 **Chemical potential for ideal gas mixtures**

The entropy $S(E, V, N_A, N_B)$ of a classical monatomic ideal gas mixture was uncovered using statistical mechanics in problem 2.16. Invert the result of that problem to find $E(S, V, N_A, N_B)$, then show that the temperature and pressure of an ideal gas mixture obey familiar results for pure ideal gases. Show that

$$\mu_A(T, p, f_A, f_B) = k_B T \ln\left[\left(\frac{h_0^2}{2\pi m_A (k_B T)^{5/3}}\right)^{3/2} p f_A\right], \tag{3.188}$$

and relate this expression to the form (3.183). Verify relation (3.172).

3.42 **Relations between equilibrium constants**

You measure the equilibrium constants for these three chemical reactions:

$$\begin{aligned} 2\,\mathrm{H_2} + \mathrm{O_2} &\iff 2\,\mathrm{H_2O} \\ \mathrm{H_2} + \mathrm{Cl_2} &\iff 2\,\mathrm{HCl} \\ \mathrm{Cl_2} + 2\,\mathrm{O_2} &\iff 2\,\mathrm{ClO_2} \end{aligned}$$

(Call those constants K_A, K_B, and K_C.) Find an expression for the equilibrium constant for the reaction

$$4\,\mathrm{ClO_2} + 2\,\mathrm{H_2O} \iff 4\,\mathrm{HCl} + 5\,\mathrm{O_2}$$

3.11 Thermodynamics Applied to Light

Another non-fluid system (see section 3.7).

See Robert E. Kelly, "Thermodynamics of blackbody radiation," *Am. J. Phys.* **49** (1981) 714–719, and Max Planck, *The Theory of Heat Radiation*, part II.

How do you get a "box of light?" This is blackbody (cavity) radiation: meaning radiation in thermal equilibrium. (Usually it's also in equilibrium with the cavity walls, but you could imagine a container with mirror walls. . .)

3.11.1 Fundamentals

The fundamental thermodynamic equation for this system involves the master function $E(S, V)$. It is

$$dE = T\,dS - p\,dV. \tag{3.189}$$

This equation differs from previously encountered master equations in that there is no term for $\mu\,dN$. From the classical perspective, this is because radiation is made up of fields, not particles. From the quantal perspective, this is because photon number is not conserved.

Thermodynamics binds one quantity to another, but it must use experiment (or statistical mechanics) to find the values being bound. For example, thermodynamics tells us that

$$C_p = C_V + TV\frac{\beta^2}{\kappa_T},$$

but it cannot calculate either C_p, or C_V, or β, or κ_T: these quantities must be found by experiment (or through a statistical mechanical calculation). The empirical result that we will employ is that for blackbody radiation,

$$p = \frac{1}{3}\frac{E}{V} = \frac{1}{3}u. \tag{3.190}$$

This equation of state is the parallel for blackbody radiation to $pV = Nk_BT$ for ideal gases. It was discovered by experiment, but it can be derived from electrodynamics as well.

3.11.2 Energy density as a function of temperature

Consider the energy as a function of volume and temperature. Because $E(V, T)$ is extensive, but in the argument list only V is extensive (recall that N doesn't appear in the argument list), we must have

$$E(V, T) = V u(T). \tag{3.191}$$

That is, the energy density u depends *only* upon temperature. What is this dependence?

We seek a differential equation for $u(T)$. Compare

$$dE = d(Vu) = V\,du + u\,dV = V\frac{du}{dT}\,dT + u\,dV \tag{3.192}$$

with

$$dE = T\,dS - p\,dV = T\,dS - \tfrac{1}{3}u\,dV. \tag{3.193}$$

Together these give us a formula for dS:

$$dS = \left(\frac{V}{T}\frac{du}{dT}\right) dT + \left[\frac{4}{3}\frac{u}{T}\right] dV. \tag{3.194}$$

The Maxwell relation associated with this differential is

$$\left.\frac{\partial(\quad)}{\partial V}\right)_T = \left.\frac{\partial[\quad]}{\partial T}\right)_V \tag{3.195}$$

or

$$\frac{1}{T}\frac{du}{dT} = \frac{4}{3}\frac{d[u/T]}{dT} = \frac{4}{3}\left[\frac{1}{T}\frac{du}{dT} - \frac{1}{T^2}u\right]. \tag{3.196}$$

A rearrangement gives

$$\frac{du}{dT} = 4\frac{u}{T} \tag{3.197}$$

or

$$4\frac{dT}{T} = \frac{du}{u}. \tag{3.198}$$

The solution is

$$4\ln T = \ln u + \text{ const} \tag{3.199}$$

whence

$$u(T) = \sigma T^4. \tag{3.200}$$

The Stefan-Boltzmann law!

3.11.3 Quasistatic adiabatic expansion of radiation

Consider a sample of radiation undergoing quasistatic adiabatic change of volume. The entropy is a constant during this process, although the value of that constant will of course depend on the particular sample that's expanding.

$$dE = T\,dS - p\,dV \tag{3.201}$$

but $dS = 0$, $E = uV$, and $p = u/3$ so

$$\begin{aligned} u\,dV + V\,du &= -\tfrac{1}{3}u\,dV \\ V\,du &= -\tfrac{4}{3}u\,dV \\ \ln u &= -\tfrac{4}{3}\ln V + \text{ const} \\ u &= KV^{-4/3} \end{aligned}$$

Recognizing that this constant will depend upon which adiabat is taken, i.e. that it will depend on the entropy, we write

$$u(S,V) = K(S)V^{-4/3}. \tag{3.202}$$

Using the Stefan-Boltzmann result $u = \sigma T^4$ we find that

$$T(S,V) = \frac{C(S)}{V^{1/3}}. \tag{3.203}$$

This explains the cooling of the universe as it expands from the initial “hot big bang” to the current “3° K microwave background.”

3.11.4 Thermodynamics of the energy spectrum

What if we consider not just the energy density per volume, but the energy density per volume and wavelength? Let

$$\bar{u}(T,\lambda)\,d\lambda \tag{3.204}$$

represent the energy per volume due to that radiation with wavelength between λ and $\lambda + d\lambda$. As you know, quantum mechanics was discovered through Planck's efforts to find a theoretical explanation for the measured function $\bar{u}(T,\lambda)$. This is not the place to describe Planck's work. Instead I want to focus on a purely thermodynamic result that was known long before Planck started his investigations.

This is Wien's law[8], which states that the function $\bar{u}(T,\lambda)$, which you'd think could have any old form, must be of the form

$$\bar{u}(T,\lambda) = T^5 f(\lambda T). \tag{3.205}$$

An immediate consequence of Wien's law is the Wien displacement theorem: The wavelength $\hat{\lambda}$ which maximizes $\bar{u}(T,\lambda)$ is inversely proportional to temperature:

$$\hat{\lambda}(T) = \frac{\text{constant}}{T}, \tag{3.206}$$

where the constant is the value of x that maximizes $f(x)$. The consequences of the Wien displacement theorem are familiar from daily life: low temperature objects (such as people) radiate largely in the infrared, moderate temperature objects (such as horseshoes in the forge) radiate largely in the red, while high temperature objects (such as the star Sirius) radiate largely in the blue.

I stated earlier that Wien's law is a purely thermodynamic result. That's almost true, but it also relies on one more fact from electrodynamics, a result called "no mode hoping":

> If the volume makes a quasistatic, adiabatic change from V_1 to V_2, then the light of wavelength in the range λ_1 to $\lambda_1 + d\lambda_1$ shifts into the range λ_2 to $\lambda_2 + d\lambda_2$ where
>
> $$\frac{\lambda_1}{V_1^{1/3}} = \frac{\lambda_2}{V_2^{1/3}}. \tag{3.207}$$

(This result may be derived rigorously from Maxwell's equations, but it's reasonable through this analogy: A string of length L vibrating in, say, its third mode, has wavelength $\lambda = \frac{3}{2}L$. If the length of the string is slowly changed, then the wave remains in its third mode, so λ/L is constant.)

Now we're ready to begin the derivation. Consider the quasistatic adiabatic expansion of light, and while that expansion is going on focus your attention on the light in wavelength range λ to $\lambda + d\lambda$. According to the "no mode hopping" result, during this expansion the quantity

$$\lambda/V^{1/3} \tag{3.208}$$

---

[8] Wien is pronounced like the English "veen".

remains constant during the expansion. Furthermore, according to equation (3.203) the quantity

$$TV^{1/3} \tag{3.209}$$

also remains constant. Multiplying these two equations, we find that the volume-independent quantity

$$T\lambda \tag{3.210}$$

remains constant during the expansion: this number characterizes the expansion.

Another such volume-independent constant can be found by repeating the reasoning of subsection 3.11.3, Quasistatic adiabatic expansion of radiation, but considering not the energy of all the radiation, but the energy of the radiation with wavelengths from λ to $\lambda + \Delta\lambda$. This energy is $E = \bar{u}V\Delta\lambda$, and the pressure due to this segment of the radiation is $p = \frac{1}{3}\bar{u}\Delta\lambda$. During a quasistatic adiabatic expansion, $dE = -p\,dV$, so

$$(V\Delta\lambda)\,d\bar{u} + (\bar{u}\Delta\lambda)\,dV + (\bar{u}V)\,d[\Delta\lambda] = -\tfrac{1}{3}\bar{u}\Delta\lambda\,dV. \tag{3.211}$$

During the expansion the volume and wavelengths are changing through (see equation 3.207)

$$\begin{aligned} \lambda &= cV^{1/3} \\ d\lambda &= c\tfrac{1}{3}V^{-2/3}\,dV = \frac{1}{3}\frac{\lambda}{V}\,dV \\ d[\Delta\lambda] &= \frac{1}{3}\frac{\Delta\lambda}{V}\,dV \end{aligned} \tag{3.212}$$

so we have

$$(V\Delta\lambda)\,d\bar{u} = -\tfrac{5}{3}\bar{u}\Delta\lambda\,dV. \tag{3.213}$$

Thus

$$\begin{aligned} V\,d\bar{u} &= -\tfrac{5}{3}\bar{u}\,dV \\ \ln\bar{u} &= -\tfrac{5}{3}\ln V + \text{ const} \\ \bar{u} &= KV^{-5/3} \end{aligned} \tag{3.214}$$

But equation (3.203) shows how a larger volume is related to a lower temperature, so the quantity

$$\frac{\bar{u}(T,\lambda)}{T^5} \tag{3.215}$$

remains constant during the expansion.

Thus we have two volume-independent ways to characterize the particular curve taken by this expansion. In the thermodynamics of light, a state is specified by two variables, so a curve is specified by only one parameter. Hence these two characterizations cannot be independent: one must be a function of the other. Thus

$$\frac{\bar{u}(T,\lambda)}{T^5} = f(\lambda T)$$

or

$$\bar{u}(T,\lambda) = T^5 f(\lambda T). \tag{3.216}$$

Wien's law.

Problems

3.43 **Heat capacity of light**

Show that, for blackbody radiation, $C_V = 4E/T$.

Resources

Thermodynamic tables. (G.N. Lewis and M. Randall) Zemansky. Practical heat engines. Callen. Fermi.

Math book. e.g. Taylor and Mann?

Picture of Smithsonian crystal on www?

Thermodynamic data (e.g. steam tables) on www?

3.12 Additional Problems

3.44 **Cool mountain air**

Model the earth's atmosphere as an ideal gas (nitrogen) in a uniform gravitational field. Ignore all winds. Let m denote the mass of a gas molecule, g the acceleration of gravity, and z the height above sea level.

a. Use ideas from Newtonian mechanics to show that the change of atmospheric pressure p with height z is

$$\frac{dp}{dz} = -\frac{mg}{k_B T(z)} p(z). \tag{3.217}$$

b. If the atmosphere is a poor conductor of heat, then the decrease in pressure with height is due to an adiabatic expansion. (*Clue:* In other words: At the bottom of the mountain, fill an insulated balloon with air at the local density, pressure, and temperature. Transport that balloon to the top of the mountain. During the journey the balloon will expand, so the density, pressure, and temperature will change. According to our assumption, during this journey the balloon's density, pressure, and temperature will match those of the atmosphere outside.) Show that under this assumption

$$\frac{dp}{dT} = \frac{\gamma}{\gamma - 1} \frac{p(T)}{T} \tag{3.218}$$

and hence that

$$\frac{dT}{dz} = -\frac{\gamma - 1}{\gamma} \frac{mg}{k_B}. \tag{3.219}$$

Evaluate this expression in kelvin per kilometer for nitrogen, which has $\gamma = 1.4$.

c. In contrast, if the atmosphere were a good conductor of heat, then temperature would be uniform. Find $p(z)$ under such circumstances. Denote the sea-level pressure and temperature by p_0 and T_0.

d. Similarly find $p(z)$ for an adiabatic atmosphere.

3.45 The speed of sound

When a sound wave passes through a fluid (liquid or gas), the period of vibration is short compared to the time necessary for significant heat flow, so the compressions may be considered adiabatic.

Analyze the compressions and rarefactions of fluid in a tube. The equilibrium mass density is ρ_0. Apply $\mathbf{F} = m\mathbf{a}$ to a slug of fluid of thickness Δx, and show that if the variations in pressure $p(x,t)$ are small then pressure satisfies the wave equation

$$\frac{\partial^2 p}{\partial t^2} = c^2 \frac{\partial^2 p}{\partial x^2} \tag{3.220}$$

where c, the speed of sound, is given by

$$c = \frac{1}{\sqrt{\rho_0 \kappa_S}}. \tag{3.221}$$

Optional: Use the results of problems 1.2 and 3.36 to show that, for an ideal gas,

$$c = \sqrt{\gamma \frac{k_B T}{m}}. \tag{3.222}$$

3.46 Thermodynamics of a plastic rod

(This problem is based on Reif problem 5.14.)

For a restricted range of lengths L and temperatures T, the tension force in a stretched plastic rod is

$$F(T,L) = aT^2(L - L_0), \tag{3.223}$$

where a is a positive constant and L_0 is the relaxed (unstretched) length of the rod. When $L = L_0$, the heat capacity C_L of the rod (measured at constant length) is given by $C_L(T, L_0) = bT$, where b is independent of temperature.

a. Write down the fundamental thermodynamic relation for this rod, expressing dE in terms of dS and dL.

b. Compute $(\partial S/\partial L)_T$. (Clue: Derive an appropriate Maxwell relation for the assembly with variables T and L.)

c. Knowing $S(T_0, L_0)$, integrate along an appropriate path to find $S(T,L)$ at any temperature and length within the range of applicability of the equation for $F(T,L)$.

d. If you start at $T = T_i$ and $L = L_i$ and then quasi-statically stretch a thermally insulated rod until it reaches length L_f, what is the final temperature T_f? Show than when $L_0 \le L_i < L_f$, the rod is cooled by this process.

e. Find the heat capacity $C_L(L,T)$ of the rod when its length is not necessarily L_0.

f. Find $(\partial T/\partial L)_S$ for arbitrary T and L. Can insulated stretches warm as well as cool the rod?

3.47 Magnetic cooling

At low temperatures, paramagnetic salts obey the Curie law

$$M = c\frac{H}{T}, \tag{3.224}$$

where c is a positive constant (see equation (3.100)). Assume that the heat capacity C_H is a constant independent of temperature and field. Suppose a sample at magnetic field H_i and temperature T_i is wrapped in insulation, and then the magnetic field is slowly reduced to zero. Find the final temperature, and show that it is less than T_i. This technique, known as "adiabatic demagnetization" is the refrigeration method used to produce the temperatures from about 1 kelvin to 1 microkelvin.

3.48 Thermodynamics of an electrochemical cell

Reif 5.16.

3.49 Thermodynamics and evolution

Read the essay "Thermodynamics and Evolution" by John W. Patterson, in *Scientists Confront Creationism*, Laurie R. Godfrey, ed. (Norton, New York, 1983), pages 99–116, on reserve in the science library.

a. When a snowflake forms, its surroundings increase in entropy ("become more disordered"). What is the name of the heat flow associated with this entropy change?

b. Patterson argues that $\Delta S < 0$ on Earth, due to biological evolution, and that $\Delta S > 0$ somewhere else in the universe in order to make up for it. Where is that entropy increase taking place?

c. Patterson feels the need to invoke "self-organization" and Prigogine (pages 110–111) to explain *how* his ram pumps could be made. Is this necessary? List two or more situations from nature in which water *does* flow uphill.

3.50 **Entropy and evolution**

Creationists sometimes claim that the second law of thermodynamics prohibits biological evolution.

a. The surface of the Sun (mean temperature 5778 K) heats the surface of the Earth (mean temperature 288 K) through visible and near-infrared radiation. The solar energy absorbed by the Earth each second is 1.732×10^{17} J. What is the entropy change per second (due to this process) of the Sun? The Earth? Does the entropy of "Sun plus Earth" increase or decrease?

b. Yet the mean temperature of the Earth changes slowly, if at all. This is because almost all of the solar energy absorbed by the Earth is then emitted through far-infrared radiation which in turn heats "outer space" — the cosmic microwave background (CMB; temperature 2.728 K). What is the entropy change per second (due to this process) of the Earth? The CMB? Does the entropy of "Earth plus CMB" increase or decrease?

c. Now refine the model by supposing that, due to evolution, the entropy of the Earth is not exactly constant, but is decreasing. (In this case the entropy of the CMB would have to be increasing faster than rate predicted in part (b).) Suppose that, due to evolution, each individual organism is 1000 times "more improbable" than the corresponding individual was 100 years ago. In other words, if Ω_i is the number of microstates consistent with the specification of an organism 100 years ago, and if Ω_f is the number of microstates consistent with the specification of today's "improved and less probable" organism, then $\Omega_f = 10^{-3}\Omega_i$. What is the corresponding change in entropy per organism?

d. The population of Earth is about 10^{18} eukaryotic individuals and 10^{32} prokaryotic individuals. If the estimate of part (c) holds for each one of them, what is the change in entropy due to evolution each second?

e. How accurately would you have to measure the entropy flux of part (b) in order to notice the diversion of entropy flux calculated in part (d)? Has any scientific quantity ever been measured to this accuracy?

f. It is generally agreed that the greatest rate of evolution fell during the Cambrian period, from 542 million years ago to 488 million years ago. During this so-called "Cambrian explosion" multicellular organisms first formed and then radiated into remarkable variety. Suppose that during the Cambrian period entropy was diverted into the evolution of living things at the rate calculated in part (d). And suppose that at the end of the Cambrian there were 10^{18} multicellular individuals. How much "improved and less probable" would each organism be, relative to its single-celled ancestor at the beginning of the Cambrian period?

The moral of the story? There's plenty of entropy to go around.

Chapter 4

Ensembles

After the last chapter's dip into thermodynamics, we return to the discussion of the principles of statistical mechanics begun in chapter 2.

4.1 The Canonical Ensemble

Examples of "systems" and "baths":

- Bottle of wine/a swimming pool.
- Sample of gas/laboratory temperature control apparatus.
- One ideal gas molecule/sample of gas.
- But *not* one interacting gas molecule/sample of gas. (The Boltzmann distribution is for systems within ensembles, not for molecules within systems.)

We denote a microstate by x. Exactly what is meant by a microstate will depend upon circumstances. For a system of point particles it means specifying all the positions and momenta. For a spin system it means specifying the "up" or "down" state of each spin. We'll see other examples later.

I'll try to use different letters for microscopic and macroscopic (thermodynamic) quantities. For example $H(\mathsf{x})$ versus E (the thermodynamic energy is $E = \langle H(\mathsf{x})\rangle$; $\mathcal{M}(\mathsf{x})$ versus $M = \langle \mathcal{M}(\mathsf{x})\rangle$.

Summary

The canonical ensemble in general:

The probability that the system is in the microstate x is proportional to the "Boltzmann factor"

$$e^{-H(\mathsf{x})/k_BT}. \tag{4.1}$$

The normalization factor is called the "partition function" or "sum over all states" (German "Zustandsumme"):

$$Z(T,V,N) = \sum_{\text{microstates } \mathsf{x}} e^{-H(\mathsf{x})/k_BT}. \tag{4.2}$$

(Note that Z is independent of x.) Thus the probability that the system is in microstate x is

$$\frac{e^{-H(\mathsf{x})/k_BT}}{Z(T,V,N)}. \tag{4.3}$$

The connection to thermodynamics is that the Helmholtz free energy is

$$F(T,V,N) = -k_BT \ln Z(T,V,N). \tag{4.4}$$

Note that in finding Z we sum over *all* microstates: the low-energy ones, the high-energy ones, the "orderly" ones (e.g. all atoms heading west, or all atoms heading east), the "disorderly" ones (e.g. atoms heading in scattered directions).

The canonical ensemble for a pure classical monatomic fluid:

The probability that the system is in the microstate Γ is proportional to the "Boltzmann factor"

$$e^{-H(\Gamma)/k_BT}. \tag{4.5}$$

Writing out all the normalizations correctly gives: the probability that the system is in some microstate within the phase space volume element $d\Gamma$ about Γ is

$$\frac{e^{-H(\Gamma)/k_BT}}{N!h_0^{3N}Z(T,V,N)}d\Gamma, \tag{4.6}$$

where the partition function is

$$Z(T,V,N) = \frac{1}{N!h_0^{3N}}\int e^{-H(\Gamma)/k_BT}\,d\Gamma. \tag{4.7}$$

(The integral runs over all of phase space.) This is an example of "partition function", namely the partition function for a pure classical monatomic fluid. It does not apply to mixtures, to crystals, to the ideal paramagnet. In contrast, the definition of "partition function" is equation (4.2), the "sum over all states" of the Boltzmann factor.

4.2 Meaning of the Term “Ensemble”

An ensemble is just a collection. For example, a musical group is an ensemble. Think of a bunch of systems filling up a huge gymnasium.

- Microcanonical ensemble: A collection of many systems, all with the same volume, particle number, particle mass, chemical composition, etc., and each with energy $E < H(x) \leq E + \Delta E$.
- Canonical ensemble: A collection of many systems, all with the same volume, particle number, particle mass, chemical composition, etc., and each connected to the same heat bath (whence each with the same temperature T).

The names (selected by J. Willard Gibbs) are pretty poor.

4.3 Classical Monatomic Ideal Gas

I’ve told you that it’s easier to do calculations in the canonical ensemble than in the microcanonical ensemble. Today I’m going to demonstrate the truth of this assertion.

Remember how we found the entropy $S(E, V, N)$ for a classical monatomic ideal gas? The hard part involved finding the volume of a shell in $3N$-dimensional space. It took us three or four hours to derive the Sackur-Tetrode formula (equation (2.32)), namely

$$S(E, V, N) = k_B N \left[\tfrac{3}{2} \ln \left(\frac{4\pi m E V^{2/3}}{3h_0^2 N^{5/3}} \right) + \tfrac{5}{2} \right]. \tag{4.8}$$

It took us another hour or so to show that the energy of this system is (equation (2.57))

$$E = \tfrac{3}{2} N k_B T \tag{4.9}$$

whence

$$S(T, V, N) = k_B N \left[\tfrac{3}{2} \ln \left(\frac{2\pi m k_B T V^{2/3}}{h_0^2 N^{2/3}} \right) + \tfrac{5}{2} \right]. \tag{4.10}$$

In this section, we’ll derive this same equation using the canonical ensemble. While the derivation is no stroll in the park, most people find it considerably easier than the microcanonical derivation.

Our strategy will be: (1) Integrate the Boltzmann factor over all phase space to find the partition function $Z(T, V, N)$. (2) Find the Helmholtz free energy using

$$F(T, V, N) = -k_B T \ln(Z(T, V, N)). \tag{4.11}$$

And finally (3) use the thermodynamic result

$$S(T, V, N) = -\left.\frac{\partial F}{\partial T}\right)_{V,N} \tag{4.12}$$

to find the entropy.

The Hamiltonian for this model system is

$$H(\Gamma) = \frac{1}{2m}(p_{x,1}^2 + p_{y,1}^2 + p_{z,1}^2 + p_{x,2}^2 + \cdots + p_{z,N}^2) + U(\mathbf{x}_1) + U(\mathbf{x}_2) + \cdots + U(\mathbf{x}_N), \tag{4.13}$$

where the potential energy function for each individual atom as a function of its location $\mathbf{x}$ is

$$U(\mathbf{x}) = \begin{cases} 0 & \text{if } \mathbf{x} \text{ is inside the container} \\ \infty & \text{if outside.} \end{cases} \tag{4.14}$$

This has been background. Now we're ready to roll up our sleeves and plunge into the work. Any questions? Okay, let's go.

The canonical partition function is

$$\begin{aligned} Z(T,V,N) &= \frac{1}{N!h_0^{3N}} \int d\Gamma\, e^{-\beta H(\Gamma)} \qquad (4.15) \\ &= \frac{1}{N!h_0^{3N}} \int_{-\infty}^{+\infty} dx_1 \int_{-\infty}^{+\infty} dy_1 \int_{-\infty}^{+\infty} dz_1 \cdots \int_{-\infty}^{+\infty} dx_N \int_{-\infty}^{+\infty} dy_N \int_{-\infty}^{+\infty} dz_N \\ &\quad \times \int_{-\infty}^{+\infty} dp_{x,1} \int_{-\infty}^{+\infty} dp_{y,1} \int_{-\infty}^{+\infty} dp_{z,1} \cdots \int_{-\infty}^{+\infty} dp_{x,N} \int_{-\infty}^{+\infty} dp_{y,N} \int_{-\infty}^{+\infty} dp_{z,N}\, e^{-\beta H(\Gamma)}. \end{aligned}$$

There are N triplets of integrals over positions and N triplets of integrals over momenta…in total, a $6N$-dimensional integral. Because the Hamiltonian consists of a sum of terms, the Boltzmann factor consists of a product of quantities:

$$e^{-\beta H(\Gamma)} = e^{-\beta(p_{x,1}^2/2m)} e^{-\beta(p_{y,1}^2/2m)} \times \cdots \times e^{-\beta(p_{z,N}^2/2m)} e^{-\beta U(\mathbf{x}_1)} e^{-\beta U(\mathbf{x}_2)} \times \cdots \times e^{-\beta U(\mathbf{x}_N)}. \tag{4.16}$$

More importantly, however, each of these quantities depends on a different set of variables. Therefore the partition function also breaks up into a product of quantities:

$$\begin{aligned} Z(T,V,N) &= \frac{1}{N!h_0^{3N}} \left[\int_{-\infty}^{+\infty} dx_1 \int_{-\infty}^{+\infty} dy_1 \int_{-\infty}^{+\infty} dz_1\, e^{-\beta U(\mathbf{x}_1)} \right] \times \cdots \times \left[\int_{-\infty}^{+\infty} dx_N \int_{-\infty}^{+\infty} dy_N \int_{-\infty}^{+\infty} dz_N\, e^{-\beta U(\mathbf{x}_N)} \right] \\ &\quad \times \left[\int_{-\infty}^{+\infty} dp_{x,1}\, e^{-\beta(p_{x,1}^2/2m)} \right] \times \cdots \times \left[\int_{-\infty}^{+\infty} dp_{z,N}\, e^{-\beta(p_{z,N}^2/2m)} \right]. \end{aligned}$$

The partition function, which in general is a $6N$-dimensional integral, has been reduced in this case to a product of N three-dimensional integrals over position and $3N$ one-dimensional integrals over momentum. (This near-miraculous simplification comes about because all of the limits of integration are constants…if the limits of integration of $p_{y,1}$ were functions of $p_{x,1}$—as they are in the microcanonical ensemble—then it wouldn't happen.)

Moreover, the N position integrals differ only in the dummy variable of integration: they all have the same value. The same holds for the $3N$ integrals over momentum. The partition function is nothing more than

$$\begin{aligned} Z(T,V,N) &= \frac{1}{N!h_0^{3N}} \left[\int_{-\infty}^{+\infty} dx \int_{-\infty}^{+\infty} dy \int_{-\infty}^{+\infty} dz\, e^{-\beta U(\mathbf{x})} \right]^N \\ &\quad \times \left[\int_{-\infty}^{+\infty} dp\, e^{-\beta(p^2/2m)} \right]^{3N}. \end{aligned} \tag{4.17}$$

It is not difficult to evaluate the two integrals remaining. The position integral ranges over all space, but for any point in space outside of the container, its integrand is

$$e^{-\beta U(\mathbf{x})} = e^{-\beta(\infty)} = 0. \tag{4.18}$$

Meanwhile, for any point in space within the container, the integrand is

$$e^{-\beta U(\mathbf{x})} = e^{-\beta(0)} = 1. \tag{4.19}$$

Thus

$$\int_{-\infty}^{+\infty} dx \int_{-\infty}^{+\infty} dy \int_{-\infty}^{+\infty} dz\, e^{-\beta U(\mathbf{x})} = \int\int\int_{\text{container}} dx_1 dy_1 dz_1\, 1 = V. \tag{4.20}$$

Meanwhile, the momentum integral is a clear cousin to the Gaussian integral (equation B.5)

$$\int_{-\infty}^{+\infty} e^{-u^2}\, du = \sqrt{\pi}. \tag{4.21}$$

Use of the substitution $u = \sqrt{\beta/2m}\, p$ in the momentum integral gives

$$\int_{-\infty}^{+\infty} dp\, e^{-\beta(p^2/2m)} = \sqrt{2m/\beta} \int_{-\infty}^{+\infty} e^{-u^2}\, du = \sqrt{2\pi m k_B T}. \tag{4.22}$$

Putting all this together gives us

$$Z(T,V,N) = \frac{V^N}{N! h_0^{3N}} \left(\sqrt{2\pi m k_B T}\right)^{3N} = \frac{1}{N!}\left(\frac{2\pi m k_B T V^{2/3}}{h_0^2}\right)^{3N/2}. \tag{4.23}$$

We've completed the first step of our three-step plan. Now we must find the free energy

$$F(T,V,N) = -k_B T \ln Z = -k_B T \ln\left[\frac{1}{N!}\left(\frac{2\pi m k_B T V^{2/3}}{h_0^2}\right)^{3N/2}\right]. \tag{4.24}$$

Something's a bit funny here. If we double V and N, we should double F, but this doesn't exactly happen: that factor of $N!$ is sure to mess things up. What's gone wrong? We ran into the same problem in when we used the microcanonical ensemble (at equation (2.24)) and it has the same solution: we must take the thermodynamic limit. For large values of N,

$$\begin{aligned} F(T,V,N) &= -k_B T \ln\left[\frac{1}{N!}\left(\frac{2\pi m k_B T V^{2/3}}{h_0^2}\right)^{3N/2}\right] \\ &= -k_B T \left[\ln\left(\frac{2\pi m k_B T V^{2/3}}{h_0^2}\right)^{3N/2} - \ln N!\right] \\ &\approx -k_B T \left[\tfrac{3}{2} N \ln\left(\frac{2\pi m k_B T V^{2/3}}{h_0^2}\right) - N\ln N + N\right]. \end{aligned}$$

But

$$-N\ln N = \tfrac{3}{2}N(-\tfrac{2}{3}\ln N) = \tfrac{3}{2}N\ln(N^{-2/3}),$$

so

$$F(T,V,N) = -k_BTN\left[\tfrac{3}{2}\ln\left(\frac{2\pi mk_BTV^{2/3}}{h_0^2N^{2/3}}\right)+1\right]. \tag{4.25}$$

This feels a lot healthier: If we double both V and N, then the ratio $(V^{2/3}/N^{2/3})$ is unchanged, so the free energy exactly doubles.

Now the final step: Take the derivative with respect to temperature to find the entropy. To do this, recognize that within the square brackets we have

$$\left[\tfrac{3}{2}\ln(T)+\text{ a lot of things independent of }T\right].$$

With this realization the derivative becomes straightforward:

$$S(T,V,N) = -\left.\frac{\partial F}{\partial T}\right)_{V,N} = k_BN\left[\tfrac{3}{2}\ln\left(\frac{2\pi mk_BTV^{2/3}}{h_0^2N^{2/3}}\right)+1\right]+k_BTN\left[\tfrac{3}{2}\frac{1}{T}\right] \tag{4.26}$$

or

$$S(T,V,N) = k_BN\left[\tfrac{3}{2}\ln\left(\frac{2\pi mk_BTV^{2/3}}{h_0^2N^{2/3}}\right)+\tfrac{5}{2}\right]. \tag{4.27}$$

Wow. This is exactly the same as expression (4.10), which came from a (considerably longer) microcanonical derivation.

We've come a long way and it is certainly appropriate to take a moment here to bask in our triumph. But while doing so, a small but troubling question might arise: Why *should* we get the same answer from a canonical and a microcanonical calculation? After all, the ensembles in question are quite distinct: In a microcanonical ensemble each system has the same energy. In a canonical ensemble the individual systems can have any energy they'd like, as reflected by states that range from crystalline to plasma. Why should we get identical entropies from such very different collections?

Loose remark: One often hears that for a gas at temperature T, the probability of an atom having energy E is proportional to the "Boltzman factor" e^{-E/k_BT}. This is true only for non-interacting atoms. If the atoms interact then the kinetic energy belongs to atoms but the potential energy belongs to atom pairs, so it's impossible to define "the energy of an atom". What is always true is that in the canonical ensemble at temperature T, the probability of a system having energy E is proportional to e^{-E/k_BT}.

4.4 Energy Dispersion in the Canonical Ensemble

The systems in the canonical ensemble are not restricted to having just one particular energy or falling within a given range of energies. Instead, systems with any energy from the ground state energy to infinity are present in the ensemble, but systems with higher energies are less probable. In this circumstance, it is important to ask not only for the mean energy, but also for the dispersion (uncertainty, fluctuation, spread, standard deviation) in energy.

Terminology: "Uncertainty" suggests that there's one correct value, but measurement errors prevent your knowing it. (For example: "You are 183.3 ± 0.3 cm tall.") "Dispersion" suggests that there are several values, each one correct. (For example: "The mean height of people in this room is 172 cm, with a dispersion (as measured by the standard deviation) of 8 cm.") "Fluctuation" is similar to "dispersion," but suggests that the value changes with time. (For example: My height fluctuates between when I slouch and when I stretch.) This book will use the term "dispersion" or, when tradition dictates, "fluctuation." Other books use the term "uncertainty."

The energy of an individual member of the ensemble we call $H(\mathsf{x})$, whereas the average energy of the ensemble members we call E:

$$\begin{aligned} H(\mathsf{x}) &= \text{microscopic energy of an individual system} && (4.28)\\ E &= \langle H(\mathsf{x})\rangle = \text{thermodynamic energy for the ensemble.} && (4.29)\end{aligned}$$

The dispersion in energy ΔE is given through

$$\begin{aligned} \Delta E^2 &= \langle (H(\mathsf{x}) - E)^2\rangle && (4.30)\\ &= \langle H^2(\mathsf{x}) - 2H(\mathsf{x})E + E^2\rangle \\ &= \langle H^2(\mathsf{x})\rangle - 2E^2 + E^2 \\ &= \langle H^2(\mathsf{x})\rangle - E^2 \\ &= \langle H^2(\mathsf{x})\rangle - \langle H(\mathsf{x})\rangle^2 && (4.31)\end{aligned}$$

This relation, which holds for the dispersion of any quantity under any type of average, is worth memorizing. Furthermore it's easy to memorize: The only thing that might trip you up is whether the result is $\langle H^2\rangle - \langle H\rangle^2$ or $\langle H\rangle^2 - \langle H^2\rangle$, but the result must be positive (it is equal to ΔE^2) and it's easy to see that the average of the squares must exceed the square of the averages (consider a list of data containing both positive and negative numbers).

Now it remains to find $\langle H^2(\mathsf{x})\rangle$. Recall that we evaluated $\langle H(\mathsf{x})\rangle$ through a slick trick ("parametric differentiation") involving the derivative

$$\left.\frac{\partial \ln Z}{\partial \beta}\right)_{\text{parameters}}, \tag{4.32}$$

namely

$$\frac{\partial \ln Z}{\partial \beta} = \frac{1}{Z}\frac{\partial Z}{\partial \beta} = \frac{1}{Z}\frac{\partial}{\partial \beta}\left(\sum_{\mathsf{x}} e^{-\beta H(\mathsf{x})}\right) = -\frac{\displaystyle\sum_{\mathsf{x}} H(\mathsf{x})e^{-\beta H(\mathsf{x})}}{\displaystyle\sum_{\mathsf{x}} e^{-\beta H(\mathsf{x})}} = -E \tag{4.33}$$

The essential part of the trick was that the derivative with respect to β pulls down an $H(\mathsf{x})$ from the exponent in the Boltzmann factor. In order to pull down two factors of $H(\mathsf{x})$, we will need to take two derivatives. Thus the average $\langle H^2(\mathsf{x})\rangle$ must be related to the second-order derivative

$$\left.\frac{\partial^2 \ln Z}{\partial \beta^2}\right)_{\text{parameters}}. \tag{4.34}$$

To see precisely how this works out, we take

$$\begin{aligned}
\frac{\partial^2 \ln Z}{\partial \beta^2} &= -\frac{\left(\sum_{\mathsf{x}} e^{-\beta H(\mathsf{x})}\right)\left(-\sum_{\mathsf{x}} H^2(\mathsf{x}) e^{-\beta H(\mathsf{x})}\right) - \left(\sum_{\mathsf{x}} H(\mathsf{x}) e^{-\beta H(\mathsf{x})}\right)\left(-\sum_{\mathsf{x}} H(\mathsf{x}) e^{-\beta H(\mathsf{x})}\right)}{\left(\sum_{\mathsf{x}} e^{-\beta H(\mathsf{x})}\right)^2} \\
&= \frac{\sum_{\mathsf{x}} H^2(\mathsf{x}) e^{-\beta H(\mathsf{x})}}{\sum_{\mathsf{x}} e^{-\beta H(\mathsf{x})}} - \left(\frac{\sum_{\mathsf{x}} H(\mathsf{x}) e^{-\beta H(\mathsf{x})}}{\sum_{\mathsf{x}} e^{-\beta H(\mathsf{x})}}\right)^2 \\
&= \langle H^2(\mathsf{x})\rangle - \langle H(\mathsf{x})\rangle^2.
\end{aligned}$$

For our purposes, this result is better than we could ever possibly have hoped. It tells us that

$$\Delta E^2 = \frac{\partial^2 \ln Z}{\partial \beta^2} = -\frac{\partial E}{\partial \beta} = -\frac{\partial E}{\partial T}\frac{\partial T}{\partial \beta}. \tag{4.35}$$

To simplify the rightmost expression, note that

$$\frac{\partial E}{\partial T} = C_V \quad \text{and} \quad \frac{\partial \beta}{\partial T} = \frac{\partial(1/k_B T)}{\partial T} = -\frac{1}{k_B T^2},$$

whence

$$\Delta E^2 = k_B T^2 C_V$$

or

$$\Delta E = T\sqrt{k_B C_V}. \tag{4.36}$$

This result is called a “fluctuation-susceptibility theorem”.

Analogy: “susceptibility” means “herd instinct”. A herd of goats is highly susceptible to external influence, because a small influence (such as a waving handkerchief) will cause the whole herd to stampede. On the other hand a herd of cows is insusceptible to external influence. . . indeed, cowherds often talk about how hard it is to get the herd into motion. A politician is susceptible if he or she is readily swayed by the winds of public opinion. The opposite of “susceptible” is “steadfast” or “stalwart”. If a herd (or politician) is highly susceptible, you expect to see large fluctuations. A herd of goats runs all over its pasture, whereas a herd of cows stays pretty much in the same place.

How does ΔE behave for large systems, that is “in the thermodynamic limit”? Because C_V is intensive, ΔE goes up like $\sqrt{N}$ as the thermodynamic limit is approached. But of course, we expect things to go to infinity in the thermodynamic limit! There will be infinite number, volume, energy, entropy, free energy, etc. The question is what happens to the relative dispersion in energy, $\Delta E/E$. This quantity goes to zero in the thermodynamic limit.

This resolves the question raised at the end of the previous section. A system in a canonical ensemble is *allowed to* have any energy from ground state to infinity. But most of the systems will not make use of that option: they will *in fact* have energies falling within a very narrow band about the mean energy. For larger and larger systems, this energy band becomes more and more narrow. *This* is why the canonical entropy is the same as the microcanonical entropy.

When a bottle of salad dressing sits out on your kitchen counter, connected to the heat bath of your kitchen, that bottle is one element of a canonical ensemble. The temperature is fixed at the temperature of the kitchen, and the energy can fluctuate. But the fluctuations are so small (in the thermodynamic limit) that they are noticeable only through highly accurate measurements. Wrap that same bottle in an insulating blanket[1] and it is now one element of a microcanonical ensemble. The energy is fixed. The concepts of microcanonical vs. canonical ensemble are dramatically different (insulated vs. thermalizing walls). The associated calculations are dramatically different ($3N$-dimensional sphere vs. gaussian integrals). But any cook knows that you don't change the flavor of salad dressing by wrapping it in an insulating blanket: those dramatic differences result always in the same physical properties.

4.5 Temperature as a Control Variable for Energy (Canonical Ensemble)

Note distinction!

$\mathcal{P}(\mathsf{x})$ is the probability of falling in a particular microstate x. This happens to be a function only of the energy of the microstate, whence this function is often called $\mathcal{P}(H(\mathsf{x}))$. (For a continuous system, $\mathcal{P}(\mathsf{x})$ corresponds to $p(\Gamma)d\Gamma$…the probability of the system falling in some phase space point within the volume $d\Gamma$ about point Γ.)

$P(H)$ is the probability of having a particular energy. It is equal to $\mathcal{P}(H(\Gamma))\Omega(H)$. ($\Omega(H)$: the number of microstates with energy H.)

Temperature as persuasion.

Temperature as an energy control parameter.

Analogy: "The Jim Smith effect." A man asks a statistician "What is the probability that a man named Milton Abramowitz will win the lottery?" The questioner, whose name is Milton Abramowitz, is disappointed when the statistician's answer is so tiny. So he tries again: "What is the probability that a man named Jim Smith will win the lottery?" The statistician replies with a number that is still small, but not quite so small as the first reply. In response, the man changes his name to Jim Smith.[2]

Because $\mathcal{P}(H(\Gamma))$ decreases rapidly with H, and $\Omega(H)$ increases rapidly with H, we expect $P(H)$ to be pretty sharply peaked near some $\langle H\rangle$ (recall the arguments of section 2.7.3). We also expect this peak to become sharper and sharper as the system becomes larger and larger (approaching "the thermodynamic limit").

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[1] Do not heat or cool the bottle before wrapping it.

[2] Only the most ardent students of American history know that Jim Smith signed the Declaration of Independence.

Even at high temperature, the most probable microstate is the ground state. However the most probable energy increases with temperature.

In the canonical ensemble (where all microstates are "accessible") the microstate most likely to be occupied is the ground state, and this is true *at any positive temperature, no matter how high.* The ground state energy is not the most probable energy, nor is the ground state typical, yet the ground state is the most probable microstate. In specific, even at a temperature of 1 000 000 K, a sample of helium is more likely to be in a particular crystalline microstate than in any particular plasma microstate. However, there are so many more plasma than crystalline microstates that (in the thermodynamic limit) the sample occupies a plasma macrostate with probability 1.

Economic analogy for temperature as an energy control parameter: strict regulation versus incentives. "Market-based approaches work more efficiently than clumsy command-and-control techniques"—Alan S. Blinder, "Needed: Planet Insurance", New York *Times*, 22 October 1997, page A23.

4.1 **Probability of microstate vs. probability of energy**

$\mathcal{P}(H)$ is the probability of being in a particular microstate with energy H, whereas $P(H)\,dH$ is the probability of being in any microstate whose energy falls within the range H to $H+dH$. The number of microstates with energy from H to $H+dH$ is $\Omega(H)\,dH$.

Following the arguments of section 2.7.1 ("Rapidly increasing character of the $\Omega(H)$ function"), assume that $\Omega(H) = cH^\nu$. (For a classical monatomic ideal gas of N atoms, $\nu = (3/2)N$.) Show that under this assumption

$$Z(T,V,N) = c(k_BT)^{\nu+1}\Gamma(\nu+1). \tag{4.37}$$

Does Z have the correct dimensions? Show that

$$\mathcal{P}(H) = \frac{e^{-H/k_BT}}{c(k_BT)^{\nu+1}\Gamma(\nu+1)} \quad \text{while} \quad P(H) = \frac{H^\nu e^{-H/k_BT}}{(k_BT)^{\nu+1}\Gamma(\nu+1)}. \tag{4.38}$$

Sketch $\Omega(H)$, $\mathcal{P}(H)$, and $P(H)$.

4.6 The Equivalence of Canonical and Microcanonical Ensembles

In a microcanonical ensemble the individual systems are all restricted, by definition, to have a given energy. In a canonical ensemble the individual systems are *allowed* to have any energy, from that of the ground state to that of an ionized plasma, but we have seen that (for large systems) they tend not to use this permission and instead they cluster within a narrow band of energies. We might expect, therefore, that a calculation performed in the microcanonical ensemble for systems at a given energy value, say 5 joules, would give the same results as a calculation performed in the canonical ensemble for systems at whatever temperature corresponds to an average energy of 5 joules.

If the canonical and microcanonical ensembles give the same results, why bother with the canonical ensemble? We will see soon (section 5.1) that calculations are much easier to perform in the canonical ensemble.

4.7 The Grand Canonical Ensemble

Grand as in the French "big" rather than as in the English "magnificent". This ensemble is "bigger" than the canonical ensemble in that there are more possible microstates.

Summary

The grand canonical ensemble for a pure classical monatomic fluid:

The probability that the system has N particles and is in the microstate Γ_N is proportional to

$$e^{-\beta(H(\Gamma_N)-\mu N)}, \tag{4.39}$$

where

$$\beta = \frac{1}{k_B T}. \tag{4.40}$$

Writing out all the normalizations correctly gives: the probability that the system has N particles and is in some microstate within the phase space volume element $d\Gamma_N$ about Γ_N is

$$\frac{e^{-\beta(H(\Gamma_N)-\mu N)}}{N!h_0^{3N}\Xi(\beta,V,\mu)}d\Gamma_N, \tag{4.41}$$

where the "grand canonical partition function" is

$$\begin{aligned}
\Xi(\beta,V,\mu) &= \sum_{N=0}^{\infty}\frac{1}{N!h_0^{3N}}\int e^{-\beta(H(\Gamma_N)-\mu N)}\,d\Gamma_N & (4.42)\\
&= \sum_{N=0}^{\infty} e^{\beta\mu N}Z(\beta,V,N). & (4.43)
\end{aligned}$$

This sum is expected to converge when μ is negative.

The connection to thermodynamics is that

$$\Pi(T,V,\mu) = -p(T,\mu)V = -k_B T\ln\Xi(T,V,\mu). \tag{4.44}$$

4.8 The Grand Canonical Ensemble in the Thermodynamic Limit

This section uncovers results that are of interest in their own right, but it also serves as an example of a mathematically rigorous argument in statistical mechanics.

Definitions. The grand partition function is

$$\Xi(T,V,\alpha) = \sum_{N=0}^{\infty} e^{-\alpha N}Z(T,V,N), \tag{4.45}$$

the Helmholtz free energy is

$$F(T,V,N) = -k_BT\ln Z(T,V,N), \tag{4.46}$$

and the chemical potential is

$$\mu(T,V,N) = \left.\frac{\partial F(T,V,N)}{\partial N}\right)_{T,V}. \tag{4.47}$$

Theorem. *Consider a grand canonical ensemble of hard-core particles at equilibrium with a bath of temperature T and "number control parameter" α. There is a "most probable value of N", called $\hat{N}$ (a function of T, V, and α), satisfying*

$$\alpha = -\frac{\mu(T,V,\hat{N})}{k_BT}, \tag{4.48}$$

such that, in the thermodynamic limit,

$$-k_BT\ln\Xi(T,V,\alpha) \to -\mu(T,V,\hat{N})\hat{N} + F(T,V,\hat{N}). \tag{4.49}$$

Strategy. The theorem assumes hard-core particles so that there will be a maximum number of particles in any given volume, whence the sum (4.45) is finite rather than infinite, and convergence questions do not arise. (Less restrictive conditions—e.g. that the repulsion between two nearby particles increases rapidly enough as they are brought together—may be used instead of the hard-core condition, but then the proof becomes more technical and less insightful.) The proof works by establishing both upper and lower bounds on sum (4.45), and then showing that, in the thermodynamic limit, these two bounds are equal.

Proof. Assume that each hard-core particle has volume v_0. Then the maximum number of particles that can fit into a container of volume V is $N^* \le V/v_0$. Thus the sum in equation (4.45) does not go to ∞, but stops at N^*.

We will need a trivial mathematical result, called "the method of the maximum term": If f_N is a sequence of positive terms, $N = 0, 1, \ldots N^*$, and if the maximum element of the sequence is $\max\{f_N\}$, then

$$\max\{f_N\} \le \sum_{N=0}^{N^*} f_N \le (N^*+1)\max\{f_N\}. \tag{4.50}$$

Applying this result to the sum (4.45), we obtain

$$\max\{e^{-\alpha N}Z_N\} \le \Xi \le (N^*+1)\max\{e^{-\alpha N}Z_N\}, \tag{4.51}$$

where Z_N is shorthand for $Z(T,V,N)$. Taking the logarithm of each side, and realizing that $\ln\max\{f\} = \max\{\ln f\}$, gives

$$\max\{-\alpha N + \ln Z_N\} \le \ln\Xi \le \ln(N^*+1) + \max\{-\alpha N + \ln Z_N\}. \tag{4.52}$$

To prepare for taking the thermodynamic limit, we divide both sides by V and employ the definition $F_N = -k_BT\ln Z_N$, resulting in

$$\max\left\{-\alpha\frac{N}{V} - \frac{F_N}{k_BTV}\right\} \le \frac{\ln\Xi}{V} \le \frac{\ln(N^*+1)}{V} + \max\left\{-\alpha\frac{N}{V} - \frac{F_N}{k_BTV}\right\}. \tag{4.53}$$

Consider the difference between these upper and lower bounds. It is clear that

$$0 \le \frac{\ln(N^* + 1)}{V} \le \frac{\ln(V/v_0 + 1)}{V}. \tag{4.54}$$

In the limit as $V \to \infty$, the right hand side above approaches 0, so

$$\frac{\ln(N^* + 1)}{V} \to 0. \tag{4.55}$$

Thus in the thermodynamic limit the lower bound approaches the upper bound, and

$$\frac{\ln \Xi}{V} \to \max\left\{-\alpha\frac{N}{V} - \frac{F_N}{k_B T V}\right\}. \tag{4.56}$$

Now we need to find the maximum of the quantity in curly brackets above. The maximum is located at $N = \hat{N}$, which we find by taking the partial derivative with respect to N and setting it equal to zero:

$$\frac{\alpha}{V} = -\frac{1}{k_B T V} \left.\frac{\partial F_N}{\partial N}\right]_{N=\hat{N}}. \tag{4.57}$$

Using the definition (4.47), the equation for $\hat{N}$ becomes

$$\alpha = -\frac{\mu(T, V, \hat{N})}{k_B T}. \tag{4.58}$$

Returning to equation (4.56), this location of $\hat{N}$ implies that, for sufficiently large values of V,

$$\frac{\ln \Xi}{V} = -\frac{\mu(T, V, \hat{N})}{k_B T}\frac{\hat{N}}{V} - \frac{F_{\hat{N}}}{k_B T V}, \tag{4.59}$$

from which the final result (4.49) follows immediately.

Resume. The system under study can exchange energy and particles with a heat bath that has "energy control parameter" $\beta = 1/k_B T$ and "number control parameter" α. The probability that the system contains exactly N particles is

$$P_N = \frac{e^{-\alpha N} Z(\beta, V, N)}{\Xi(\beta, V, \alpha)}. \tag{4.60}$$

The proof shows that, in the thermodynamic limit, there is one particular value of N, namely $\hat{N}$, for which P_N approaches 1. All the other P_N's, of course, approach 0. The condition for locating $\hat{N}$ is just that it gives the maximum value of P_N... this condition gives rise to equation (4.48). Once $\hat{N}$ is located, the result $P_{\hat{N}} \to 1$ becomes equation (4.49).

4.9 Summary of Major Ensembles

	boundary	variables	probability of microstate	p.f.	master function
microcanonical	adiabatic (no-skid)	E, V, N	$\frac{d\Gamma}{N! h_0^{3N}} \frac{1}{\Omega}$ or 0	Ω	$S(E, V, N) = k_B \ln \Omega$
canonical	heat bath	T, V, N	$\frac{d\Gamma e^{-\beta H(\Gamma)}}{N! h_0^{3N}} \frac{1}{Z}$	Z	$F(T, V, N) = -k_B T \ln Z$
grand canonical	heat bath, with holes	T, V, μ	$\frac{d\Gamma_N e^{-\beta H(\Gamma_N) - \alpha N}}{N! h_0^{3N}} \frac{1}{\Xi}$	Ξ	$\Pi(T, V, \mu) = -k_B T \ln \Xi$

In all cases, the partition function (p.f. in the above table) is the normalization factor

$$\text{p.f.} = \sum_{\text{microstates}} \text{unnormalized probability.}$$

4.10 Quantal Statistical Mechanics

How shall we define a partition function for quantal systems? A reasonable first guess is that

$$Z(T, \text{parameters}) = \sum_{\text{all quantal states}} e^{-\beta E}. \qquad [\![\text{first guess}]\!]$$

This guess runs into problems immediately. Most quantal states are not energy eigenstates, so it's not clear how to interpret "E" for such states. Another difficulty—harder to see—arises because there are many more quantal states than classical states, so the guess above is in some sense counting too many states. It's hard to see how it could have the correct classical limit. (Indeed, a mathematical investigation of the above guess would reveal that it doesn't even have the correct thermodynamic limit—if you were to calculate the Helmholtz free energy from the above guess, the resulting $F(T, V, N)$ would increase far faster than linearly with system size.)

A second guess might be

$$Z(T, \text{parameters}) = \sum_{\text{all energy eigenstates}} e^{-\beta E}. \qquad [\![\text{second guess}]\!]$$

This avoids the problem of how to interpret E for non-energy eigenstates, but there still seems to be an over-counting of states in the case of an energy degeneracy: If two energy eigenstates are separate in energy by any amount, no matter how small, those two energy eigenstates will contribute two terms to the above sum. But if the energy separation vanishes, then all linear combinations of the two states are also energy eigenstates, and each of this infinite number of combinations will enter into the sum.

Finally we arrive at a workable definition for quantal partition function, namely

$$Z(T, \text{parameters}) = \sum_{\text{energy eigenbasis } n} e^{-\beta E_n}. \tag{4.61}$$

Note that this is a sum over an *energy eigenbasis*, not over *energy eigenvalues.* These two sums differ through degeneracy: If $E_6 = E_5$, then two equal terms enter into the sum. More formally: if $N(m)$ is the degeneracy of eigenvalue m, that is, the number of linearly independent states with energy E_m, then

$$Z(T, \text{parameters}) = \sum_{\text{energy eigenvalues } m} N(m) e^{-\beta E_m}. \tag{4.62}$$

The above argument has a strange, *ex post facto* character: We define the quantal partition function not from first principles, but to insure that it has properties that we consider desirable (namely, that it avoids subtle interpretation issues, it posses the expected classical limit, and it has desirable behavior at level crossings). Linear combinations of energy eigenstates are quantal states just as legitimate as energy eigenstates, so why do we ignore them in the sum? The argument reminds me of politics at its worst: "I'm going to pass this law because I want it, even though I can't support it with any rationale." The resulting definition of partition function is strange in that it seems to select the energy eigenbasis as some sort of God-given basis, "better" than any other basis. In fact, the result is not as bad as it seems. It turns out (see problem 4.2) that our definition can be rephrased in a basis-independent manner as

$$Z(T, \text{parameters}) = \sum_{\text{energy eigenbasis } n} e^{-\beta E_n} = \sum_{\text{any basis } j} \langle j | e^{-\beta \hat{H}} | j \rangle. \tag{4.63}$$

If you don't know what it means to exponentiate the Hamiltonian operator $\hat{H}$, don't worry. For this book—and for most practical calculations—the most effective definition is the form on the left. The point is simply that the definition of partition function *can* be cast into the basis-independent form on the right. The energy eigenbasis is *not* special.

In this chapter we have often found, first, results about probabilities, and second, connections to thermodynamics. This section has so far dealt with only the second element. What do these results imply for probabilities? I will often say things like "The probability of having energy E_m is

$$\frac{N(m) e^{-\beta E_m}}{Z}."$$

On the face of it, this statement is absurd, because most of the microstates aren't energy eigenstates so they don't have any energy at all. What I mean is "If the energy is measured, the probability of finding energy E_m is

$$\frac{N(m) e^{-\beta E_m}}{Z}."$$

I will often use the first statement rather than the long and formal second statement. I do so, however, fully realizing that the first statement is wrong and that I use it just as convenient shorthand for the second statement. You may use this shorthand too, as long as you don't mean it.

> The ultimate source of such problems is that the English language was invented by people who did not understand quantum mechanics, hence they never produced concise, accurate phrases to describe quantal phenomena. In the same way, the ancient phrase "Search the four corners of the Earth" is still colorful and practical, and is used today even by those who know that the Earth isn't flat.

Similarly, I will often say "The probability of being in the energy eigenstate $\eta_n(\mathbf{x}_1, \ldots, \mathbf{x}_N)$ with energy E_n is

$$\frac{e^{-\beta E_n}}{Z}.\text{"}$$

But what I really mean is "If the microstate is projected onto a basis which includes the energy eigenstate $\eta_n(\mathbf{x}_1, \ldots, \mathbf{x}_N)$, then the probability of projecting onto that state is

$$\frac{e^{-\beta E_n}}{Z}.\text{"}$$

4.2 **The trace**

Show that for any operator $\hat{A}$, the "trace" of $\hat{A}$, defined as

$$\text{trace}\{\hat{A}\} \equiv \sum_{\text{any basis } j} \langle j|\hat{A}|j\rangle, \tag{4.64}$$

is independent of basis. What is the trace in terms of the matrix representation of the operator?

4.3 **Entropy in the canonical ensemble**

From the partition function (4.61), one can find the free energy F and hence the entropy S. Show that the entropy obtained in this manner equals

$$S(T) = -k_B \sum_n p_n \ln p_n, \tag{4.65}$$

where

$$p_n = \frac{e^{-\beta E_n}}{Z(T)} \tag{4.66}$$

is the probability that the system is in its nth energy eigenstate (using the shorthand mentioned above). This expression for the entropy is particularly useful in information theory. (Clue: Work forward from $S = -\partial F/\partial T$ and backwards from equation (4.65) to meet at the middle.)

4.4 **Entropy in the microcanonical ensemble**

[You must work the previous problem before working this one.] What are the state probabilities p_n, analogous to (4.66), for an system in the microcanonical ensemble? Devise a suitable quantal replacement for the microcanonical definition of entropy (2.7). Cast your replacement into the form of a function of the microcanonical probabilities p_n. Is formula (4.65) correct in the microcanonical ensemble?

4.11 Ensemble Problems I

4.5 **Classical monatomic ideal gas in the canonical ensemble**

In section 5.1 we will show that the canonical partition function of a classical monatomic ideal gas is

$$Z(T, V, N) = \frac{1}{N!}\left[\frac{V}{\lambda^3(T)}\right]^N, \tag{4.67}$$

where

$$\lambda(T) \equiv \frac{h_0}{\sqrt{2\pi m k_B T}}. \tag{4.68}$$

a. Show that in the thermodynamic limit, the Helmholtz free energy per particle is

$$\frac{F(T,V,N)}{N} = -k_B T \left[\ln\left(\frac{V/N}{\lambda^3(T)} \right) + 1 \right]. \tag{4.69}$$

b. Differentiate with respect to T to find $S(T,V,N)$.

c. Change variables to $S(E,V,N)$ using $E = \frac{3}{2} N k_B T$, and compare the resulting expression to the entropy derived in class through the microcanonical ensemble.

4.6 **Number fluctuations in the grand canonical ensemble**

Calculate ΔN, the root mean square fluctuations in the particle number, for a system in the grand canonical ensemble. (Clue: Take derivatives with respect to μ.) Show that this result is related to the isothermal compressibility κ_T through

$$\frac{\Delta N}{N} = \sqrt{\frac{k_B T \kappa_T}{V}}. \tag{4.70}$$

(Clue: Use the results of problem 3.34.)

4.7 **Classical monatomic ideal gas in the grand canonical ensemble**

a. Use the fact that

$$Z(T,V,N) = \frac{1}{N!} \left[\frac{V}{\lambda^3(T)} \right]^N, \tag{4.71}$$

to find $\Xi(T,V,\mu)$ for the classical monatomic ideal gas.

b. Use the connection to thermodynamics for the grand canonical ensemble, namely

$$p(T,\mu)V = k_B T \ln \Xi(T,V,\mu), \tag{4.72}$$

to show that for any substance

$$N(T,V,\mu) = k_B T \left.\frac{\partial \ln \Xi}{\partial \mu}\right)_{T,V}. \tag{4.73}$$

c. Derive the ideal gas equation of state in the grand canonical ensemble.

4.8 **Isobaric ensemble**

This problem encourages you to think about an ensemble with a specified temperature, pressure, and particle number. A physical model to keep in mind is a collection of systems each with the same number of particles and all connected to the same heat bath but enclosed in balloons rather than in rigid boxes. I want you to guess the answers to the following questions rather than produce mathematical or verbal arguments. If you are uncomfortable making guesses in a physics problem assignment then do only the first two parts.

a. Given that T, p, and N are fixed, what quantities fluctuate?

b. In going from the canonical to the isobaric ensemble, what control parameter (comparable to $\beta = 1/k_BT$ or $\alpha = -\mu/k_BT$) must be introduced, and how is it related to the pressure?

c. What is the (unnormalized) probability of finding the system in microstate x with energy $H(x)$ and volume $V(x)$?

d. What is the relevant state sum (comparable to Z or Ξ), and how is it related to the thermodynamic master function $G(T, p, N)$?

e. The relevant fluctuation-susceptibility relation connects the fluctuations in volume to what susceptibility?

f. Write out the fluctuation-susceptibility relation, using B to represent a product of several unguessable intensive quantities but writing out the extensive quantities explicitly.

g. What are the dimensions of B? Can you use this knowledge to guess at the unguessable?

4.9 **Fluctuation-susceptibility relation for a magnetic system**

In the Ising model for a magnet, the spins are located at fixed sites (labeled by i), and can point either up or down ($s_i = \pm 1$). The Ising Hamiltonian is

$$\mathcal{H} = \mathcal{H}_0(s_1, \ldots, s_N) - mH \sum_{i=1}^{N} s_i, \tag{4.74}$$

where m is the magnetic moment of each spin, H is the applied magnetic field, and $\mathcal{H}_0$ represents some spin-spin interaction energy, the details of which are not important here except for the fact that it is independent of H. The microscopic magnetization, which varies from configuration to configuration, is

$$\mathcal{M}(s_1, \ldots, s_N) = m \sum_i s_i, \tag{4.75}$$

while the macroscopic (or thermodynamic) magnetization is the canonical average over all such microscopic magnetizations:

$$M(T, H) = \langle \mathcal{M} \rangle. \tag{4.76}$$

The magnetic susceptibility—easily measured experimentally—is

$$\chi_T(T, H) = \left.\frac{\partial M}{\partial H}\right)_T. \tag{4.77}$$

Show that in the canonical ensemble the fluctuations in magnetization are related to the susceptibility by

$$\Delta M = \sqrt{k_B T \chi_T}. \tag{4.78}$$

4.10 Two definitions of magnetization

The previous problem gave a statistical mechanical definition of magnetization:

$$M(T,H) = \langle \mathcal{M} \rangle, \tag{4.79}$$

while equation (3.100) gave a thermodynamic definition:

$$M(S,H) = -\left.\frac{\partial E}{\partial H}\right)_S . \tag{4.80}$$

Show that these two definitions give equivalent results.

4.11 Values for the approach to the thermodynamic limit

In problem 2.13, "The approach to the thermodynamic limit," you were given a value of $EV^{2/3}/h_0^2$ and told that it was appropriate "for a gas at room temperature and atmospheric pressure." Justify this value as

$$EV^{2/3}/h_0^2 = [\tfrac{3}{2}(k_BT)^{5/3}/(p^{2/3}h^2)]N^{5/3} \tag{4.81}$$

4.12 Integrals by parametric differentiation

To find the mean energy or energy dispersion in the canonical ensemble, we introduced the "slick trick" of differentiating with respect to β. This trick, called parametric differentiation, is in fact useful in a number of circumstances. For example, in a graduate electrodynamics class I was once assigned a problem (Jackson, *Classical Electrodynamics*, problem 14.5(b)) for which I needed to evaluate

$$\int_0^{2\pi} \frac{\cos^2\theta}{(1+b\sin\theta)^5}\,d\theta \tag{4.82}$$

where b is a constant with $|b| < 1$. My classmates and I tried everything: substitutions, partial fractions, conversion to a contour integral in the complex plane, and, most popular of all, "look it up in reference books". I puzzled over it for a dozen hours before giving up. When the solutions were handed out, I expected to find many pages devoted to evaluating the integral. Instead I found a two-line argument that began with the known integral (see Dwight 858.546 or Gradshteyn and Ryzhik 3.644.4)

$$\int_0^{2\pi} \frac{\cos^2\theta}{a+b\sin\theta}\,d\theta = \frac{2\pi}{a+\sqrt{a^2-b^2}} \tag{4.83}$$

and then took a fourth derivative. What was the argument, and what is the value of the integral?

4.13 Parametric differentiation in quantum mechanics

The previous problem showed how parametric differentiation could be useful in electrodynamics. This one shows how it can be useful in quantum mechanics. In quantum mechanics, an infinite square well of width π has energy eigenfunctions

$$\eta_n(x) = \sqrt{\frac{2}{\pi}}\sin(nx) \quad n = 1,2,3,\ldots. \tag{4.84}$$

One frequently needs to evaluate matrix elements such as

$$\langle n|x^2|m\rangle = \frac{2}{\pi}\int_0^\pi \sin(nx)x^2\sin(mx)\,dx. \tag{4.85}$$

Show how this integral—as well as a host of other useful matrix elements—can be obtained easily from the well known result

$$\int_0^\pi \sin(ax)\sin(bx)\,dx = \frac{1}{2}\left[\frac{\sin[(a-b)\pi]}{a-b} - \frac{\sin[(a+b)\pi]}{a+b}\right] \qquad a \neq \pm b. \tag{4.86}$$

4.14 Polymers

A primitive model for a polymer is a random walk on a simple cubic lattice. A random walk consists of n steps (or "links") starting at ("anchored to") the origin. (In this model a polymer unit can step back onto a lattice site already occupied by a different polymer unit. This unrealistic feature is corrected in a more sophisticated model, the so-called "self avoiding walk.")

a. Show that the number of distinct walks consisting of n links is $N_n = 6^n$. Does this formula hold when $n = 0$?

For many purposes it is valuable to consider the ensemble of *all* random walks, regardless of their size. In this ensemble there is a "size control parameter" α such that the probability of finding a walk x consisting of $n(\mathsf{x})$ links is proportional to $e^{-\alpha n(\mathsf{x})}$. (Thus *longer* walks are *less* probable in this ensemble, but there are more of them.) The partition function associated with this model is

$$\Xi(\alpha) = \sum_{\text{walks } \mathsf{x}} e^{-\alpha n(\mathsf{x})}. \tag{4.87}$$

b. Show that the mean walk size in this ensemble is a function of α given through

$$\langle n\rangle = -\frac{\partial \ln \Xi(\alpha)}{\partial \alpha}. \tag{4.88}$$

c. Show that

$$\Xi(\alpha) = \frac{1}{1-6e^{-\alpha}} \qquad \text{and that} \qquad \langle n\rangle = \frac{6}{e^\alpha - 6}. \tag{4.89}$$

Clue: The geometric series sums to

$$1 + x + x^2 + x^3 + \cdots = \frac{1}{1-x} \qquad \text{when} \qquad |x| < 1.$$

d. What is the smallest possible value of the control parameter α? Does large α correspond to long polymers or short polymers?

e. Show that the dispersion in n is given through

$$(\Delta n)^2 = \frac{\partial^2 \ln \Xi}{\partial \alpha^2}, \tag{4.90}$$

whence

$$\frac{\Delta n}{\langle n\rangle} = \sqrt{\frac{e^\alpha}{6}} = \sqrt{\frac{1}{\langle n\rangle} + 1}. \tag{4.91}$$

Thus the relative dispersion decreases for longer polymers.

(See also loops: S. Leibler, R.R.P. Singh, and M.E. Fisher, "Thermodynamic behavior of two-dimensional vesicles," *Phys. Rev. Lett.* **59** (1987) 1989–1992; C. Richard, A.J. Guttmann, and I. Jensen, "Scaling function and universal amplitude combinations for self-avoiding polygons," *J. Phys.* A **34** (2001) L495–501.)

4.15 **A class of new ensembles**

Any mechanical parameter in the Hamiltonian can be "traded in" for a control parameter. This problem details the procedure if the mechanical parameter is intensive and an intrinsically positive quantity. Examples to keep in mind are 1) the particle mass, 2) the spacing between planes of a high temperature superconductor, or 3) the natural frequency of vibration for a diatomic molecule modeled as a simple harmonic oscillator. In honor of this last example I will call the parameter ω. In the "micro-ω" ensemble, all of the systems in the ensemble have a particular value of the parameter. In the "grand-ω" ensemble, the systems in the ensemble have a variety of values for the parameter, but larger values are less probable. In fact, the probability is proportional to $e^{-\gamma N\omega}$, where γ is a "control parameter" which can be adjusted to set the mean value of ω to any desired positive value. We suspect that, in the thermodynamic limit, the results of the two ensembles will be identical when the mean value of ω in the grand-ω ensemble is the same as the fixed value of ω in the micro-ω ensemble.

a. The thermodynamic assembly corresponding to the micro-ω ensemble has as master function the Helmholtz free energy $F(T,V,N,\omega)$. Using the definition

$$B(T,V,N,\omega) = -\left.\frac{\partial F}{\partial \omega}\right)_{T,V,N}, \tag{4.92}$$

write out the differential equation for dF.

b. Execute a Legendre transformation to an assembly with master function

$$K(T,V,N,B) = F + B\omega, \tag{4.93}$$

and show that in this assembly, the function (not variable!) ω is

$$\omega(T,V,N,B) = \left.\frac{\partial K}{\partial B}\right)_{T,V,N}. \tag{4.94}$$

In the grand-ω ensemble, the probability that a system has a parameter falling within $d\omega$ about ω is

$$\frac{e^{-\gamma N\omega} Z(T,V,N,\omega)\, d\omega}{\int_0^\infty e^{-\gamma N\omega'} Z(T,V,N,\omega')\, d\omega'}. \tag{4.95}$$

Define the partition function

$$Y(T,V,N,\gamma) = \frac{1}{\omega_0}\int_0^\infty e^{-\gamma N\omega} Z(T,V,N,\omega)\, d\omega, \tag{4.96}$$

where ω_0 is an arbitrary constant with the dimensions of ω whose only purpose is to make Y dimensionless. Presumably, the relationship between thermodynamics and statistical mechanics in the grand-ω ensemble is

$$K = -k_B T \ln Y, \tag{4.97}$$

by analogy to the similar relation in the canonical ensemble. We will assume this relationship and use it, first to find the relationship between the statistical mechanical γ and the thermodynamic B and second to show that the statistical mechanical equation (4.96) is consistent with the thermodynamic equation (4.93).

c. Show that, in the grand-ω ensemble,

$$\langle\omega\rangle = -\frac{1}{N}\frac{\partial \ln Y}{\partial\gamma} \tag{4.98}$$

and

$$\Delta\omega^2 = \frac{1}{N^2}\frac{\partial^2 Y}{\partial\gamma^2}. \tag{4.99}$$

Note that $\langle\omega\rangle$ and $\Delta\omega$ are functions of T, V, N, and γ.

d. Compare equations (4.94) and (4.98) and conclude that, if (4.97) is to hold, then

$$B = Nk_BT\gamma. \tag{4.100}$$

e. Show that

$$\Delta\omega = \sqrt{k_BT \left.\frac{\partial\omega}{\partial B}\right)_{T,V,N}}. \tag{4.101}$$

f. We suspect that, in the thermodynamic limit $N, V \to \infty$, $\ln Y \sim N$. If true, show that $\langle\omega\rangle$ is intensive (independent of N) whereas $\Delta\omega$ falls like $1/\sqrt{N}$.

g. To evaluate $Y(\gamma)$ in the thermodynamic limit, write

$$Y(T,V,N,\gamma) = \frac{1}{\omega_0}\int_0^\infty e^{-\gamma N\omega} Z(T,V,N,\omega)\, d\omega \approx e^{-\gamma N\langle\omega\rangle} Z(T,V,N,\langle\omega\rangle)\frac{\Delta\omega}{\omega_0}. \tag{4.102}$$

Take logarithms to show that

$$\ln Y \approx -\gamma N\langle\omega\rangle + \ln Z + \ln(\Delta\omega/\omega_0), \tag{4.103}$$

and argue that in the thermodynamic limit the last term becomes negligible. Finally conclude that

$$K = k_BT\gamma N\langle\omega\rangle + F \tag{4.104}$$

or, in light of relationship (4.100),

$$K = F + B\langle\omega\rangle, \tag{4.105}$$

which should be compared to equation (4.93).

We have shown only that this ensemble scheme is "not inconsistent". It is not obviously wrong, but of course this does not prove that it is right. A flawless general proof would require detailed mathematical reasoning, but proofs for particular situations are outlined in the next problem and in problem 4.18.

4.16 The grand-ω ensemble for the classical monatomic ideal gas

Apply the concepts of the previous problem to the classical monatomic ideal gas where the mechanical parameter ω is the particle mass. In particular, find expressions

a. for $B(T, V, N, m)$,
b. for $m(T, V, N, B)$,
c. and for $\langle m \rangle$ and Δm as functions of T, V, N, and γ.

4.17 **An ensemble of your own**
Any mechanical parameter in the Hamiltonian can be traded in for a control parameter. Can you think up a good problem *using* this fact where the parameter is, say, an applied magnetic field? Or the spring constant (or relaxed length) between two atoms in a diatomic molecule (or in the Einstein model)? Or the moment of inertia of a diatomic molecule modeled as a dumbbell? Or a parameter in the Lennard-Jones potential? Or the size of hard-sphere atoms? Or the spacing between atoms in a crystal?

4.12 Ensemble Problems II

The remaining problems in this chapter deal with the same "principles" issues that the others do, but they assume some familiarity with physical and mathematical topics that we have not yet treated. I place them here because of their character, but I do not expect you to do them at this moment. Instead I list their prerequisites and I hope you will come back to them later.

4.18 **The grand-ω ensemble for the simple harmonic oscillator**
(Prerequisite: Problems 4.15 and 5.7.) Problem 4.15 introduced a class of ensembles in which mechanical parameters in the Hamiltonian were not fixed but rather allowed to fluctuate under the control of some parameters γ. Apply this concept to the diatomic molecules of problem 5.7, using the natural frequency of vibration as the mechanical parameter. Develop the suggestive arguments of problem 4.15 into a mathematically rigorous proof.

4.19 **Particles in a bowl**
(Prerequisite: Chapter 5.) I can't count how many times I've waved my hands and told you that the precise character of the boundaries should be irrelevant to the bulk properties found by statistical mechanics. Now you have a chance to prove it (for a restricted situation of course).

a. Consider N non-interacting, classical point particles moving subject to the potential energy function $U(\mathbf{r}) = Kr^2/2$. Evaluate the classical partition function $Z_b(T, K, N)$ and compare it to the partition function $Z_h(T, V, N)$ for N particles in a hard-walled container of volume V.
b. For what V (as a function of K) will the two partition functions in part (a.) be the same?
c. The "bowl" container has no stiff walls, so it is possible for a particle to be located at any distance from the origin. But is it not likely that a particle will get too far away. Calculate the rms radius $\sqrt{\langle r^2 \rangle}$. (Use equipartition?)
d. Suppose the hard-walled container is spherical with radius R. Place the origin at the center of the sphere and find the rms radius $\sqrt{\langle r^2 \rangle}$.

e. For the V corresponding to K in the sense of part (b.), compare the two rms radii.

Extra: Do this problem quantum mechanically. (Clue: Notice the mathematical similarity between this problem and the Einstein model of lattice vibrations.)

4.20 **Quantal monatomic ideal gas**

(Prerequisite: Chapter 6.) We have many times considered the problem of N non-interacting classical point particles in a box of edge length $L = V^{1/3}$. Now we will solve the problem for quantum mechanical particles.

The partition function is $Z = \sum e^{-\beta E}$, where the sum is taken over the many-particle energy eigenstates $\Psi(\mathbf{r}_1, \ldots, \mathbf{r}_N)$. Ignore symmetry-under-interchange requirements so that such states are specified by a simple listing of the component one-particle levels (or orbitals) $\eta_{\mathbf{k}}(\mathbf{r})$. Thus Ψ can be specified by simply listing the relevant $\mathbf{k}$ values of its component levels. Show then that

$$Z = \frac{1}{N!}\left(\sum_{\mathbf{k}} e^{-\beta E_k}\right)^N \tag{4.106}$$

where $E_k = \hbar^2 k^2/2m$ and the sum is over all $\mathbf{k}$ permitted by periodic boundary conditions. Evaluate the sum (in the thermodynamic limit) by turning it into an integral. Compare the resulting partition function with that of a classical monatomic ideal gas.

4.21 **Quantal monatomic ideal gas in the microcanonical ensemble**

Consider the situation of the above problem but calculate the microcanonical partition function $\Omega(E, V, N)$. Compare with the classical result.

Chapter 5

Classical Ideal Gases

End of principles, beginning of applications. There is still more that could be done with principles, but "the proof of the pudding is in the eating". And in this case the pudding is excellent eating indeed. . . calculations made from statistical mechanics theory give results that are actually more accurate than experiment.

This chapter considers ideal (i.e. non-interacting) gases made up of atoms or molecules that may have internal structure (i.e. not point particles). The internal degrees of freedom will be treated either classically or quantally, but the translational degrees of freedom will always be treated classically.

5.1 Classical Monatomic Ideal Gases

We have already found the Helmholtz free energy of the classical monatomic ideal gas (section 4.3). I think you will agree that the canonical calculation is considerably easier than the corresponding microcanonical calculation. Here we will review the calculation, then go back and investigate just what caused the solution to be so much easier, and this investigation will lead to an important theorem.

5.1.1 Solving the problem

The energy

$$H(\Gamma) = \frac{1}{2m}(p_{x,1}^2 + p_{y,1}^2 + p_{z,1}^2 + p_{x,2}^2 + \cdots + p_{z,N}^2) + U(\mathbf{x}_1) + U(\mathbf{x}_2) + \cdots + U(\mathbf{x}_N) \tag{5.1}$$

is a sum of terms, each involving different variables, so the Boltzmann factor

$$e^{-\beta H(\Gamma)} = e^{-\beta(p_{x,1}^2/2m)} e^{-\beta(p_{y,1}^2/2m)} \times \cdots \times e^{-\beta(p_{z,N}^2/2m)} e^{-\beta U(\mathbf{x}_1)} e^{-\beta U(\mathbf{x}_2)} \times \cdots \times e^{-\beta U(\mathbf{x}_N)} \tag{5.2}$$

is a product of factors, each involving different variables. Thus the partition function, which in general is an integral in a $6N$-dimensional space, factors into 3- and 1-dimensional integrals

$$\begin{aligned} Z(T,V,N) &= \frac{1}{N!h^{3N}}\left[\int_{-\infty}^{+\infty} dx_1 \int_{-\infty}^{+\infty} dy_1 \int_{-\infty}^{+\infty} dz_1\, e^{-\beta U(\mathbf{x}_1)}\right] \times \cdots \times \left[\int_{-\infty}^{+\infty} dx_N \int_{-\infty}^{+\infty} dy_N \int_{-\infty}^{+\infty} dz_N\, e^{-\beta U(\mathbf{x}_N)}\right] \\ &\times \left[\int_{-\infty}^{+\infty} dp_{x,1}\, e^{-\beta(p_{x,1}^2/2m)}\right] \times \cdots \times \left[\int_{-\infty}^{+\infty} dp_{z,N}\, e^{-\beta(p_{z,N}^2/2m)}\right]. \end{aligned}$$

This doesn't happen in the microcanonical calculation!

Moreover, we found it easy to evaluate the N three-dimensional position integrals and the $3N$ one-dimensional momentum integrals. The result was

$$Z(T,V,N) = \frac{V^N}{N!h^{3N}}\left[\sqrt{2\pi m k_B T}\right]^{3N}. \tag{5.3}$$

The result above is correct, but it is not the most convenient form for the partition function. There are lots of variables and constants floating around, many of them with hard-to-remember dimensions. The quantity Z is in fact dimensionless, but that's not obvious from the expression. For this reason is customary to define the quantity

$$\lambda(T) = \frac{h}{\sqrt{2\pi m k_B T}}, \tag{5.4}$$

called the "thermal de Broglie wavelength". Like any wavelength, it has the dimensions of length, and the notation $\lambda(T)$ suggests this. It is, of course, an intensive quantity. In terms of the thermal de Broglie wavelength, the partition function for the classical monatomic ideal gas is

$$Z(T,V,N) = \frac{1}{N!}\left(\frac{V}{\lambda^3(T)}\right)^N. \tag{5.5}$$

If a particle of mass m has kinetic energy k_BT, then it has momentum $\sqrt{2mk_BT}$ and thus a quantum-mechanical de Broglie wavelength of

$$\lambda = \frac{h}{p} = \frac{h}{\sqrt{2mk_BT}}. \tag{5.6}$$

The definition (5.4) above slips in an extra dimensionless factor of $\sqrt{\pi} = 1.77$ just to make the result (5.5) easier to remember and to work with. Physically, the thermal de Broglie wavelength represents the quantal smearing of each individual point particle. Thus if the mean separation between atoms is much greater than $\lambda(T)$, we expect that the classical approximation will be a good one. If the mean separation is less than or about equal to $\lambda(T)$, we expect that a quantal treatment will be required.

After doing any calculation is it useful to perform a "debriefing" to figure out why—in general rather than technical terms—the calculation went the way it did. Almost everyone agrees that this canonical calculation is a lot easier than the corresponding microcanonical calculation to find $\Omega(E,V,N)$ for the classical monatomic ideal gas. But what was the particular feature that made it so much easier? Surely it was the factorization of the Boltzmann factor and the subsequent factorization of the partition function. This enabled us to perform one- and three-dimensional integrals rather than the $3N$-dimensional integral required (see appendix D) for the microcanonical calculation. Is there anything that can be said more generally about this feature?

5.1.2 Theorem on decoupling Hamiltonians

Indeed there is. Suppose a Hamiltonian is a sum of two pieces

$$H(\Gamma) = H_1(\Gamma_1) + H_2(\Gamma_2), \tag{5.7}$$

where Γ_1 and Γ_2 are *exclusive.* (That is, the phase space variables in the list Γ_1 and the phase space variables in the list Γ_2 together make up the whole list Γ, and no variable appears in both lists.) The Hamiltonian $H(\Gamma)$ is then said to "decouple" into the two parts $H_1(\Gamma_1)$ and $H_2(\Gamma_2)$.[1] Then it is easy to see that the partition function will factor into two parts:

$$Z(T, V, N) = \frac{1}{N!h^{3N}} \int d\Gamma\, e^{-\beta H(\Gamma)} = \frac{1}{N!h^{3N}} \int d\Gamma_1\, e^{-\beta H(\Gamma_1)} \int d\Gamma_2\, e^{-\beta H(\Gamma_2)}. \tag{5.8}$$

If the Hamiltonian decouples into three parts, then this reasoning can be used to show that the partition function breaks into three factors. And so forth.

For example, the Hamiltonian of the classical monatomic ideal gas that we have just investigated decouples into $4N$ pieces,

$$H(\Gamma) = \frac{p_{x,1}^2}{2m} + \frac{p_{y,1}^2}{2m} + \cdots + \frac{p_{z,N}^2}{2m} + U(\mathbf{x}_1) + U(\mathbf{x}_2) + \cdots + U(\mathbf{x}_N). \tag{5.9}$$

Each term of the form $p^2/2m$ in the Hamiltonian leads to a factor of $h/\lambda(T)$ in the partition function...each term of the form $U(\mathbf{x})$ leads to a factor of V. Thus our theorem on decoupling Hamiltonians shows that the partition function is

$$Z(T, V, N) = \frac{1}{N!h^{3N}} \left(\frac{h}{\lambda(T)}\right)^{3N} V^N. \tag{5.10}$$

If the particles *do* interact, then the potential energy part of the Hamiltonian does not break up into exclusive pieces, but the kinetic energy part still does. Thus for an interacting gas with potential energy of interaction

$$U_N(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N), \tag{5.11}$$

the partition function is

$$Z(T, V, N) = \frac{1}{N!\lambda^{3N}(T)} \int_{-\infty}^{+\infty} dx_1 \cdots \int_{-\infty}^{+\infty} dz_N\, e^{-\beta U_N}. \tag{5.12}$$

Although the potential energy part of the problem is now excruciatingly difficult, our theorem on decoupling Hamiltonians assures us that the kinetic energy part is just as easy to handle for an interacting as for a non-interacting gas.

5.1 **Gas with pair interactions**

For a pure classical monatomic gas that interacts only through pair interactions (i.e. for which there are no three-body or higher interactions) the Hamiltonian is

$$H(\Gamma) = \sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{2m} + \sum_{i=1}^{N} U_A(\mathbf{x}_i) + \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} U_B(\mathbf{x}_i, \mathbf{x}_j), \tag{5.13}$$

---

[1] Alternatively, the two parts of the Hamiltonian are called "uncoupled". These terms derive from the ordinary English word "to couple", meaning to join or to connect.

where $U_A(\mathbf{x})$ is the potential energy due to the interaction between a particle at point $\mathbf{x}$ and the container, and $U_B(\mathbf{x},\mathbf{y})$ is the potential energy due to the interaction between a particle at point $\mathbf{x}$ and a particle at point $\mathbf{y}$. The potential energy thus breaks up into a sum of $N + N(N-1)/2$ pieces. Does the decoupling theorem apply?

5.2 Classical Diatomic Ideal Gases

Rigid linear model. The partition function is

$$Z(T,V,N) = \frac{1}{N!}\left[\frac{V}{\lambda^3(T)}\left(\frac{4\pi^3 I k_B T}{h^2}\right)\right]^N \tag{5.14}$$

General results for separation of Z into translational (center of mass) and internal degrees of freedom. Term “internal specific heat”.

5.3 Heat Capacity of an Ideal Gas

5.3.1 The equipartition theorem

Equipartition theorem. (For classical systems.) Suppose the Hamiltonian $H(\Gamma)$ decouples into one piece involving a single phase space variable—call it H_1, plus another piece which involves all the other phase space variables—call it $H_2(\Gamma_2)$. Suppose further that the energy depends quadratically upon this single phase space variable, and that this variable may take on values from $-\infty$ to $+\infty$. Then, in classical statistical mechanics, the mean contribution to the energy due to that single variable is

$$\langle H_1\rangle = \tfrac{1}{2}k_B T. \tag{5.15}$$

Notice how general this theorem is. The remaining piece of the Hamiltonian, $H_2(\Gamma_2)$, might decouple further or it might not. The phase space variable entering H_1 might be a momentum,

$$H_1(p) = \frac{p^2}{2m}, \tag{5.16}$$

or an angular momentum,

$$H_1(\ell) = \frac{\ell^2}{2I}, \tag{5.17}$$

or even a position coordinate, as in the simple harmonic oscillator energy

$$H_1(x) = \tfrac{1}{2}kx^2. \tag{5.18}$$

Furthermore, in all these circumstances, the mean energy is *independent* of the particular parameters m or I or k... it depends only upon the temperature. This explains the origin of the name “equipartition”: the mean translational energy due to motion in the x direction is equal to the mean rotational energy due to the change of θ, and this holds true even if the gas is a mixture of molecules with different masses and different moments of inertia. The energy is equally partitioned among all these different ways of holding energy.

Proof. We will write

$$H_1(p) = ap^2, \tag{5.19}$$

although the variable might not be a linear momentum. Then the average of H_1 is

$$\langle H_1 \rangle = \frac{\int d\Gamma\, H_1 e^{-\beta H(\Gamma)}}{\int d\Gamma\, e^{-\beta H(\Gamma)}} = \frac{\int_{-\infty}^{+\infty} dp\, H_1 e^{-\beta H_1} \int d\Gamma_2\, e^{-\beta H_2(\Gamma_2)}}{\int_{-\infty}^{+\infty} dp\, e^{-\beta H_1} \int d\Gamma_2\, e^{-\beta H_2(\Gamma_2)}}. \tag{5.20}$$

Clearly, the integrals over Γ_2 cancel in this last expression. (This explains why the form of H_2 is irrelevant to the theorem.) We are left with

$$\langle H_1 \rangle = \frac{\int_{-\infty}^{+\infty} dp\, ap^2 e^{-\beta ap^2}}{\int_{-\infty}^{+\infty} dp\, e^{-\beta ap^2}}. \tag{5.21}$$

These two integrals could be evaluated in terms of Gamma functions (see appendix C), but they don't need to be evaluated yet. Think for a moment about our "slick trick" of parametric differentiation... using it we can write

$$\langle H_1 \rangle = -\frac{d}{d\beta} \ln \left[\int_{-\infty}^{+\infty} dp\, e^{-\beta ap^2} \right]. \tag{5.22}$$

The integral that remains is of Gaussian character and we *could* evaluate it using the results of Appendix B. But before rushing in to integrate, let's employ the substitution $u = \sqrt{\beta a}\, p$ to find

$$\langle H_1 \rangle = -\frac{d}{d\beta} \ln \left[\frac{1}{\sqrt{\beta a}} \int_{-\infty}^{+\infty} du\, e^{-u^2} \right] = -\frac{d}{d\beta} \left\{ \ln \left[\frac{1}{\sqrt{\beta}} \right] + \ln \left[\frac{1}{\sqrt{a}} \int_{-\infty}^{+\infty} du\, e^{-u^2} \right] \right\}. \tag{5.23}$$

This last expression shows that there's no need to evaluate the integral. Whatever its value is, it is some number, not a function of β, so when we take the derivative with respect to β the term involving that number will differentiate to zero. Similarly for the constant a, which explains why the equipartition result is independent of that prefactor. We are left with

$$\langle H_1 \rangle = -\frac{d}{d\beta} \ln \frac{1}{\sqrt{\beta}} = \frac{1}{2} \frac{d}{d\beta} \ln \beta = \frac{1}{2} \frac{1}{\beta} \tag{5.24}$$

or, finally, the desired equipartition result

$$\langle H_1 \rangle = \tfrac{1}{2} k_B T. \tag{5.25}$$

5.3.2 Applications of equipartition; Comparison with experiment

5.3.3 Crossover between classical and quantal behavior; Freeze out

At high temperatures, typical thermal energies are much greater than level spacings. Transitions from one level to another are very easy to do and the granular character of the quantized energies can be ignored. This is the classical limit, and equipartition holds!

At low temperatures, typical thermal energies are less that the level spacing between the ground state and the first excited state. There is so little thermal energy around that the molecule cannot even be excited out of its ground state. Virtually all the molecules are in their ground states, and the excited states might as well just not exist.

In classical mechanics, a diatomic molecule offered a small amount of rotational energy will accept that energy and rotate slowly. But in quantum mechanics, a diatomic molecule offered a small amount of rotational energy will reject that energy and remain in the ground state, because the energy offered is not enough to lift it into the first excited state.[2] The quantal diatomic molecule does not rotate at all at low temperatures, so it behaves exactly like a monatomic molecule with only center-of-mass degrees of freedom.

In short, we explain the high-temperature rotational specific heat ($c_V^{\mathrm{rot}} = k_B$) through equipartition. We explain the low-temperature rotational specific heat (c_V^{rot} vanishes) through difficulty of promotion to the first quantal excited state. This fall-off of specific heat as the temperature is reduced is called "freeze out".

The crossover between the high-temperature and low-temperature regimes occurs in the vicinity of a characteristic temperature θ at which the typical thermal energy is equal to energy separation between the ground state and the first excited state. If the energies of these two states are ϵ_0 and ϵ_1 respectively, then we define the characteristic crossover temperature through

$$k_B\theta \equiv \epsilon_1 - \epsilon_0. \tag{5.26}$$

5.2 Generalized equipartition theorem and the ultra-relativistic gas

a. Suppose the Hamiltonian $H(\Gamma)$ decouples into two pieces

$$H(\Gamma) = a|p|^n + H_2(\Gamma_2) \tag{5.27}$$

where p is some phase space variable that may take on values from $-\infty$ to $+\infty$, and where Γ_2 represents all the phase space variables except for p. (Note that the absolute value $|p|$ is needed in order to avoid, for example, taking the square root of a negative number in the case $n = 1/2$.) Show that, in classical statistical mechanics, the mean contribution to the energy due to that single variable is

$$\langle a|p|^n\rangle = \tfrac{1}{n}k_BT. \tag{5.28}$$

b. In special relativity, the energy of a free (i.e. non-interacting) particle is given by

$$\sqrt{(mc^2)^2 + (pc)^2}, \tag{5.29}$$

where c is the speed of light. As you know, when $v \ll c$ this gives the non-relativistic kinetic energy KE $\approx mc^2 + p^2/2m$. In the "ultra-relativistic" limit, where v is close to c, the energy is approximately pc. What is the heat capacity of a gas of non-interacting ultra-relativistic particles?

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[2] This paragraph is written in the "shorthand" language discussed on page 113, as if energy eigenstates were the only allowed quantal states.

c. Estimate the crossover temperature between the non-relativistic and ultra-relativistic regimes.

5.3 **Another generalization of equipartition**
Consider the same situation as the equipartition theorem in the text, but now suppose the single phase space variable takes on values from 0 to $+\infty$. What is the corresponding result for $\langle H_1 \rangle$?

5.4 **Equipartition and the virial theorem**
Look up the term "virial theorem" in a classical mechanics textbook. Is there any relation between the virial theorem of classical mechanics and the equipartition theorem of classical statistical mechanics?

Box: The $\mathcal{O}$ Notation

Approximations are an important part of physics, and an important part of approximation is to ensure their reliability and consistency. The $\mathcal{O}$ notation (pronounced "the big-oh notation") is an important and practical tool for making approximations reliable and consistent.

The technique is best illustrated through an example. Suppose you desire an approximation for

$$f(x) = \frac{e^{-x}}{1-x} \tag{5.30}$$

valid for small values of x, that is, $x \ll 1$. You know that

$$e^{-x} = 1 - x + \tfrac{1}{2}x^2 - \tfrac{1}{6}x^3 + \cdots \tag{5.31}$$

and that

$$\frac{1}{1-x} = 1 + x + x^2 + x^3 + \cdots, \tag{5.32}$$

so it seems that reasonable approximations are

$$e^{-x} \approx 1 - x \tag{5.33}$$

and

$$\frac{1}{1-x} \approx 1 + x, \tag{5.34}$$

whence

$$\frac{e^{-x}}{1-x} \approx (1-x)(1+x) = 1 - x^2. \tag{5.35}$$

Let's try out this approximation at $x_0 = 0.01$. A calculator shows that

$$\frac{e^{-x_0}}{1-x_0} = 1.0000503\ldots \tag{5.36}$$

while the value for the approximation is

$$1 - x_0^2 = 0.9999000. \tag{5.37}$$

This is a very poor approximation indeed. . . the deviation from $f(0) = 1$ is even of the wrong sign!

Let's do the problem over again, but this time keeping track of exactly how much we've thrown away while making each approximation. We write

$$e^{-x} = 1 - x + \tfrac{1}{2}x^2 - \tfrac{1}{6}x^3 + \cdots \tag{5.38}$$

as

$$e^{-x} = 1 - x + \tfrac{1}{2}x^2 + \mathcal{O}(x^3), \tag{5.39}$$

where the notation $\mathcal{O}(x^3)$ stands for the small terms that we haven't bothered to write out explicitly. The symbol $\mathcal{O}(x^3)$ means "terms that are about the magnitude of x^3, or smaller" and is pronounced "terms of order x^3". The $\mathcal{O}$ notation will allow us to make controlled approximations in which we keep track of exactly how good the approximation is.

Similarly, we write

$$\frac{1}{1-x} = 1 + x + x^2 + \mathcal{O}(x^3), \tag{5.40}$$

and find the product

$$\begin{aligned}
f(x) &= \left[1 - x + \tfrac{1}{2}x^2 + \mathcal{O}(x^3)\right] \times \left[1 + x + x^2 + \mathcal{O}(x^3)\right] && (5.41)\\
&= \quad \left[1 - x + \tfrac{1}{2}x^2 + \mathcal{O}(x^3)\right] && (5.42)\\
&\quad + \left[1 - x + \tfrac{1}{2}x^2 + \mathcal{O}(x^3)\right] x && (5.43)\\
&\quad + \left[1 - x + \tfrac{1}{2}x^2 + \mathcal{O}(x^3)\right] x^2 && (5.44)\\
&\quad + \left[1 - x + \tfrac{1}{2}x^2 + \mathcal{O}(x^3)\right] \mathcal{O}(x^3). && (5.45)
\end{aligned}$$

Note, however, that $x \times \frac{1}{2}x^2 = \mathcal{O}(x^3)$, and that $x^2 \times \mathcal{O}(x^3) = \mathcal{O}(x^3)$, and so forth, whence

$$\begin{aligned}
f(x) &= \quad \left[1 - x + \tfrac{1}{2}x^2 + \mathcal{O}(x^3)\right] && (5.46)\\
&\quad + \left[x - x^2 + \mathcal{O}(x^3)\right] && (5.47)\\
&\quad + \left[x^2 + \mathcal{O}(x^3)\right] && (5.48)\\
&\quad + \mathcal{O}(x^3) && (5.49)\\
&= 1 + \tfrac{1}{2}x^2 + \mathcal{O}(x^3). && (5.50)
\end{aligned}$$

Thus we have the approximation

$$f(x) \approx 1 + \tfrac{1}{2}x^2. \tag{5.51}$$

Furthermore, we know that this approximation is accurate to terms of order $\mathcal{O}(x^2)$ (i.e. that the first neglected terms are of order $\mathcal{O}(x^3)$). Evaluating this approximation at $x_0 = 0.01$ gives

$$1 + \tfrac{1}{2}x_0^2 = 1.0000500, \tag{5.52}$$

far superior to our old approximation (5.35).

What went wrong on our first try? The $-x^2$ in approximation (5.35) is the same as the $-x^2$ on line (5.47). However, lines (5.46) and (5.48) demonstrate that there were other terms of about the same size (that is, other "terms of order x^2") that we neglected in our first attempt.

The $\mathcal{O}$ notation is superior to the "dot notation" (such as $\cdots$) in that dots stand for "a bunch of small terms", but the dots don't tell you just how small they are. The symbol $\mathcal{O}(x^3)$ also stands for "a bunch of small terms", but in addition it tells you precisely how small those terms are. The $\mathcal{O}$ notation allows us to approximate in a consistent manner, unlike the uncontrolled approximations where we ignore a "small term" without knowing whether we have already retained terms that are even smaller.

End of Box: The $\mathcal{O}$ Notation

5.4 Specific Heat of a Hetero-nuclear Diatomic Ideal Gas

The classical partition function is

$$Z = \frac{1}{N!}\left[\frac{V}{\lambda^3(T)}\frac{1}{h^2}\int_0^{\pi} d\theta \int_0^{2\pi} d\varphi \int_{-\infty}^{+\infty} d\ell_\theta \int_{-\infty}^{+\infty} d\ell_\varphi \, e^{-\beta(\ell_\theta^2+\ell_\varphi^2)/2I}\right]^N. \tag{5.53}$$

Let's make sure we have the quantum mechanics of one molecule straight before we jump into treating 6.02×10^{23} molecules: First of all, we consider *hetero*-nuclear rather than homo-nuclear diatomic molecules (such as CO or HCl rather than H_2 or N_2) because in the latter there are additional issues due to the Pauli principle. Let's just avoid these issues on our first encounter. The quantal energy eigenvalues are

$$\epsilon_{\text{rot}} = \ell(\ell+1)\frac{\hbar^2}{2I} \qquad \ell = 0, 1, 2, \ldots, \tag{5.54}$$

with

$$\text{degeneracy}_\ell = 2\ell + 1. \tag{5.55}$$

Thus the quantal "characteristic temperature" θ (or Θ_{rot}) is

$$k_B\theta \equiv \epsilon_1 - \epsilon_0 = \frac{\hbar^2}{I}. \tag{5.56}$$

And, finally, the quantal partition function is

$$Z = \frac{1}{N!}\left[\frac{V}{\lambda^3(T)}\sum_{\ell=0}^{\infty}(2\ell+1)e^{-\beta\ell(\ell+1)\hbar^2/2I}\right]^N. \tag{5.57}$$

It saves a lot of writing to define the "rotational partition function"

$$\zeta(T) \equiv \zeta^{\text{rot}}(T) \equiv \sum_{\ell=0}^{\infty}(2\ell+1)e^{-\beta\ell(\ell+1)\hbar^2/2I} = \sum_{\ell=0}^{\infty}(2\ell+1)e^{-\ell(\ell+1)\theta/2T}. \tag{5.58}$$

The expression on the far right is the one that I like to use... instead of having a lot of variables like T, $\hbar$, and I floating around just waiting to get misplaced, everything is neatly packaged into the ratio θ/T, which is obviously dimensionless.

Now, for *any* partition function of the form

$$Z = \frac{1}{N!}\left[\frac{V}{\lambda^3(T)}\zeta(T)\right]^N = Z_{\text{mono}}\zeta^N(T). \tag{5.59}$$

We have

$$F = -k_B T \ln Z = \underbrace{-k_B T \ln Z_{\text{mono}}}_{F_{\text{mono}}} \underbrace{-k_B T N \ln \zeta}_{N f^{\text{rot}}} \tag{5.60}$$

and

$$e^{\text{rot}} = \frac{\partial(f^{\text{rot}}/T)}{\partial(1/T)} = -\frac{\partial \ln \zeta}{\partial \beta} \qquad c_V^{\text{rot}} = \frac{\partial e^{\text{rot}}}{\partial T}. \tag{5.61}$$

Because the rotational partition function depends on temperature only through the combination θ/T, it makes sense to use that variable for derivatives:

$$e^{\text{rot}} = \frac{\partial(f^{\text{rot}}/T)}{\partial(1/T)} = \frac{\partial(-k_B T \ln\zeta/T)}{\partial(1/T)} = -k_B \frac{\partial \ln\zeta}{\partial(1/T)} = -k_B\theta\frac{\partial \ln\zeta}{\partial(\theta/T)} \tag{5.62}$$

and

$$c_V^{\text{rot}} = \frac{\partial e^{\text{rot}}}{\partial T} = \frac{\partial e^{\text{rot}}}{\partial(\theta/T)}\frac{\partial(\theta/T)}{\partial T} = -\frac{\theta}{T^2}\frac{\partial e^{\text{rot}}}{\partial(\theta/T)}. \tag{5.63}$$

Now back to the evaluation of $\zeta(T)$. It is quite easy to prove that the infinite sum for $\zeta(T)$ converges. You will then be tempted to find an expression for $\zeta(T)$ in terms of well-known functions like polynomials or exponentials. If you try this, you will not find any simple expression. Instead of manipulating $\zeta(T)$ into some combination of familiar functions, we will have to become familiar with it on our own. It can be evaluated and plotted on a computer just by adding up a finite number of terms in the defining infinite sum. But doing so is not the most productive way to approach an understanding of this function... given a plot of $\zeta(T)$, how would you find the specific heat due to rotation? A better way to approach the problem is to find how the partition function $\zeta(T)$ (and hence the specific heat $c_V^{\text{rot}}(T)$) behaves at low and high temperatures.

At low temperatures, we expand in terms of the small variable $e^{-\theta/T}$ to find

$$\begin{aligned}\zeta(T) &= 1 + 3e^{-\theta/T} + 5e^{-3\theta/T} + 7e^{-6\theta/T} + \cdots \\ &= 1 + 3e^{-\theta/T} + 5e^{-3\theta/T} + \mathcal{O}(e^{-6\theta/T}).\end{aligned} \tag{5.64}$$

The notation $\mathcal{O}(x^N)$ is read "terms of order x^N". (See the box on page 129.) Now for small variables ϵ the logarithm is

$$\ln(1+\epsilon) = \epsilon - \tfrac{1}{2}\epsilon^2 + \tfrac{1}{3}\epsilon^3 - \tfrac{1}{4}\epsilon^4 + \mathcal{O}(\epsilon^5), \tag{5.65}$$

whence

$$\begin{aligned}
\ln\zeta(T) &= 3e^{-\theta/T} + 5e^{-3\theta/T} + \mathcal{O}(e^{-6\theta/T}) \\
&\quad -\tfrac{1}{2}[3e^{-\theta/T} + 5e^{-3\theta/T} + \mathcal{O}(e^{-6\theta/T})]^2 \\
&\quad\quad +\tfrac{1}{3}[3e^{-\theta/T} + 5e^{-3\theta/T} + \mathcal{O}(e^{-6\theta/T})]^3 \\
&\quad\quad\quad +\mathcal{O}(e^{-4\theta/T}) \qquad (5.66)\\
&= 3e^{-\theta/T} + 5e^{-3\theta/T} + \mathcal{O}(e^{-6\theta/T}) \\
&\quad -\tfrac{1}{2}[9e^{-2\theta/T} + 30e^{-4\theta/T} + \mathcal{O}(e^{-6\theta/T})] \\
&\quad\quad +\tfrac{1}{3}[27e^{-3\theta/T} + 135e^{-5\theta/T} + \mathcal{O}(e^{-6\theta/T})] \\
&\quad\quad\quad +\mathcal{O}(e^{-4\theta/T}) \qquad (5.67)\\
&= 3e^{-\theta/T} - \tfrac{9}{2}e^{-2\theta/T} + 14e^{-3\theta/T} + \mathcal{O}(e^{-4\theta/T}). \qquad (5.68)
\end{aligned}$$

Note that in going from equation (5.67) to equation (5.68) it would have been impossible to make sure that all of the several expansions were kept to equivalent orders of accuracy had we used $+\cdots$ rather than the $\mathcal{O}$ notation.

Now it is easy to use equations (5.62) and (5.63) to find

$$e^{\text{rot}} = -k_B\theta[-3e^{-\theta/T} - 9e^{-2\theta/T} - 42e^{-3\theta/T} + \mathcal{O}(e^{-4\theta/T})] \tag{5.69}$$

and

$$c_V^{\text{rot}} = k_B\left(\frac{\theta}{T}\right)^2[3e^{-\theta/T} - 18e^{-2\theta/T} + 126e^{-3\theta/T} + \mathcal{O}(e^{-4\theta/T})]. \tag{5.70}$$

(Note that if we had used equations (5.61) instead, it would have been a lot more work.) The specific heat vanishes at zero temperature, and it increases *exponentially* slowly with increasing temperature. This is a very slow growth indeed…not only is the slope zero, but the second derivative is zero, the third derivative is zero, indeed *all* orders of derivative vanish at the origin.

What about high temperatures? We have discussed the fact that at high temperatures the rotational specific heat will approach the classical equipartition value of k_B, but *how* will it approach the limiting value? In other words, what are the deviations from the high temperature limit? We can answer these questions by approximating the sum by an integral. The *Euler-MacLaurin formula* states that if $f(x) \to 0$, $f'(x) \to 0$, $f''(x) \to 0$, etc. as $x \to \infty$, then

$$\sum_{\ell=0}^{\infty} f(\ell) \approx \int_0^\infty f(x)\,dx + \tfrac{1}{2}f(0) - \tfrac{1}{12}f'(0) + \tfrac{1}{720}f'''(0) - \tfrac{1}{30240}f^{(\text{v})}(0) + \cdots. \tag{5.71}$$

In our case,

$$f(x) = (2x+1)e^{-x(x+1)\theta/2T}, \tag{5.72}$$

so

$$\int_0^\infty f(x)\,dx = 2\frac{T}{\theta}$$

$$\begin{aligned}
f(0) &= 1 \\
f'(0) &= 2-\frac{\theta}{2T} \\
f'''(0) &= -6\frac{\theta}{T}+\mathcal{O}\left(\frac{\theta}{T}\right)^2 \\
f^{(\mathrm{v})}(0) &= \mathcal{O}\left(\frac{\theta}{T}\right)^2 .
\end{aligned}$$

Thus we have

$$\zeta(T) \approx 2\frac{T}{\theta}+\frac{1}{3}+\frac{1}{30}\frac{\theta}{T}+\mathcal{O}\left(\frac{\theta}{T}\right)^2 \tag{5.73}$$

$$\ln\zeta(T) \approx -\ln\frac{\theta}{2T}+\frac{1}{6}\frac{\theta}{T}+\frac{1}{360}\left(\frac{\theta}{T}\right)^2+\mathcal{O}\left(\frac{\theta}{T}\right)^3 \tag{5.74}$$

$$e^{\mathrm{rot}} \approx -k_B\theta\left[-\frac{T}{\theta}+\frac{1}{6}+\frac{1}{180}\frac{\theta}{T}+\mathcal{O}\left(\frac{\theta}{T}\right)^2\right] \tag{5.75}$$

$$c_V^{\mathrm{rot}} \approx k_B\left[1+\frac{1}{180}\left(\frac{\theta}{T}\right)^2+\mathcal{O}\left(\frac{\theta}{T}\right)^3\right]. \tag{5.76}$$

For high temperatures the specific heat is nearly equal to its classical value, and the quantity grows slightly larger as the temperature decreases.

Note: The $\approx$ sign in the above formulas represents "asymptotic equality". The infinite series on the right does not necessarily converge, and even if it does then it might not converge to the quantity on the left. However a finite truncation of the sum can be a good approximation for the quantity on the left, and that approximation grows better and better with increasing temperature (i.e. smaller values of θ/T).

5.5 Chemical Reactions Between Gases

5.6 Problems

5.5 **Decoupling quantal Hamiltonians**

Prove the "decoupling Hamilton implies factoring partition function" theorem of section 5.1.2 for quantal systems.

5.6 **Schottky anomaly**

A molecule can be accurately modeled by a quantal two-state system with ground state energy 0 and excited state energy ϵ. Show that the internal specific heat is

$$c_V^{\mathrm{int}}(T)=k_B\left(\frac{\epsilon}{k_BT}\right)^2\frac{e^{-\epsilon/k_BT}}{(1+e^{-\epsilon/k_BT})^2}. \tag{5.77}$$

Sketch this specific heat as a function of k_BT/ϵ. How does the function behave when $k_BT \ll \epsilon$ and $k_BT \gg \epsilon$?

5.7 **Simple harmonic oscillator**

Suppose a molecule can be accurately modeled as a harmonic oscillator of natural frequency ω.

a. Find the expected internal energy of one such molecule, written as a sum of the ground state energy plus a temperature-dependent part.

b. Show that the internal specific heat is

$$c_V^{\text{int}}(T) = k_B \left(\frac{\hbar\omega}{k_B T} \right)^2 \frac{e^{-\hbar\omega/k_B T}}{(1 - e^{-\hbar\omega/k_B T})^2}. \tag{5.78}$$

c. Show that at low temperatures ($k_B T \ll \hbar\omega$),

$$c_V^{\text{int}}(T) \approx k_B \left(\frac{\hbar\omega}{k_B T} \right)^2 e^{-\hbar\omega/k_B T}, \tag{5.79}$$

whereas at high temperatures ($k_B T \gg \hbar\omega$),

$$c_V^{\text{int}}(T) \approx k_B. \tag{5.80}$$

d. (Optional.) Show that the leading quantal correction to the high-temperature specific heat is

$$c_V^{\text{int}}(T) = k_B[1 - \tfrac{1}{12}x^2 + \mathcal{O}(x^3)], \quad \text{where} \quad x = \frac{\hbar\omega}{k_B T}. \tag{5.81}$$

e. Sketch the internal specific heat as a function of $k_B T/\hbar\omega$.

5.8 **Conceptual comparison**

a. Explain qualitatively why the results of the two previous problems are parallel at low temperatures.

b. (Harder.) Explain qualitatively both high temperature results. (Clue: At high temperatures, the average energy per particle in the Schottky case approaches $\epsilon/2$. Why?)

5.9 **Simple harmonic oscillator — entropy**

I was speaking with someone who claimed that thermodynamics didn't apply to systems of interacting atoms, or to living things, or to anything other than the ideal gas. He challenged me "What's the entropy of a pendulum? The answer is that entropy doesn't apply to a pendulum!" Answer his question for a pendulum in the simple harmonic oscillator approximation, with natural frequency ω and temperature T.

5.10 **Kinetic energy in air**

What is the kinetic energy is a cubic liter of air (mostly nitrogen and oxygen) at one atmosphere pressure and room temperature? At one atmosphere pressure and temperature 600 K? Use classical mechanics, and express your answer both in joules and in the commercial unit kilowatt-hours. (*Clue:* If you calculate the average kinetic energy of one molecule, you're working way too hard.) Why doesn't anyone exploit all this valuable energy lying around in every cubic meter of air?

5.11 Compressibility of a diatomic gas

Find the isothermal compressibility κ_T for an ideal diatomic gas, where each molecule is modeled as a dumbbell with moment of inertia I.

5.12 Systems with a small number of states

(This problem requires *no calculation!* All the answers can be found in your head.) A collection of non-interacting particles is in thermal equilibrium. Each particle has only three energy eigenvalues, namely 0, ϵ, and 4ϵ.

a. What is the criterion for "high temperature" in this situation?

b. Suppose there are three non-degenerate energy eigenstates. At high temperatures, what is the average energy of each particle? (Clue: The answer is *not* 4ϵ.)

c. Now suppose that the lower two energy eigenstates are non-degenerate, but that there are two independent states with energy 4ϵ. What is the average energy per particle at high temperatures in this case?

5.13 Anharmonic oscillator

The energy eigenvalues of a simple harmonic oscillator are equally spaced, and we have explored the consequences of this for the heat capacity of a collection of harmonic oscillators. Suppose an anharmonic oscillator is approximately harmonic (with natural frequency ω_0) for small energies, but that for large energies (greater than, say, E_x) the eigenvalues become *more* closely spaced as energy increases. At temperatures greater than E_x/k_B, will the heat capacity of a collection of such anharmonic oscillators be greater than or less than that of a collection of harmonic oscillators with the same natural frequency ω_0? Why?

5.14 Descriptive features of models

(This problem is stolen from a GRE Physics test.)

Two possible models for a diatomic ideal gas are the rigid dumbbell (model R; two point particles connected by a rigid rod) and the springy dumbbell (model S; two point particles connected by a spring). In classical statistical mechanics, which of the following statements is true?

a. Model R has a specific heat $c_V = \frac{3}{2}k_B$.

b. Model S has a smaller specific heat than model R.

c. Model S is always correct.

d. Model R is always correct.

e. The choice between models R and S depends on the temperature.

5.15 An n-state system, qualitatively

A model molecule has n equally-spaced energy levels, all of them non-degenerate, with energy spacing ϵ. Thus as n varies from 2 to ∞ this model interpolates between the Schottky system of problem 5.6 and the simple harmonic oscillator of problem 5.7.

a. Find a low-temperature approximation for the specific heat that is independent of n.

b. At high temperatures, the specific heat approaches zero. What is the criterion for "high temperature"?

c. At high temperatures, what is the expected energy of this model?

d. There is a theorem stating that at any fixed positive temperature, the specific heat must increase with increasing n. Assume this theorem and use it to prove that as n increases, the maximum in the specific heat versus temperature curve becomes higher.

5.16 **An n-state system, quantitatively**

Show that the system of the previous problem has internal specific heat

$$c_V^{\text{int}}(T) = k_B \left[\left(\frac{\epsilon}{k_B T} \right)^2 \frac{e^{-\epsilon/k_B T}}{(1 - e^{-\epsilon/k_B T})^2} - \left(\frac{n\epsilon}{k_B T} \right)^2 \frac{e^{-n\epsilon/k_B T}}{(1 - e^{-n\epsilon/k_B T})^2} \right]. \tag{5.82}$$

Does this expression have the proper limits when $n = 2$ and when $n \to \infty$?

Chapter 6

Quantal Ideal Gases

6.1 Introduction

In the previous chapter, we found that at high temperatures, an ideal gas of diatomic molecules with spring interactions has a heat capacity of $\frac{7}{2}k_B$ per molecule: $\frac{3}{2}k_B$ from the translational degrees of freedom, k_B from the rotational degrees of freedom, and k_B from the spring degrees of freedom. If the temperature is decreased, the spring degrees of freedom become governed by quantum mechanics rather than classical mechanics, the equipartition theorem no longer holds, and eventually these degrees of freedom "freeze out" and contribute nothing to the heat capacity: the total heat capacity per molecule becomes $\frac{5}{2}k_B$. If the temperature is decreased still further, the story is repeated for the rotational degrees of freedom and eventually they freeze out. What happens if the temperature is decreased yet again? Do the translational degrees of freedom then freeze out as well? The answer is "sort of", but the crossover from the classical to the quantal regime is complicated in this case by the quantal requirement of interchange symmetry. This requirement gives rise to a much richer and more interesting crossover behavior than is provided by simple freeze out.

6.2 The Interchange Rule

Before turning to statistical mechanics, let us review the quantal "interchange rule". The wavefunction for a system of three particles is a function of three variables: $\psi(\mathsf{x}_A, \mathsf{x}_B, \mathsf{x}_C)$. [The symbol x represents whatever is needed to specify the state: For a spinless particle in one dimension x represents the coordinate x or, if you are working in momentum space, the coordinate p. For a particle with spin moving in three dimensions, x represents (x, y, z, m_z), or perhaps (p_x, p_y, p_z, m_x).] If the three particles are identical, then the wavefunction must be either symmetric under the interchange of any pair of variables,

$$\psi(\mathsf{x}_A, \mathsf{x}_B, \mathsf{x}_C) = +\psi(\mathsf{x}_B, \mathsf{x}_A, \mathsf{x}_C) = +\psi(\mathsf{x}_B, \mathsf{x}_C, \mathsf{x}_A), \qquad \text{etc.,} \tag{6.1}$$

or else antisymmetric under the interchange of any pair of variables,

$$\psi(\mathsf{x}_A, \mathsf{x}_B, \mathsf{x}_C) = -\psi(\mathsf{x}_B, \mathsf{x}_A, \mathsf{x}_C) = +\psi(\mathsf{x}_B, \mathsf{x}_C, \mathsf{x}_A), \qquad \text{etc.} \tag{6.2}$$

The foregoing assertion is an empirical rule that cannot be derived from any of the other principles of quantum mechanics. (Indeed there is currently considerable interest in *anyons*, hypothetical particles that obey all the principles of quantum mechanics except the interchange rule.) The rule holds for all quantal states, not just energy eigenstates. It holds for interacting as well as for non-interacting particles. And the rule has a number of surprising consequences, both within the domain of quantum mechanics and atomic physics, and, as well shall soon see in detail, within the domain of statistical mechanics.

The sign of the interchange symmetry, either + or −, is governed only by the type of particle involved: for pions it is always +, for electrons it is always −. Particles for which the sign is always + are called *bosons*, and those for which it is always − are called *fermions*. It is an experimental fact that particles with integral spin s are bosons and those with half integral spin s are fermions.

6.2.1 Problems

6.1 **The interchange rule in another representation**

Full information about the state of three identical spinless particles is contained not only in the configurational wave function $\psi(\mathbf{x}_A, \mathbf{x}_B, \mathbf{x}_C)$ but also in the momentum space wave function

$$\tilde{\psi}(\mathbf{p}_A, \mathbf{p}_B, \mathbf{p}_C) = \frac{1}{(2\pi\hbar)^{9/2}} \int d^3x_A \int d^3x_B \int d^3x_C \psi(\mathbf{x}_A, \mathbf{x}_B, \mathbf{x}_C) e^{-i(\mathbf{p}_A\cdot\mathbf{x}_A + \mathbf{p}_B\cdot\mathbf{x}_B + \mathbf{p}_C\cdot\mathbf{x}_C)/\hbar}. \tag{6.3}$$

Show that if one representation is symmetric (or antisymmetric), then the other one is as well.

6.2 **Symmetrization**

Show that for any function $f(x, y, z)$, the function

$$f_S(x, y, z) = f(x, y, z) + f(x, z, y) + f(z, x, y) + f(z, y, x) + f(y, z, x) + f(y, x, z) \tag{6.4}$$

is symmetric under the interchange of any pair of variables. How many such pairs are there? Is there a similar algorithm for building up an antisymmetric function from any garden-variety function?

6.3 Quantum Mechanics of Independent Identical Particles

This chapter considers collections of independent (i.e. non-interacting) identical monatomic particles. It does not treat mixtures or diatomic molecules. Notice that "independent" means only that the particles do not interact with each other. In contrast, each particle individually may interact with some background potential, such as a square well or harmonic oscillator potential. Later on (in section 6.5) we will restrict our consideration to particles that interact only with the walls of their container ("free particles"), but for now we treat the more general case.

Doing quantal statistical mechanics requires a basis of states to sum over. In this section we consider the only the quantum mechanics of our situation in order to produce an energy eigenbasis. . . we defer all questions of statistical mechanics to the next section.

Most of our discussion in this section is phrased in terms of the three-particle problem rather than the N-particle problem. The use of a specific number lends the advantage of concreteness, and three is the smallest number that generalizes readily to the N-particle case.

6.3.1 A basis for non-identical particles

Consider first a single particle moving in the background potential. Elementary quantum mechanics deals with this situation, and it tells us that there will be a certain number M of (possibly degenerate) energy eigenstates. (Usually M will be infinite, but there are advantages to calling it M and maintaining the ability to take the limit $M \to \infty$.) The rth energy eigenstate has energy ϵ_r and is represented by the wavefunction $\eta_r(\mathsf{x})$, where x denotes the arguments of the wavefunction: Thus for a spinless particle, x could stand for x, y, z or p_x, p_y, p_z or even p_x, y, p_z. For a particle with spin s, x could stand for expressions like x, y, z, s_z or p_x, p_y, p_z, s_x.

We will soon use these one-particle energy eigenstates as building blocks to construct energy eigenstates for the N-particle situation, i.e. energy eigenstates for the entire system. Thus we will frequently be talking about both "one-particle energy eigenstates" and "N-particle energy eigenstates" in the same sentence, and both phrases are mouthfulls. To make our sentences shorter and clearer—and to emphasize the dramatic distinction between these two entities—we will adopt the common convention of referring to the one-particle energy eigenstates as "levels" and to the N-particle energy eigenstates as "states". (Some books use the term "orbitals" rather than "levels".) Thus we have for the one-particle energy eigenproblem:

$$\begin{array}{rcccccc} \text{levels:} & \eta_1(\mathsf{x}) & \eta_2(\mathsf{x}) & \cdots & \eta_r(\mathsf{x}) & \cdots & \eta_M(\mathsf{x}) \\ \text{energies:} & \epsilon_1 & \epsilon_2 & \cdots & \epsilon_r & \cdots & \epsilon_M \end{array}$$

Now consider more than one particle—let's say three particles—moving independently and all subject to the same background potential. If the particles are not identical (say one helium, one argon, and one neon atom), then the three-body energy eigenbasis will contain elements ("states") such as

$$\eta_r(\mathsf{x}_A)\eta_s(\mathsf{x}_B)\eta_t(\mathsf{x}_C) \quad \text{with energy} \quad \epsilon_r + \epsilon_s + \epsilon_t. \tag{6.5}$$

(If the particles interacted, then this would still be a state of the system, but it would not be an energy eigenstate.) We will represent this state by the notation $|r, s, t\rangle$:

$$\eta_r(\mathsf{x}_A)\eta_s(\mathsf{x}_B)\eta_t(\mathsf{x}_C) \quad \Longleftrightarrow \quad |r, s, t\rangle. \tag{6.6}$$

Of course, degeneracies now *must* exist: the energy of $|r, s, t\rangle$ is the same as the energy of $|s, r, t\rangle$. The entire basis consists of M^3 such states (more generally, for the case of N independent particles, M^N), namely:

$$
\begin{gathered}
|\,1\,,\ 1\ ,\ 1\ \rangle \\
|\,2\,,\ 1\ ,\ 1\ \rangle \\
|\,1\,,\ 2\ ,\ 1\ \rangle \\
|\,1\,,\ 1\ ,\ 2\ \rangle \\
|\,3\,,\ 1\ ,\ 1\ \rangle \\
\vdots \\
|\,3\,,\ 2\ ,\ 1\ \rangle \\
|\,3\,,\ 1\ ,\ 2\ \rangle \\
\vdots \\
|\,4\,,\ 2\ ,\ 1\ \rangle \\
\vdots \\
|\mathrm{M},\ \mathrm{M},\ \mathrm{M}\ \rangle
\end{gathered}
$$

Out of these M^3 states we can build up (by addition and scalar multiplication) any wavefunction, i.e. any normalized function of $(\mathsf{x}_A, \mathsf{x}_B, \mathsf{x}_C)$. This is exactly what we want for non-identical particles. But for identical particles we don't want to be able to build *any* wavefunction. Because of the interchange rule, the only relevant wavefunctions are those symmetric (or antisymmetric) under the interchange of any pair of coordinates, for example

$$\psi(\mathsf{x}_A, \mathsf{x}_B, \mathsf{x}_C) = \pm\psi(\mathsf{x}_C, \mathsf{x}_B, \mathsf{x}_A), \tag{6.7}$$

and hence these are the only kind of wavefunctions we want to be able to build. In other words, we need an energy eigenbasis consisting only of symmetric (or antisymmetric) wavefunctions.

6.3.2 A basis for identical particles

Fortunately, there exists a general procedure for constructing symmetric (or antisymmetric) functions out of garden-variety (or "non-symmetrized") functions, and this procedure will enable us to build the two desired basis sets. For functions of three variables the procedure (which is readily generalized to N variables) works like this: Given a function $f(x_A, x_B, x_C)$, the new function

$$f(x_A,x_B,x_C)+f(x_A,x_C,x_B)+f(x_C,x_A,x_B)+f(x_C,x_B,x_A)+f(x_B,x_C,x_A)+f(x_B,x_A,x_C) \tag{6.8}$$

is surely symmetric under the interchange of any pair of variables, and the new function

$$f(x_A,x_B,x_C)-f(x_A,x_C,x_B)+f(x_C,x_A,x_B)-f(x_C,x_B,x_A)+f(x_B,x_C,x_A)-f(x_B,x_A,x_C) \tag{6.9}$$

is surely antisymmetric. These two procedures are called "symmetrization" and "antisymmetrization" (or sometimes "alternation") respectively. It is of course possible that the resulting function vanishes, but this does not invalidate the procedure, because zero functions are both symmetric *and* antisymmetric!

When applied to a quantal wavefunction $\psi(\mathsf{x}_A, \mathsf{x}_B, \mathsf{x}_C)$, these processes result in the symmetric wavefunction

$$\hat{S}\psi(\mathsf{x}_A, \mathsf{x}_B, \mathsf{x}_C) \equiv A_s[\psi(\mathsf{x}_A, \mathsf{x}_B, \mathsf{x}_C)+\psi(\mathsf{x}_A, \mathsf{x}_C, \mathsf{x}_B)+\psi(\mathsf{x}_C, \mathsf{x}_A, \mathsf{x}_B)+\psi(\mathsf{x}_C, \mathsf{x}_B, \mathsf{x}_A)+\psi(\mathsf{x}_B, \mathsf{x}_C, \mathsf{x}_A)+\psi(\mathsf{x}_B, \mathsf{x}_A, \mathsf{x}_C)] \tag{6.10}$$

and in the antisymmetric wavefunction

$$\hat{A}\psi(\mathsf{x}_A, \mathsf{x}_B, \mathsf{x}_C) \equiv A_a[\psi(\mathsf{x}_A, \mathsf{x}_B, \mathsf{x}_C)-\psi(\mathsf{x}_A, \mathsf{x}_C, \mathsf{x}_B)+\psi(\mathsf{x}_C, \mathsf{x}_A, \mathsf{x}_B)-\psi(\mathsf{x}_C, \mathsf{x}_B, \mathsf{x}_A)+\psi(\mathsf{x}_B, \mathsf{x}_C, \mathsf{x}_A)-\psi(\mathsf{x}_B, \mathsf{x}_A, \mathsf{x}_C)] \tag{6.11}$$

where the constants A_s and A_a are inserted simply to insure normalization. Note that the operators $\hat{S}$ and $\hat{A}$ defined above are *linear*, whence *a basis for symmetric wavefunctions may be obtained by symmetrizing every element of an ordinary, non-symmetrized, basis*, and similarly for antisymmetric wavefunctions.

For functions of three variables that factorize into three functions of one variable, i.e. functions of the form (6.5), these definitions can be expressed even more simply because, for example, swapping η_s and η_t is the same as swapping x_B and x_C. Thus, if $|r, s, t\rangle$ is an energy eigenstate, then

$$\hat{S}|r, s, t\rangle \equiv A_s[|r, s, t\rangle + |r, t, s\rangle + |t, r, s\rangle + |t, s, r\rangle + |s, t, r\rangle + |s, r, t\rangle] \tag{6.12}$$

is a symmetric state with the same energy, while

$$\hat{A}|r, s, t\rangle \equiv A_a[|r, s, t\rangle - |r, t, s\rangle + |t, r, s\rangle - |t, s, r\rangle + |s, t, r\rangle - |s, r, t\rangle] \tag{6.13}$$

in an antisymmetric state with the same energy.

It is easy to see that the symmetrization process is unaffected by the order of the letters, i.e. that

$$\hat{S}|r, s, t\rangle = \hat{S}|r, t, s\rangle \quad \text{etc.,} \tag{6.14}$$

whence, for example, the states $|1, 1, 2\rangle$, $|1, 2, 1\rangle$, and $|2, 1, 1\rangle$ all symmetrize to the same state. Similarly in antisymmetrization the order of the letters affects only the sign of the result,

$$\hat{A}|r, s, t\rangle = -\hat{A}|r, t, s\rangle = \hat{A}|t, r, s\rangle \quad \text{etc.,} \tag{6.15}$$

but this result is considerably more profound: It shows not only that, for example, $\hat{A}|1, 2, 3\rangle$ is the same state as $\hat{A}|3, 2, 1\rangle$, but also that

$$\hat{A}|3, 1, 1\rangle = -\hat{A}|3, 1, 1\rangle \tag{6.16}$$

whence $\hat{A}|3, 1, 1\rangle = 0$, and, in general, that $|r, s, t\rangle$ antisymmetrizes to zero unless r, s, and t are all distinct.

Now we construct a basis for symmetric wavefunctions by applying the operator $\hat{S}$ to every element of our non-symmetrized basis on page 141. We obtain

$\hat{S}|\,1\,,\;1\;,\;1\,\rangle$

$\hat{S}|\,2\,,\;1\;,\;1\,\rangle$

~~$\hat{S}|\,1\,,\;2\;,\;1\,\rangle$~~

~~$\hat{S}|\,1\,,\;1\;,\;2\,\rangle$~~

$\hat{S}|\,3\,,\;1\;,\;1\,\rangle$

$\vdots$

$\hat{S}|\,3\,,\;2\;,\;1\,\rangle$

~~$\hat{S}|\,3\,,\;1\;,\;2\,\rangle$~~

$\vdots$

$\hat{S}|\,4\,,\;2\;,\;1\,\rangle$

$\vdots$

$\hat{S}|\mathrm{M},\;\mathrm{M},\;\mathrm{M}\rangle$

where the crossed out elements are those that have already appeared earlier in the list. It is clear that there are fewer elements in this basis than there are in the non-symmetrized basis, although it is a challenge to count them exactly. The number of elements turns out to be

$$\frac{(M)(M+1)(M+2)}{3!}, \tag{6.17}$$

or, for the N-particle rather than the three-particle case,

$$\left(\begin{array}{c} M+N-1 \\ N \end{array} \right). \tag{6.18}$$

where the binomial coefficient symbol is defined through

$$\left(\begin{array}{c} m \\ n \end{array} \right) \equiv \frac{m!}{n!(m-n)!}. \tag{6.19}$$

We construct a basis for antisymmetric wavefunctions in the same way. The result is

~~$\hat{A}|1\,,\ 1\ ,\ 1\ \rangle$~~

~~$\hat{A}|2\,,\ 1\ ,\ 1\ \rangle$~~

~~$\hat{A}|1\,,\ 2\ ,\ 1\ \rangle$~~

~~$\hat{A}|1\,,\ 1\ ,\ 2\ \rangle$~~

~~$\hat{A}|3\,,\ 1\ ,\ 1\ \rangle$~~

$$\vdots$$

$\hat{A}|\,3\,,\ 2\ ,\ 1\ \rangle$

~~$\hat{A}|3\,,\ 1\ ,\ 2\ \rangle$~~

$$\vdots$$

$\hat{A}|\,4\,,\ 2\ ,\ 1\ \rangle$

$$\vdots$$

~~$\hat{A}|M,\ M,\ M\rangle$~~

where now the crossed out elements have either appeared earlier in the list or else are equal to zero. There are even fewer elements in this basis than there were in the symmetrized basis. In fact there are exactly

$$\frac{(M)(M-1)(M-2)}{3!}, \tag{6.20}$$

such elements or, for the case of N particles,

$$\left(\begin{array}{c} M \\ N \end{array} \right) \equiv \frac{M!}{N!(M-N)!} \tag{6.21}$$

elements.

For the case $N = 2$, there are $M(M+1)/2$ elements the symmetric basis and $M(M-1)/2$ elements in the antisymmetric basis, so the sum is M^2, the number of elements in the non-symmetrized basis. In fact, for $N = 2$, the set resulting from the conjunction of the symmetric and antisymmetric bases is a basis for the entire set of any function of two variables. This is related to the fact that any two-variable function can be written as the sum of a symmetric function and an antisymmetric function. I point out these results to emphasize that they apply for the two-variable case only, and are not general properties of symmetric and antisymmetric functions. For $N \geq 3$, the conjunction of the symmetric and antisymmetric bases does *not* span the set of all N-variable functions.

6.3.3 The occupation number representation

We have seen that in order to specify an element of the symmetric or the antisymmetric basis that we have just produced, it is not necessary to specify the order of the one-particle level building blocks. For example $\hat{A}|4,9,7\rangle$ is the same state as $\hat{A}|4,7,9\rangle$, so there's no need to pay attention to the order in which the 4, 7, and 9 appear. This observation permits the "occupation number" representation of such states, in which we specify the basis state simply by listing the one-particle levels that are used as building blocks to make up that state. Or, equivalently but more commonly, we specify the basis state by listing the number n_r of one-body levels of each type r that are used as building blocks. (And, of course, we must also specify whether we're considering the symmetric or the antisymmetric basis.) Thus, for example:

level r:	1	2	3	4	5	6	$\cdots$	M
$\hat{S}\|3,3,4\rangle$ has n_r:	0	0	2	1	0	0	$\cdots$	0
$\hat{A}\|1,3,4\rangle$ has n_r:	1	0	1	1	0	0	$\cdots$	0

The second line in this table means that the state $\hat{S}|3,3,4\rangle$ is built by starting with the three levels $\eta_3(\mathsf{x}_A)$, $\eta_3(\mathsf{x}_B)$, and $\eta_4(\mathsf{x}_A)$, multiplying them together, and then symmetrizing. Sometimes you will hear this state described by the phrase "there are two particles in level 3 and one particle in level 4", but that can't be literally true... the three particles are identical, and if they could be assigned to distinct levels they would not be identical! Phrases such as the one above[1] invoke the "balls in buckets" picture of N-particle quantal wavefunctions: The state $\hat{S}|3,3,4\rangle$ is pictured as two balls in bucket number 3 and one ball in bucket number 4. It is all right to use this picture and this phraseology, as long as you don't believe it. Always keep in mind that it is a shorthand for a more elaborate process of building up states from levels by multiplication and symmetrization.

The very term "occupation number" for n_r is a poor one, because it so strongly suggests the balls-in-buckets picture. A somewhat better name for n_r is "occupancy", and I will sometimes use it. If you can think of a better name, please tell me.

To summarize the occupation number representation: an element of the symmetric basis is specified by the list

$$n_r, \qquad \text{for} \qquad r = 1, 2, \ldots M, \qquad \text{where} \qquad n_r \text{ is } 0, 1, 2, \ldots, \tag{6.22}$$

and an element of the antisymmetric basis is specified by the list

$$n_r, \qquad \text{for} \qquad r = 1, 2, \ldots M, \qquad \text{where} \qquad n_r \text{ is 0 or 1.} \tag{6.23}$$

The total number of particles in such a state is

$$N = \sum_{r=1}^{M} n_r, \tag{6.24}$$

and the energy of the state is

$$E = \sum_{r=1}^{M} n_r \epsilon_r. \tag{6.25}$$

Finally, since we have been devoting so much attention to energy eigenstates, I remind you that there do exist states other than energy states. (Expand on this paragraph and insert a reference to the caveat concerning meaning of $e^{-\beta E}$ for arbitrary states on page 113.)

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[1] For example, phrases like "the level is filled" or "the level is empty" or "the level is half-filled".

6.3.4 Problems

6.3 **Bases in quantum mechanics**
We have just produced an energy eigenbasis for independent non-identical particles, one for independent bosons, and one for independent fermions. In each case did we produce the only possible energy eigenbasis or just one of several possible energy eigenbases? If the particles interact, the states in question will no longer constitute an energy eigenbasis. But will they constitute a basis?

6.4 **Symmetrization in the N-variable case**
Equations (6.8) and (6.9) contain algorithms for constructing (anti)symmetric functions of three variables by summing up six terms. How do these equations generalize to functions of N variables and, in particular, how many terms appear in each sum?

6.5 **Symmetrizing the symmetric**
The non-symmetrized state $|r, s, t\rangle$ is already symmetric in the case that $r = s = t$. What happens if you attempt to symmetrize this already symmetric state through the procedure (6.12)? What if you attempt to antisymmetrize it through the procedure (6.13)?

6.6 **Normalization constants**
Find the normalization constants A_s and A_a in equations (6.12) and (6.13). Be sure your formula works for the case of $\hat{S}|3, 3, 5\rangle$ and $\hat{S}|4, 4, 4\rangle$. Generalize your result to the N-particle case, where the answer is a function of $n_1, n_2, \ldots, n_M$ as well as N.

6.7 **Algorithms for permutations**
Invent some problem concerning the Heap algorithm for generating permutations. Better just give a reference to Sedgwick's paper.

6.8 **Algorithms to list basis states**
Come up with some algorithm for producing the three sets of basis states that we have discussed, preferably in some useful order (where "useful" is to be defined by you). Your algorithm should generalize readily to the N-particle case.

6.9 **Number of basis elements**
Perform the counts (6.18) and (6.21). (Clue: Do it first for $N = 3$, then for N arbitrary.)

6.4 Statistical Mechanics of Independent Identical Particles

6.4.1 Partition function

Now that we have an energy eigenbasis, the obvious thing to do is to calculate the canonical partition function

$$Z(\beta) = \sum_{\text{states}} e^{-\beta E}, \tag{6.26}$$

where for fermions and bosons, respectively, the term "state" implies the occupation number lists:

fermions	$(n_1, n_2, \cdots, n_M)$, $n_r = 0, 1$, subject to $\sum_r n_r = N$
bosons	$(n_1, n_2, \cdots, n_M)$, subject to $\sum_r n_r = N$

As we have seen, it is difficult to even count these lists, much less enumerate them and perform the relevant sum! It can be done, but there is a trick that renders it unnecessary. (Don't be ashamed if you don't see the trick…neither did Einstein or Fermi. They both did it the hard, canonical way.)

The trick here, as in so many places in statistical mechanics, is to use the grand canonical ensemble. In this ensemble, the partition function is

$$\Xi(\beta,\mu) = \sum_{\text{states}} e^{-\beta E+\beta\mu N} = \sum_{\text{states}} e^{-\beta\sum_r(n_r\epsilon_r-\mu n_r)} = \sum_{\text{states}}\prod_{r=1}^{M} e^{-\beta n_r(\epsilon_r-\mu)} \tag{6.27}$$

where the term "state" now implies the occupation number lists *without any restriction on total particle number:*

fermions	$(n_1, n_2, \cdots, n_M)$, $n_r = 0, 1$
bosons	$(n_1, n_2, \cdots, n_M)$

Writing out the sum over states explicitly, we have for fermions

$$\Xi(\beta,\mu) = \sum_{n_1=0}^{1}\sum_{n_2=0}^{1}\cdots\sum_{n_M=0}^{1}\prod_{r=1}^{M} e^{-\beta n_r(\epsilon_r-\mu)} \tag{6.28}$$

$$= \left[\sum_{n_1=0}^{1} e^{-\beta n_1(\epsilon_1-\mu)}\right]\left[\sum_{n_2=0}^{1} e^{-\beta n_2(\epsilon_2-\mu)}\right]\cdots\left[\sum_{n_M=0}^{1} e^{-\beta n_M(\epsilon_M-\mu)}\right]. \tag{6.29}$$

A typical factor in the product is

$$\left[\sum_{n_r=0}^{1} e^{-\beta n_r(\epsilon_r-\mu)}\right] = 1 + e^{-\beta(\epsilon_r-\mu)}, \tag{6.30}$$

so for fermions

$$\Xi(\beta,\mu) = \prod_{r=1}^{M} 1 + e^{-\beta(\epsilon_r-\mu)}. \tag{6.31}$$

Meanwhile, for bosons, the explicit state sum is

$$\Xi(\beta,\mu) = \sum_{n_1=0}^{\infty}\sum_{n_2=0}^{\infty}\cdots\sum_{n_M=0}^{\infty}\prod_{r=1}^{M} e^{-\beta n_r(\epsilon_r-\mu)} \tag{6.32}$$

$$= \left[\sum_{n_1=0}^{\infty} e^{-\beta n_1(\epsilon_1-\mu)}\right]\left[\sum_{n_2=0}^{\infty} e^{-\beta n_2(\epsilon_2-\mu)}\right]\cdots\left[\sum_{n_M=0}^{\infty} e^{-\beta n_M(\epsilon_M-\mu)}\right], \tag{6.33}$$

and a typical factor in the product is

$$\left[\sum_{n_r=0}^{\infty} e^{-\beta n_r(\epsilon_r-\mu)}\right] = 1 + [e^{-\beta(\epsilon_r-\mu)}] + [e^{-\beta(\epsilon_r-\mu)}]^2 + [e^{-\beta(\epsilon_r-\mu)}]^3 + \cdots \tag{6.34}$$

$$= \frac{1}{1-e^{-\beta(\epsilon_r-\mu)}}, \tag{6.35}$$

where in the last line we have summed the geometric series under the assumption that $\epsilon_r > \mu$. Thus for bosons

$$\Xi(\beta, \mu) = \prod_{r=1}^{M} \frac{1}{1 - e^{-\beta(\epsilon_r - \mu)}}. \tag{6.36}$$

The two results are compactly written together as

$$\Xi(\beta, \mu) = \prod_{r=1}^{M} [1 \pm e^{-\beta(\epsilon_r - \mu)}]^{\pm 1}, \tag{6.37}$$

where the + sign refers to fermions and the − sign to bosons.

6.4.2 Mean occupation numbers

In our previous work, we have always found the partition function and worked from there. Surprisingly, however, for the situation of quantal ideal gases it is more useful to find the mean occupation numbers, such as

$$\langle n_5 \rangle = \frac{\sum_{\text{states}} n_5 e^{-\beta(E-\mu N)}}{\sum_{\text{states}} e^{-\beta(E-\mu N)}} = \frac{\sum_{\text{states}} n_5 e^{-\beta \sum_r (n_r \epsilon_r - n_r \mu)}}{\Xi(\beta, \mu)}. \tag{6.38}$$

Note that the averages $\langle n_r \rangle$ are functions of β and μ (as well as of r) but it is notationally clumsy to show that dependence.

How can such averages be evaluated? A slick trick would be helpful here! Consider the derivative

$$\frac{\partial \ln \Xi}{\partial \epsilon_5} = \frac{1}{\Xi} \frac{\partial \Xi}{\partial \epsilon_5} = \frac{1}{\Xi} \sum_{\text{states}} (-\beta n_5) e^{-\beta \sum_r (n_r \epsilon_r - n_r \mu)} = -\beta \langle n_5 \rangle. \tag{6.39}$$

Using the explicit expression (6.37) for Ξ (where the + sign refers to fermions and the − sign to bosons), this gives

$$\begin{aligned}
\langle n_5 \rangle &= -\frac{1}{\beta} \frac{\partial \ln \Xi}{\partial \epsilon_5} && (6.40)\\
&= -\frac{1}{\beta} \left\{ \frac{\partial}{\partial \epsilon_5} \sum_{r=1}^{M} \ln[1 \pm e^{-\beta(\epsilon_r - \mu)}]^{\pm 1} \right\} && (6.41)\\
&= -\frac{1}{\beta} \left\{ \frac{\partial}{\partial \epsilon_5} \ln[1 \pm e^{-\beta(\epsilon_5 - \mu)}]^{\pm 1} \right\} && (6.42)\\
&= -\frac{1}{\beta} \left\{ \pm \frac{\pm(-\beta) e^{-\beta(\epsilon_5 - \mu)}}{[1 \pm e^{-\beta(\epsilon_5 - \mu)}]} \right\} && (6.43)\\
&= \frac{1}{e^{\beta(\epsilon_5 - \mu)} \pm 1}, && (6.44)
\end{aligned}$$

leaving us with the final result

$$\langle n_r \rangle = \frac{1}{e^{\beta(\epsilon_r - \mu)} \pm 1}. \tag{6.45}$$

As before, the + sign refers to fermions and the − sign to bosons.

The mean occupation numbers play such an important role that it is easy to forget that they are only averages, that there will be fluctuations, that for a given T and μ not all states will have exactly $\langle n_5 \rangle$ building blocks of level 5 (see problem 6.13). Keep this in mind if you ever find yourself saying "occupation number" rather than "mean occupation number".

In practice, these results from the grand canonical ensemble are used as follows: One uses these results to find quantities of interest as functions of temperature, volume, and chemical potential, such as the pressure $p(T, V, \mu)$. But most experiments are done with a fixed number of particles N, so at the very end of your calculation you will want to find $\mu(T, V, N)$ in order to express your final answer as $p(T, V, N)$. You can find $\mu(T, V, N)$ by demanding that

$$N = \sum_{r=1}^{M} \langle n_r \rangle = \sum_{r=1}^{M} \frac{1}{e^{\beta(\epsilon_r - \mu)} \pm 1}. \tag{6.46}$$

In other words, the quantity μ serves as a parameter to insure normalization, very much as the quantity Z serves to insure normalization in the canonical ensemble through

$$1 = \sum_n \frac{e^{-\beta E_n}}{Z}. \tag{6.47}$$

You might wonder, in fact, about the relation between the canonical probability

$$\frac{e^{-\beta E_n}}{Z}, \tag{6.48}$$

which we have seen many times before, and the recently derived occupancy probability

$$\frac{1}{N} \frac{1}{e^{\beta(\epsilon_r - \mu)} \pm 1}. \tag{6.49}$$

The first result applies to both interacting and non-interacting systems, both classical and quantal. The second applies only to non-interacting quantal systems. Why do we need a new probability? What was wrong with our derivation (in section 4.1) of the canonical probability that requires us to replace it with an occupancy probability? The answer is that nothing was wrong and that the occupancy probability doesn't replace the canonical probability. The canonical probability and the occupancy probability answer different questions. The first finds the probability that the entire system is in the many-body state n. The second finds the probability that the one-body level r is used as a building block in constructing the many-body state. Indeed, although we derived the occupancy probability result through a grand canonical argument, it is also possible to derive the occupancy probabilities from strict canonically arguments, proof that these two probabilities can coexist peacefully.

6.4.3 The Boltzmann limit

This is the limit where particles are far enough apart that overlap of wavefunction is minimal, so we needn't worry about symmetrization or antisymmetrization. Equivalently, it is the limit where $\langle n_r \rangle \ll 1$ for all r.

6.4.4 Problems

6.10 **Evaluation of the grand canonical partition function**

Can you find a simple expression for $\Xi(\beta, \mu)$ for non-interacting particles in a one-dimensional harmonic well? For non-interacting particles in a one-dimensional infinite square well? For any other potential? Can you do anything valuable with such an expression once you've found it?

6.11 **Entropy of quantal ideal gases**

This problem derives an expression for the entropy of a quantal ideal gas in terms of the mean occupation numbers $\langle n_r \rangle$. (Compare problem 4.3.) Throughout the problem, in the symbols $\pm$ and $\mp$, the top sign refers to fermions and the bottom sign refers to bosons.

a. Use the connection between thermodynamics and statistical mechanics to show that, for any system,

$$\frac{S(T,V,\mu)}{k_B} = \ln \Xi - \beta \frac{\partial \ln \Xi}{\partial \beta}. \tag{6.50}$$

b. Show that for the quantal ideal gas,

$$\ln \Xi(T,V,\mu) = \mp \sum_r \ln(1 \mp \langle n_r \rangle). \tag{6.51}$$

c. The mean occupation numbers $\langle n_r \rangle$ are functions of T, V, and μ (although it is notationally clumsy to show this dependence). Show that

$$\begin{aligned} \beta \left. \frac{\partial \langle n_r \rangle}{\partial \beta} \right)_{V,\mu} &= -\beta(\epsilon_r - \mu)\langle n_r \rangle (1 \mp \langle n_r \rangle) \\ &= -[\ln(1 \mp \langle n_r \rangle) - \ln\langle n_r \rangle]\langle n_r \rangle (1 \mp \langle n_r \rangle). \end{aligned} \tag{6.52}$$

d. Finally, show that

$$S(T,V,\mu) = -k_B \sum_r [\langle n_r \rangle \ln\langle n_r \rangle \pm (1 \mp \langle n_r \rangle) \ln(1 \mp \langle n_r \rangle)]. \tag{6.53}$$

e. Find a good approximation for this expression in the Boltzmann limit, $\langle n_r \rangle \ll 1$.

f. (Optional.) Find an expression for C_V in terms of the quantities $\langle n_r \rangle$.

6.12 **Isothermal compressibility of quantal ideal gases**

a. Show that in a quantal ideal gas, the isothermal compressibility is

$$\kappa_T = \frac{1}{\rho k_B T} \left[1 \mp \frac{\sum_r \langle n_r \rangle^2}{\sum_r \langle n_r \rangle} \right], \tag{6.54}$$

where as usual the top sign refers to fermions and the bottom sign to bosons. (Clue: Choose the most appropriate expression for κ_T from those uncovered in problem 3.34.)

b. Compare this expression to that for a classical ("Maxwell-Boltzmann") ideal gas.

c. The negative sign in the expression for fermions opens the possibility that κ_T could be negative. Prove that this potential horror never happens.

d. Do the relative sizes of the three compressibilites (fermion, classical, boson) adhere to your qualitative expectations? (Compare problem 6.29.)

6.13 **Dispersion in occupation number**

Find an expression analogous to (6.45) giving the dispersion in the occupation numbers. (Clue: A slick trick would be helpful here.) Answer:

$$\Delta n_r = \frac{1}{e^{\beta(\epsilon_r-\mu)/2} \pm e^{-\beta(\epsilon_r-\mu)/2}} = \sqrt{\langle n_r\rangle(1 \mp \langle n_r\rangle)} \tag{6.55}$$

6.5 Quantum Mechanics of Free Particles

"Particle in a box." Periodic boundary conditions. k-space. In the thermodynamic limit, the dots in k-space become densely packed, and it seems appropriate to replace sums over levels with integrals over k-space volumes. (In fact, there is at least one situation (see equation 6.76) in which this replacement is *not* correct.)

Density of levels in k-space:

$$\frac{V}{8\pi^3} \qquad \text{(worth memorizing).} \tag{6.56}$$

Energy density of levels:

$$\text{number of one-body levels with } \epsilon_r \text{ from } \mathcal{E} \text{ to } \mathcal{E}+d\mathcal{E} \equiv G(\mathcal{E})\,d\mathcal{E} = V\frac{\sqrt{2m^3}}{2\pi^2\hbar^3}\sqrt{\mathcal{E}}\,d\mathcal{E}. \tag{6.57}$$

How to use energy density of levels:

$$\sum_r f(\epsilon_r) \approx \int_0^\infty G(\mathcal{E})f(\mathcal{E})\,d\mathcal{E} \tag{6.58}$$

and this approximation (usually) becomes exact in the thermodynamic limit.

6.5.1 Problems

6.14 **Free particles in a box**

We argued that, for a big box, periodic boundary conditions would give the same results as "clamped boundary conditions". Demonstrate this by finding the density of levels for three-dimensional particle in a box problem.

6.15 **Density of levels for bound particles**

What is the density of levels $G(\mathcal{E})$ for a one-dimensional harmonic oscillator with spring constant K? For a three-dimensional isotropic harmonic oscillator?

6.16 **Density of levels in d dimensions**

What is the density of levels $G(\mathcal{E})$ for free particles subject to periodic boundary conditions in a world of d dimensions?

6.6 Fermi-Dirac Statistics

In three dimensions, the chemical potential μ *decreases* with temperature. Why? It is clear that at $T = 0$, $\mu = \mathcal{E}_F > 0$. But as the temperature rises the gas approaches the classical limit, for which $\mu < 0$ (see problem 2.23). This is not proof, but it makes sense that μ should decrease with increasing temperature. A proof is available but surprisingly difficult.

6.6.1 Problems

6.17 **Qualitative origin of $\mathcal{E}_F$**

(This problem is stolen from a GRE Physics test.)

The mean kinetic energy of electrons in metals at room temperature is usually many times the thermal energy k_BT. Which of the following can best be used to explain this fact?

a. The time-energy uncertainty relation.
b. The Pauli exclusion principle.
c. The degeneracy of the energy levels.
d. The Born approximation.
e. The wave-particle duality.

6.18 **Fermion gas in two dimensions**

(This problem is based on one in Ashcroft and Mermin, page 53.)

Consider a gas of free, independent, spin-$\frac{1}{2}$ fermions in two dimensions. The gas is contained within an area (or two dimensional volume) of A.

a. What is the density of one-particle levels in k-space?
b. How does the Fermi energy $\mathcal{E}_F$ depend upon the density N/A?
c. Use $\sum_r \langle n_r \rangle = N$ to show that

$$\mu + k_BT \ln(1 + e^{-\mu/k_BT}) = \mathcal{E}_F. \tag{6.59}$$

Notice that the chemical potential μ decreases with temperature.

6.19 **Dependence of chemical potential on temperature**

Show that for independent (not necessarily free) fermions, the $\mu(T)$ curve has slope (when N and V are constant)

$$\frac{d\mu}{dT} = -\frac{1}{T}\frac{\int_0^\infty G(\mathcal{E})\mathrm{sech}^2(\beta(\mathcal{E}-\mu)/2)(\mathcal{E}-\mu)\,d\mathcal{E}}{\int_0^\infty G(\mathcal{E})\mathrm{sech}^2(\beta(\mathcal{E}-\mu)/2)\,d\mathcal{E}}. \tag{6.60}$$

Can you use this result to show that the chemical potential must decrease with temperature? I can't.

6.20 **Thermodynamics of the fermion gas**

Consider a collection of free and independent spin-$\frac{1}{2}$ fermions. Do *not* assume that the temperature vanishes.

a. Use the fundamental grand canonical result $\Pi = -k_B T \ln \Xi$ to show that

$$p(T,\mu)V = k_B T \int_0^\infty G(\mathcal{E}) \ln(1 + e^{\beta(\mu-\mathcal{E})})\, d\mathcal{E}. \tag{6.61}$$

b. Use the expression for $G(\mathcal{E})$ and the change of variable $x = \beta\mathcal{E}$ to find

$$p(T,\mu) = (k_B T)^{5/2} \left[\frac{\sqrt{2m^3}}{\pi^2\hbar^3}\right] \int_0^\infty \sqrt{x} \ln(1 + e^{\beta\mu} e^{-x})\, dx. \tag{6.62}$$

c. Integrate by parts to obtain

$$p(T,\mu) = \frac{2}{3}(k_B T)^{5/2} \left[\frac{\sqrt{2m^3}}{\pi^2\hbar^3}\right] \int_0^\infty \frac{x^{3/2}}{e^x e^{-\beta\mu} + 1} dx. \tag{6.63}$$

(Do not attempt to evaluate the integral that remains.)

d. Meanwhile, show that the total energy

$$E(T,V,\mu) = \int_0^\infty G(\mathcal{E}) f(\mathcal{E}) \mathcal{E}\, d\mathcal{E} \tag{6.64}$$

is given by

$$E(T,V,\mu) = V(k_B T)^{5/2} \left[\frac{\sqrt{2m^3}}{\pi^2\hbar^3}\right] \int_0^\infty \frac{x^{3/2}}{e^x e^{-\beta\mu} + 1} dx. \tag{6.65}$$

Thus the pressure and energy are related by

$$pV = \tfrac{2}{3}E, \tag{6.66}$$

which is exactly the same relationship they have in the classical monatomic ideal gas! (See problem 6.28.)

6.21 **Thermodynamics at zero temperature**

Use the result of the previous problem to show that at absolute zero the pressure of a gas of free and independent spin-$\frac{1}{2}$ fermions does not vanish (as it does for a classical ideal gas). Instead, the zero-temperature pressure is $\frac{2}{5}\rho\mathcal{E}_F$. Show also that the isothermal compressibility is $\frac{3}{5}(1/p)$. Interpret this last result by discussing the relative softness of air and steel at room temperature.

6.22 **Mass-radius relation for white dwarf stars**

(This problem is modified from Kittel and Kroemer, *Thermal Physics*, second edition, page 216.)

A white dwarf star (see Kittel and Kroemer, pp. 196–198) consists of highly compressed hydrogen in which the atoms have ionized into independent protons and electrons. In most cases it is a good model to assume that the electrons are free and independent non-relativistic fermions at zero temperature. Consider a white dwarf of mass M and radius R, containing N electrons.

a. Show that to a very good approximation, $N = M/m_p$, where m_p is the mass of a proton.

b. Show that the gravitational potential energy of a uniform sphere of mass M and radius R is $-cGM^2/R$, where G is the gravitational constant and c is a dimensionless constant. (In fact $c = \frac{3}{5}$ but this is tedious to show.)

c. Show that the kinetic energy of the electrons is

$$\text{KE} = \frac{9}{20}\left(\frac{3\pi^2}{2}\right)^{1/3}\frac{\hbar^2}{m_e m_p^{5/3}}\frac{M^{5/3}}{R^2}, \tag{6.67}$$

where m_e is the mass of an electron.

d. If the potential and kinetic energies satisfy

$$\text{KE} = -\tfrac{1}{2}\text{PE}, \tag{6.68}$$

as required by the virial theorem of mechanics, show that

$$RM^{1/3} = \text{ a constant of approximate value } 10^{17} \text{ m kg}^{1/3}. \tag{6.69}$$

Evaluate the constant assuming that $c = \frac{3}{5}$. Note that the radius *decreases* as the mass *increases.*

e. If the white dwarf has the mass of the sun (2×10^{30} kg), what is its radius (in km)? Compare this to the radius of our sun.

f. Neutron stars (observed as pulsars) are also zero temperature fermion gases, but in this case the fermions are neutrons rather than electrons. Derive the mass-radius relation for a neutron star, and use it to find the radius of a neutron star with the mass of the sun.

6.7 Bose-Einstein Statistics

Perhaps you thought the Fermi-Dirac results were strange: Non-interacting particles forming a collection as hard as steel. . . room temperature being effectively zero. Wait until you see the Bose-Einstein results.

6.7.1 Theory

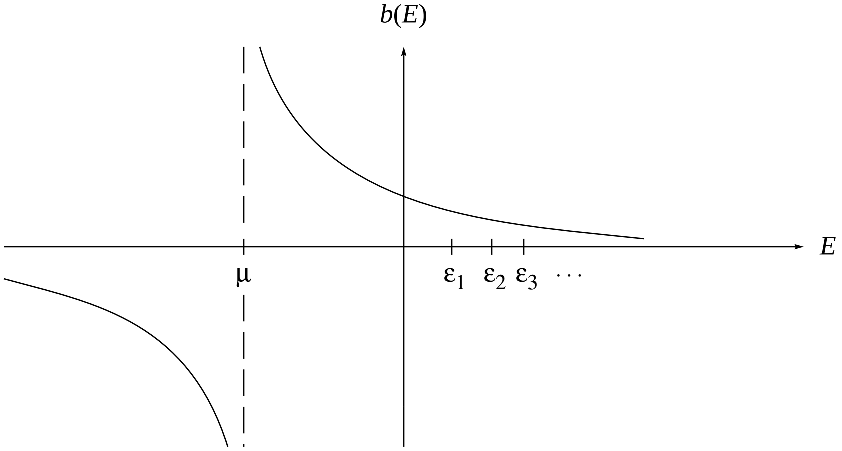
For independent bosons, whether free or subject to an external potential, the mean occupation number function is

$$b(\mathcal{E}) = \frac{1}{e^{\beta(\mathcal{E}-\mu)} - 1}. \tag{6.70}$$

To begin to understand this function, note that

when:	we have:
$\mathcal{E} < \mu$	$b(\mathcal{E})$ negative
$\mathcal{E} = \mu$	$b(\mathcal{E}) = \infty$
$\mathcal{E} > \mu$	$b(\mathcal{E})$ positive

Thus this function has the general character sketched below:



The normalization requirement

$$N = \sum_r b(\epsilon_r) \tag{6.71}$$

goes over to, whenever $b(\mathcal{E})$ is smooth on the scale of the separation between energy levels,

$$N = \int_0^\infty b(\mathcal{E}) G(\mathcal{E})\, d\mathcal{E} \tag{6.72}$$

where (from equation 6.57)

$$G(\mathcal{E}) = V \left[\frac{\sqrt{2m^3}}{2\pi^2\hbar^3} \right] \sqrt{\mathcal{E}}.$$

In the thermodynamic limit the separation between energy levels goes to zero, so your first thought would be that substituting the integral for the sum would always be legitimate. This first thought is correct *except* at the point $\mathcal{E} = \mu$, where $b(\mathcal{E})$ goes to infinity and cannot be smooth.

The correct integral replacement for the normalization sum is

$$N = \int_0^\infty G(\mathcal{E}) \frac{1}{e^{\beta(\mathcal{E}-\mu)} - 1}\, d\mathcal{E} \qquad \text{when } \mu < 0 \tag{6.73}$$

$$N = \langle n_1 \rangle + \int_0^\infty G(\mathcal{E}) \frac{1}{e^{\beta\mathcal{E}} - 1}\, d\mathcal{E} \qquad \text{when } \mu = 0. \tag{6.74}$$

The crossover between these two behaviors comes when

$$\begin{aligned} N &= \int_0^\infty G(\mathcal{E}) \frac{1}{e^{\beta\mathcal{E}} - 1}\, d\mathcal{E} \\ &= V \left[\frac{\sqrt{2m^3}}{2\pi^2\hbar^3} \right] \int_0^\infty \sqrt{\mathcal{E}} \frac{1}{e^{\beta\mathcal{E}} - 1}\, d\mathcal{E} \end{aligned}$$

$$
\begin{aligned}
&= V\left[\frac{\sqrt{2m^3}}{2\pi^2\hbar^3}\right](k_BT)^{3/2}\int_0^\infty \frac{\sqrt{x}}{e^x-1}\,dx\\
&= V\left[\frac{\sqrt{2m^3}}{2\pi^2\hbar^3}\right](k_BT)^{3/2}\left\{\frac{\sqrt{\pi}}{2}\zeta(\tfrac{3}{2})\right\},
\end{aligned}
$$

where the evaluation of the integral at the last step is performed in problem 6.26 and where the Riemann zeta function is defined by

$$\zeta(s)=\sum_{n=1}^{\infty}\frac{1}{n^s}\qquad\text{and}\qquad \zeta(\tfrac{3}{2})=2.612375348\ldots.$$

Shifting focus from chemical potential to temperature, the crossover occurs at temperature T_0 where

$$T_0(\rho)=\frac{2\pi}{\zeta^{2/3}(\frac{3}{2})}\frac{\hbar^2}{k_Bm}\rho^{2/3}. \tag{6.75}$$

The normalization condition is

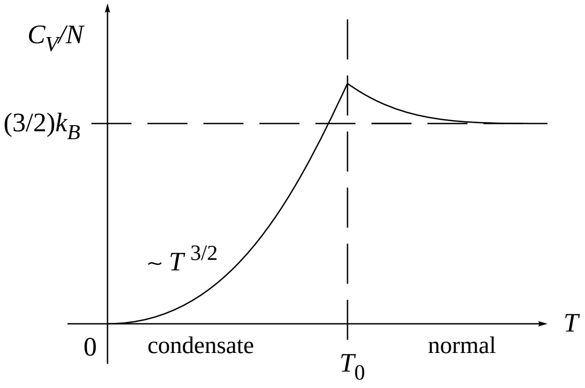
$$
\begin{aligned}
N &= \int_0^\infty G(\mathcal{E})\frac{1}{e^{\beta(\mathcal{E}-\mu)}-1}\,d\mathcal{E} &&\text{when } T>T_0(\rho)\\
N &= \langle n_1\rangle + V\left[\frac{\sqrt{2m^3}}{2\pi^2\hbar^3}\right](k_BT)^{3/2}\left\{\frac{\sqrt{\pi}}{2}\zeta(\tfrac{3}{2})\right\} &&\text{when } T<T_0(\rho)
\end{aligned}
$$

or

$$N = \int_0^\infty G(\mathcal{E})\frac{1}{e^{\beta(\mathcal{E}-\mu)}-1}\,d\mathcal{E} \qquad \text{when } T>T_0(\rho) \tag{6.76}$$

$$N = \langle n_1\rangle + N\left[\frac{T}{T_0(\rho)}\right]^{3/2} \qquad \text{when } T<T_0(\rho). \tag{6.77}$$

The first equation, applying to $T>T_0(\rho)$, can be converted to an expression for $\mu(T,V,N)$, from which all thermodynamics can be derived. For $T<T_0(\rho)$ it is always true that $\mu=0$, but with sufficient cleverness you can again derive all thermodynamics. Because these are two dramatically different procedures, we should expect that each part will behave quite differently, i.e. we expect a sudden change of behavior as the temperature drops through T_0. I will leave this pleasant but arduous project for your future, but I'll show you just one result: the expression for heat capacity as a function of temperature.



The abrupt transition at $T_0(\rho)$ is called Bose-Einstein condensation and the material at temperatures below $T_0(\rho)$ is called the Bose condensate. These terms are unfortunate: they conjure images of a gas condensing into a liquid, in which circumstance the atoms separate into two different classes: those in the liquid and those remaining in the vapor. This suggests that in Bose-Einstein condensation too there are two classes of particles: those in the ground level and those in the excited levels. This picture is totally false. It is incorrect to say "one particle is in the ground level, another is in the fourth excited level". In truth the individual particles are not in individual levels at all: instead the whole system is in a state produced by multiplying together the individual level wavefunctions ("building blocks") and then symmetrizing them. The literature of Bose-Einstein statistics is full of statements like "at temperatures below T_0, any particle added to the system goes into the ground level." Such statements are wrong. They should be replaced with statements like "at temperatures below T_0, any increase in particle number occurs through an increase in $\langle n_1 \rangle$, the mean occupancy of the ground level." Or alternatively, "at temperatures below T_0, it is very likely that many of the building blocks from which the system wavefunction is built are the ground level." Or again, to be absolutely precise, "at temperatures below T_0, if the energy is measured then it is very likely that many of the building blocks from which the resulting energy eigenfunction is built are the ground level."

6.7.2 Experiment

References: M.H. Anderson, J.R. Ensher, M.R. Matthews, C.E. Wieman, E.A. Cornell, "Observation of Bose-Einstein condensation in a dilute atomic vapor", *Science*, **269** (14 July 1995) 198–201; Randall G. Hullet at Rice; Malcolm W. Browne, "Two groups of physicists produce matter that Einstein postulated", New York *Times*, 14 July 1995, page 1.

6.7.3 Problems

6.23 **Character of the Bose function**

What are the limits of the Bose function $b(\mathcal{E})$ (equation 6.70) as $\mathcal{E} \to \pm\infty$? Is the curvature of the function greater when the temperature is high or when it is low?

6.24 **Thermodynamics of the Bose condensate**

For temperatures less than the Bose condensation temperature T_0, find the energy, heat capacity, and entropy of an ideal gas of spin-zero bosons confined to a volume V. Write your answers in terms of the dimensionless integral

$$I = \int_0^\infty \frac{x^{3/2}}{e^x - 1}\, dx \tag{6.78}$$

but don't bother to evaluate it. Show that

$$C_V = \frac{5}{2}\frac{E}{T} \quad \text{and} \quad S = \frac{5}{3}\frac{E}{T}. \tag{6.79}$$

6.25 **More thermodynamics of the Bose condensate**

For the system of the previous problem, show that

$$F = -\frac{2}{3}E \quad \text{and} \quad p = \frac{2}{3}\frac{E}{V}. \tag{6.80}$$

From this show that at low temperatures, the pressure of a collection of free and independent bosons goes like $p \sim T^{5/2}$. (This is always less than the classical pressure $p \sim T$.)

6.26 **An integral important for Bose condensation**

Show that

$$\int_0^\infty \frac{x^{1/2}}{e^x - 1}dx = \zeta(\tfrac{3}{2})\frac{\sqrt{\pi}}{2} \tag{6.81}$$

where

$$\zeta(s) = \sum_{n=1}^{\infty} \frac{1}{n^s}. \tag{6.82}$$

Clue:

$$\frac{1}{e^x - 1} = \frac{1}{e^x(1 - e^{-x})} = e^{-x}\sum_{n=0}^{\infty} e^{-nx} \quad \text{for} \quad x > 0. \tag{6.83}$$

6.8 Specific Heat of the Ideal Fermion Gas

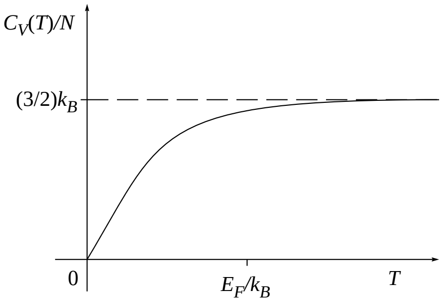
There is a "set of the pants" heuristic argument showing that at low temperatures,

$$C_V(T) \approx k_B G(\mathcal{E}_F)(k_B T). \tag{6.84}$$

This argument is not convincing in detail as far as the magnitude is concerned and, indeed, we will soon find that it is wrong by a factor of $\pi^2/3$. On the other hand it is quite clear that the specific heat will increase linearly with T at low temperatures. From equipartition, the classical result is

$$C_V^{\text{classical}} = \tfrac{3}{2}Nk_B, \tag{6.85}$$

and we expect this result to hold at high temperature. Thus our overall expectation is that the specific heat will behave as sketched below.



How can we be more precise and rigorous? That is the burden of this section.

Reminders:

$$\begin{aligned} f(\mathcal{E}) &= \frac{1}{e^{(\mathcal{E}-\mu)/k_BT}+1} && (6.86)\\ \mathcal{E}_F &= \frac{\hbar^2}{2m}\left(3\pi^2\frac{N}{V}\right)^{2/3} && (6.87)\\ G(\mathcal{E}) &= V\frac{\sqrt{2m^3}}{\pi^2\hbar^3}\sqrt{\mathcal{E}} = N\frac{3}{2}\frac{1}{\mathcal{E}_F^{3/2}}\sqrt{\mathcal{E}} && (6.88) \end{aligned}$$

The expressions for N and E are

$$\begin{aligned} N(T,V,\mu) &= \int_0^\infty G(\mathcal{E})f(\mathcal{E})\,d\mathcal{E} &&= V\frac{\sqrt{2m^3}}{\pi^2\hbar^3}\int_0^\infty \mathcal{E}^{1/2}f(\mathcal{E})\,d\mathcal{E}\\ E(T,V,\mu) &= \int_0^\infty \mathcal{E}G(\mathcal{E})f(\mathcal{E})\,d\mathcal{E} &&= V\frac{\sqrt{2m^3}}{\pi^2\hbar^3}\int_0^\infty \mathcal{E}^{3/2}f(\mathcal{E})\,d\mathcal{E}. \end{aligned} \qquad (6.89)$$

Remember how to use these expressions: The first we will invert to find $\mu(T,V,N)$, then we will plug this result into the second to find $E(T,V,N)$. As a preliminary, recognize that we can clean up some messy expressions in terms of the physically significant constant $\mathcal{E}_F$ by writing these two expressions as

$$\begin{aligned} 1 &= \frac{3}{2}\frac{1}{\mathcal{E}_F^{3/2}}\int_0^\infty \mathcal{E}^{1/2}f(\mathcal{E})\,d\mathcal{E} && (6.90)\\ \frac{E}{N} &= \frac{3}{2}\frac{1}{\mathcal{E}_F^{3/2}}\int_0^\infty \mathcal{E}^{3/2}f(\mathcal{E})\,d\mathcal{E}. && (6.91) \end{aligned}$$

In short, we must evaluate integrals like

$$\int_0^\infty \frac{\mathcal{E}^{\alpha-1}}{e^{(\mathcal{E}-\mu)/k_BT}+1}d\mathcal{E} \qquad (6.92)$$

with the dimensions of [energy]$^\alpha$. To make these more mathematical and less physical, convert to the dimensionless quantities

$$\begin{aligned} x &= \mathcal{E}/k_BT && (6.93)\\ x_0 &= \mu/k_BT && (6.94) \end{aligned}$$

to find

$$\int_0^\infty \frac{\mathcal{E}^{\alpha-1}}{e^{(\mathcal{E}-\mu)/k_BT}+1}d\mathcal{E} = (k_BT)^\alpha \int_0^\infty \frac{x^{\alpha-1}}{e^{x-x_0}+1}dx. \qquad (6.95)$$

Define the dimensionless integral

$$A_\alpha(x_0) = \int_0^\infty \frac{x^{\alpha-1}}{e^{x-x_0}+1}dx. \qquad (6.96)$$

so that

$$\begin{aligned} 1 &= \frac{3}{2}\frac{(k_BT)^{3/2}}{\mathcal{E}_F^{3/2}}A_{3/2}(\mu/k_BT) && (6.97)\\ \frac{E}{N} &= \frac{3}{2}\frac{(k_BT)^{5/2}}{\mathcal{E}_F^{3/2}}A_{5/2}(\mu/k_BT). && (6.98) \end{aligned}$$

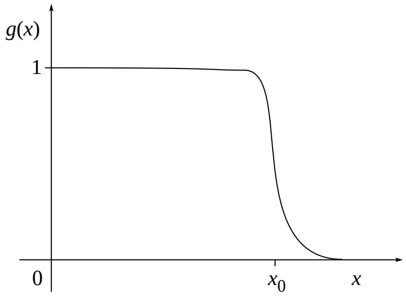
Let us pause before rushing forward. You might think that we should turn to Mathematica (or to a table of integrals) and try to evaluate these integrals in terms of well-known functions like exponentials and Bessel functions. Even if we could do this, it wouldn't help: The result would just be an incomprehensible morass of functions, and to try to understand it we would need to, among other things, look at the low-temperature limit and the high-temperature limit. Since we are particularly interested in the low-temperature behavior, let's just set out to find the low-temperature series in the first place. The meaning of "low temperature" in this context is $k_BT \ll \mu$ or $x_0 = \mu/k_BT \gg 1$, so we suspect a series like

$$E(T) = E(T=0) + \frac{E_1}{x_0} + \frac{E_2}{x_0^2} + \cdots. \tag{6.99}$$

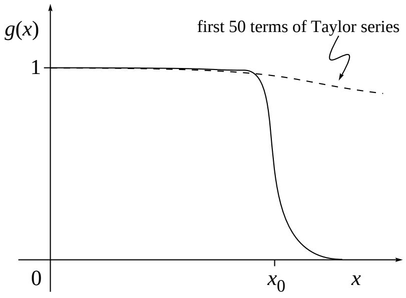
Whenever we have previously searched for such a series (for example, when we investigated internal specific heat of the rigid dumbbell, section 5.4, or the simple harmonic oscillator, problem 5.7) we had good luck using a Taylor series expansion about the origin. In this case, any such technique is doomed to failure, for the following reason: We need a good approximation for the function

$$g(x) = \frac{1}{e^{x-x_0}+1}, \tag{6.100}$$

a function that is very flat near the origin.



In fact, this function is so flat at the origin that, even if we kept dozens of terms in its Taylor series expansion about the origin, the Taylor approximation would be quite poor.



Indeed, all of the *action* associated with this function happens near $x = x_0$. (We saw earlier, in our heuristic discussion, that the low-temperature specific heat was due entirely to promotion of a few electrons near the Fermi energy.) Thus an accurate low-temperature approximation will necessarily involve expansions around $x = x_0$, not around $x = 0$.

Arnold Sommerfeld was aware this situation and had the genius to recognize that a change in focus would solve the problem. Specifically, the focus needs to change from the function $g(x)$ to its derivative $g'(x)$, because the derivative is very small for all x except near $x = x_0$, where the action is. In specific, he noted that

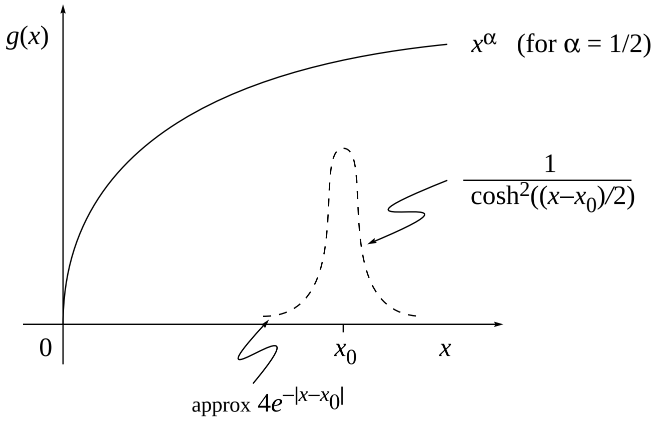
$$\begin{aligned} g'(x) &= -\frac{e^{x-x_0}}{(e^{x-x_0}+1)^2} \\ &= -\frac{1}{(e^{-(x-x_0)/2}+e^{(x-x_0)/2})^2} \\ &= -\frac{1}{4\cosh^2((x-x_0)/2)}. \end{aligned}$$

The last form makes clear the remarkable fact that $g'(x)$ is even under reflections about x_0.

How can we use these facts about $g'(x)$ to solve integrals involving $g(x)$? Through integration by parts.

$$\begin{aligned} A_\alpha(x_0) &= \int_0^\infty x^{\alpha-1} g(x)\,dx \\ &= \left[\frac{x^\alpha}{\alpha} g(x)\right]_0^\infty - \int_0^\infty \frac{x^\alpha}{\alpha} g'(x)\,dx \\ &= \frac{1}{4\alpha}\int_0^\infty \frac{x^\alpha}{\cosh^2((x-x_0)/2)}\,dx \end{aligned} \tag{6.101}$$

It's now easy to plot the pieces of the integrand, and to see that the integrand nearly vanishes except near $x = x_0$.



Because x^α varies slowly near $x = x_0$, it makes sense to expand it in a Taylor series about $x = x_0$:

$$\begin{array}{ccccccccc} f(x) & = & f(x_0) & + & f'(x_0)(x-x_0) & + & \frac{1}{2}f''(x_0)(x-x_0)^2 & + & \cdots \\ x^\alpha & = & x_0^\alpha & + & \alpha x_0^{\alpha-1}(x-x_0) & + & \frac{1}{2}\alpha(\alpha-1)x_0^{\alpha-2}(x-x_0)^2 & + & \cdots \end{array}$$

So

$$\begin{aligned} 4\alpha A_\alpha(x_0) &= \int_0^\infty \frac{x^\alpha}{\cosh^2((x-x_0)/2)}dx \\ &= x_0^\alpha \int_0^\infty \frac{1}{\cosh^2((x-x_0)/2)}dx + \alpha x_0^{\alpha-1}\int_0^\infty \frac{(x-x_0)}{\cosh^2((x-x_0)/2)}dx \\ &\qquad + \tfrac{1}{2}\alpha(\alpha-1)x_0^{\alpha-2}\int_0^\infty \frac{(x-x_0)^2}{\cosh^2((x-x_0)/2)}dx + \cdots. \end{aligned}$$

Let's think about how to evaluate integrals like

$$\int_0^\infty \frac{(x-x_0)^n}{\cosh^2((x-x_0)/2)}dx. \tag{6.102}$$

The denominator is even in the variable $(x - x_0)$, while the numerator is either even or odd in the variable $(x - x_0)$. If the lower limit were $-\infty$ instead of 0, half of these integrals would vanish… an immense labor savings! Now, of course, the lower limit isn't $-\infty$, but on the other hand if we extended the lower limit from 0 to $-\infty$, we wouldn't pick up much error, because the integrand nearly vanishes when x is negative. In fact, the error introduced is

$$\int_{-\infty}^0 \frac{(x-x_0)^n}{\cosh^2((x-x_0)/2)}dx = \int_{-\infty}^\infty \frac{(x-x_0)^n}{\cosh^2((x-x_0)/2)}dx - \int_0^\infty \frac{(x-x_0)^n}{\cosh^2((x-x_0)/2)}dx, \tag{6.103}$$

and the scale of this error is about the value of the integrand at $x = 0$, namely

$$\frac{(-x_0)^n}{\cosh^2(x_0/2)} \approx (-x_0)^n(4e^{-x_0}).$$

We could find more accurate approximations for this error, but there's no need to. We know the error is of order e^{-x_0} and we're interested in case that $x_0 \gg 1$. This error is utterly negligible. Remember that we expect an answer of the form

$$E(T) = E(T=0) + \frac{E_1}{x_0} + \frac{E_2}{x_0^2} + \cdots, \tag{6.104}$$

and that (in the limit as $x_0 \to \infty$) the error e^{-x_0} is *smaller* than any of these terms… even smaller than E_{492}/x_0^{492}. From now on we will change the lower limit of integration from 0 to $-\infty$, with the understanding that this replacement will introduce a negligible error. Thus, most of the remaining formulas in this section will show not equality, but rather "asymptotic equality", denoted by the symbol $\approx$.

(Perhaps I'm being too glib, because while this error is indeed small, I introduce it an infinite number of times. This is the kind of problem you might want to take to your friendly neighborhood applied mathematician. These folks can usually solve the problem more easily than you can and they often appreciate your bringing neat problems to them.)

Using these ideas, we write

$$\begin{aligned}
4\alpha A_\alpha(x_0) &= \int_0^\infty \frac{x^\alpha}{\cosh^2((x-x_0)/2)}dx \\
&= x_0^\alpha \int_0^\infty \frac{1}{\cosh^2((x-x_0)/2)}dx + \alpha x_0^{\alpha-1}\int_0^\infty \frac{(x-x_0)}{\cosh^2((x-x_0)/2)}dx \\
&\qquad +\tfrac{1}{2}\alpha(\alpha-1)x_0^{\alpha-2}\int_0^\infty \frac{(x-x_0)^2}{\cosh^2((x-x_0)/2)}dx+\cdots \\
&\approx x_0^\alpha \int_{-\infty}^\infty \frac{1}{\cosh^2((x-x_0)/2)}dx + \alpha x_0^{\alpha-1}\int_{-\infty}^\infty \frac{(x-x_0)}{\cosh^2((x-x_0)/2)}dx \\
&\qquad +\tfrac{1}{2}\alpha(\alpha-1)x_0^{\alpha-2}\int_{-\infty}^\infty \frac{(x-x_0)^2}{\cosh^2((x-x_0)/2)}dx+\cdots
\end{aligned}$$

Because the integrals extend from $-\infty$ to $+\infty$, it is easy to change the variable of integration to $x-x_0$, and then symmetry dictates that

$$\int_{-\infty}^\infty \frac{(x-x_0)^n}{\cosh^2((x-x_0)/2)}d(x-x_0)=0 \qquad \text{for all odd } n.$$

Using the substitution $u=(x-x_0)/2$, we have

$$4\alpha A_\alpha(x_0)\approx x_0^\alpha\left[2\int_{-\infty}^\infty \frac{1}{\cosh^2(u)}du+\frac{4\alpha(\alpha-1)}{x_0^2}\int_{-\infty}^\infty \frac{u^2}{\cosh^2(u)}du+\cdots\right] \tag{6.105}$$

The first integral can be found in Dwight and is

$$\int_{-\infty}^\infty \frac{1}{\cosh^2(u)}du=2.$$

The second is Gradshteyn 3.527.5, namely

$$\int_{-\infty}^\infty \frac{u^2}{\cosh^2(u)}du=\frac{\pi^2}{6}.$$

Consequently

$$A_\alpha(x_0)\approx\frac{x_0^\alpha}{\alpha}\left[1+\frac{\pi^2}{6}\frac{\alpha(\alpha-1)}{x_0^2}+\mathcal{O}\left(\frac{1}{x_0^4}\right)\right]. \tag{6.106}$$

This is the desired series in powers of $1/x_0$…and surprisingly, all the odd powers vanish! This result is known as "the Sommerfeld expansion".

Now we apply this formula to equation (6.97) to obtain the function $\mu(T)$:

$$\begin{aligned}
1 &\approx \frac{\mu^{3/2}}{\mathcal{E}_F^{3/2}}\left[1+\frac{\pi^2}{8}\left(\frac{k_BT}{\mu}\right)^2+\mathcal{O}\left(\frac{k_BT}{\mu}\right)^4\right] \\
\mu^{3/2} &\approx \mathcal{E}_F^{3/2}\left[1+\frac{\pi^2}{8}\left(\frac{k_BT}{\mu}\right)^2+\mathcal{O}\left(\frac{k_BT}{\mu}\right)^4\right]^{-1} \\
\mu &\approx \mathcal{E}_F\left[1+\frac{\pi^2}{8}\left(\frac{k_BT}{\mu}\right)^2+\mathcal{O}\left(\frac{k_BT}{\mu}\right)^4\right]^{-2/3} \\
&= \mathcal{E}_F\left[1-\frac{\pi^2}{12}\left(\frac{k_BT}{\mu}\right)^2+\mathcal{O}\left(\frac{k_BT}{\mu}\right)^4\right]
\end{aligned}$$

This equation tells us a lot: It confirms that at $T = 0$, we have $\mu = \mathcal{E}_F$. It confirms that at T increases from zero, the chemical potential μ decreases. However it doesn't directly give us an expression for $\mu(T)$ because μ appears on both the left and right sides. On the other hand, it does show us that μ deviates from $\mathcal{E}_F$ by an amount proportional to $(k_BT/\mu)^2$, which is small. How small?

$$\begin{aligned}
\left(\frac{k_BT}{\mu}\right)^2 &\approx \frac{(k_BT)^2}{\mathcal{E}_F^2\left[1-\frac{\pi^2}{12}\left(\frac{k_BT}{\mu}\right)^2+\mathcal{O}\left(\frac{k_BT}{\mu}\right)^4\right]^2} \\
&= \frac{(k_BT)^2}{\mathcal{E}_F^2\left[1-\frac{\pi^2}{6}\left(\frac{k_BT}{\mu}\right)^2+\mathcal{O}\left(\frac{k_BT}{\mu}\right)^4\right]} \\
&= \left(\frac{k_BT}{\mathcal{E}_F}\right)^2\left[1+\frac{\pi^2}{6}\left(\frac{k_BT}{\mu}\right)^2+\mathcal{O}\left(\frac{k_BT}{\mu}\right)^4\right]
\end{aligned}$$

In other words, it is small in the sense that

$$\left(\frac{k_BT}{\mu}\right)^2 \approx \left(\frac{k_BT}{\mathcal{E}_F}\right)^2+\mathcal{O}\left(\frac{k_BT}{\mathcal{E}_F}\right)^4 \tag{6.107}$$

and that

$$\mathcal{O}\left(\frac{k_BT}{\mu}\right)^4 \approx \mathcal{O}\left(\frac{k_BT}{\mathcal{E}_F}\right)^4 \tag{6.108}$$

This gives us the desired formula for μ as a function of T:

$$\mu(T) \approx \mathcal{E}_F\left[1-\frac{\pi^2}{12}\left(\frac{k_BT}{\mathcal{E}_F}\right)^2+\mathcal{O}\left(\frac{k_BT}{\mathcal{E}_F}\right)^4\right]. \tag{6.109}$$

This result verifies our previous heuristic arguments: $\mu(T)$ declines as the temperature increases, and it does so slowly (i.e. to second order in $k_BT/\mathcal{E}_F$).

Now apply expansion (6.106) for A_α to equation (6.98) to find the energy $E(T, V, \mu)$:

$$\frac{E}{N} \approx \frac{3}{5}\frac{\mu^{5/2}}{\mathcal{E}_F^{3/2}}\left[1+\frac{5\pi^2}{8}\left(\frac{k_BT}{\mu}\right)^2+\mathcal{O}\left(\frac{k_BT}{\mu}\right)^4\right]. \tag{6.110}$$

Using equations (6.107) and (6.108):

$$\frac{E}{N} \approx \frac{3}{5}\frac{\mu^{5/2}}{\mathcal{E}_F^{3/2}}\left[1+\frac{5\pi^2}{8}\left(\frac{k_BT}{\mathcal{E}_F}\right)^2+\mathcal{O}\left(\frac{k_BT}{\mathcal{E}_F}\right)^4\right]. \tag{6.111}$$

Now it's time to plug $\mu(T, V, N)$ into $E(T, V, \mu)$ to find $E(T, V, N)$: Use equation (6.109) for $\mu(T, V, N)$, and find

$$\begin{aligned}
\mu(T)^{5/2} &\approx \mathcal{E}_F^{5/2}\left[1-\frac{\pi^2}{12}\left(\frac{k_BT}{\mathcal{E}_F}\right)^2+\mathcal{O}\left(\frac{k_BT}{\mathcal{E}_F}\right)^4\right]^{5/2} \\
&= \mathcal{E}_F^{5/2}\left[1-\frac{5\pi^2}{24}\left(\frac{k_BT}{\mathcal{E}_F}\right)^2+\mathcal{O}\left(\frac{k_BT}{\mathcal{E}_F}\right)^4\right].
\end{aligned} \tag{6.112}$$

Using (6.112) in (6.111) gives

$$\frac{E}{N} \approx \frac{3}{5}\mathcal{E}_F \left[1 - \frac{5\pi^2}{24}\left(\frac{k_BT}{\mathcal{E}_F}\right)^2 + \mathcal{O}\left(\frac{k_BT}{\mathcal{E}_F}\right)^4\right]\left[1 + \frac{5\pi^2}{8}\left(\frac{k_BT}{\mathcal{E}_F}\right)^2 + \mathcal{O}\left(\frac{k_BT}{\mathcal{E}_F}\right)^4\right] \tag{6.113}$$

whence

$$E \approx \frac{3}{5}N\mathcal{E}_F\left[1 + \frac{5\pi^2}{12}\left(\frac{k_BT}{\mathcal{E}_F}\right)^2 + \mathcal{O}\left(\frac{k_BT}{\mathcal{E}_F}\right)^4\right]. \tag{6.114}$$

Wow! At long last we're able to say

$$C_V = \left.\frac{\partial E}{\partial T}\right)_{N,V} = \left.\frac{\partial E}{\partial(k_BT/\mathcal{E}_F)}\right)_{N,V}\left(\frac{k_B}{\mathcal{E}_F}\right) \tag{6.115}$$

whence

$$C_V \approx \frac{3}{5}Nk_B\left[\frac{5\pi^2}{6}\left(\frac{k_BT}{\mathcal{E}_F}\right) + \mathcal{O}\left(\frac{k_BT}{\mathcal{E}_F}\right)^3\right], \tag{6.116}$$

or, for low temperatures.

$$C_V \approx \frac{\pi^2}{2}Nk_B\left(\frac{k_BT}{\mathcal{E}_F}\right). \tag{6.117}$$

Was all this worth it, just to get a factor of $\pi^2/3$? Perhaps not, but our analysis gives us more than the factor. It gives us a better understanding of the ideal fermion gas and a deeper appreciation for the significance of the thin "action region" near $\mathcal{E} = \mathcal{E}_F$.

6.9 Additional Problems

6.27 **What if there were no interchange rule?**

Suppose that the interchange rule did not apply, so that the basis on page 141 were the correct one for three identical particles. (Alternatively, consider a gas of N non-identical particles.) Find and sketch the heat capacity as a function of temperature.

6.28 **Pressure and energy density**

(This problem was inspired by Reif problem 9.5.)

Any non-relativistic monatomic ideal gas, whether classical or quantal, satisfies

$$p = \frac{2}{3}\frac{E}{V}. \tag{6.118}$$

This remarkable fact can be demonstrated most easily in the canonical ensemble. (Throughout this problem the particle number is fixed so the N dependence of functions is never mentioned explicitly.)

a. Use $E = \frac{3}{2}Nk_BT$ to demonstrate the relation for the classical monatomic ideal gas.

b. From thermodynamics, show that

$$E(T,V) = -\left.\frac{\partial \ln Z}{\partial \beta}\right)_V \quad \text{and} \quad p(T,V) = \frac{1}{\beta}\left.\frac{\partial \ln Z}{\partial V}\right)_T. \tag{6.119}$$

c. Argue that temperature and energy eigenvalues enter into the canonical partition function as quotients:

$$\ln Z(T,V) = \mathcal{F}(\beta\epsilon_1, \beta\epsilon_2, \ldots, \beta\epsilon_M). \tag{6.120}$$

d. Show that in non-relativistic quantum mechanics the free particle energy eigenvalues depend on box volume through

$$\frac{\partial \epsilon_r}{\partial V} = -\frac{2}{3}\frac{\epsilon_r}{V}. \tag{6.121}$$

e. Use the last three items together to prove the pressure-energy density relation.

f. How are the pressure and energy density related for blackbody radiation? At what stage does the above proof break down in this case?

6.29 **Pressure comparison**

(This problem is modified from one in a GRE Physics test.)

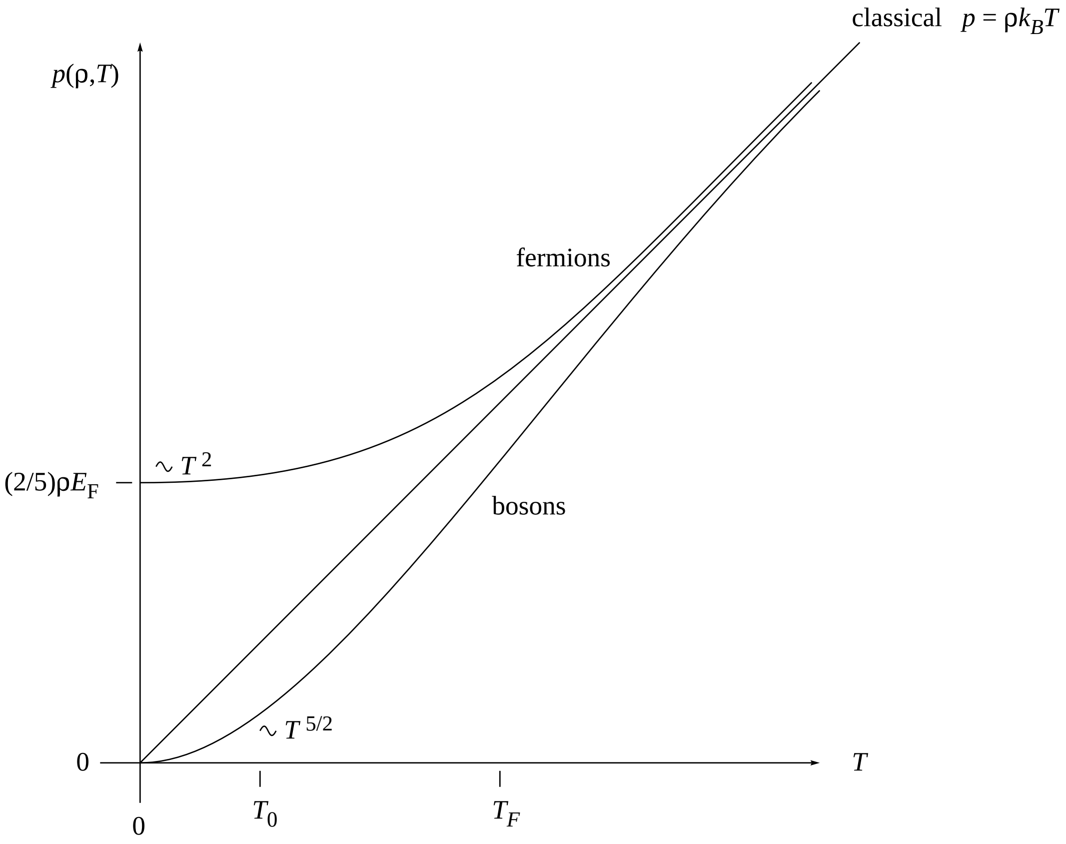
Consider three systems of non-interacting identical particles, each with the same T, V, and N. In one system the particles are fermions, in another they are bosons, and in a third they behave classically. Which system has the greatest pressure? Which has the smallest?

6.30 **Challenge**

For many years I suspected that the chemical potential μ of an ideal gas would have to decrease or at least remain constant when the temperature increased (with V and N constant). I tried proving this in a number of ways, and in my attempts I came across several interesting facts (such as the results of problem 3.37 and part (f.) of problem 6.11) but I was never been able to prove the desired result. That's because the result is false! The chemical potential increases with temperature for ideal fermions in one dimension. Can you show this?

Appendix

Even though we haven't been able to derive everything on this graph, I can't resist showing you the equation of state (that is, pressure as a function of density and temperature), for ideal fermions, ideal classical particles, and ideal bosons.



Chapter 7

Harmonic Lattice Vibrations

7.1 The Problem

7.1 **The harmonic Hamiltonian**

The Hamiltonian for lattice vibrations, in the harmonic approximation, is

$$\mathcal{H} = \tfrac{1}{2}\sum_{i=1}^{3N} m_i \dot{x}_i^2 + \tfrac{1}{2}\sum_{i=1}^{3N}\sum_{j=1}^{3N} x_i A_{ij} x_j. \tag{7.1}$$

Notice that this Hamiltonian allows the possibility that atoms at different lattice sites might have different masses. Accept the fact that any real symmetric matrix S can be diagonalized through an orthogonal transformation, i.e. that for any such S there exists a matrix B whose inverse is its transpose and such that

$$\mathsf{B}\mathsf{S}\mathsf{B}^{-1} \tag{7.2}$$

is diagonal. Show that the Hamiltonian can be cast into the form

$$\mathcal{H} = \tfrac{1}{2}\sum_{r=1}^{3N} (\dot{q}_r^2 + D_r q_r^2) \tag{7.3}$$

by a linear change of variables. (Clue: As a first step, introduce the change of variable $z_i = \sqrt{m_i} x_i$.)

7.2 Statistical Mechanics of the Problem

7.2 **Thermal energy versus kinetic energy**

According to the Fall 2001 Review Draft of *Ohio's Academic Content Standards for Science* (page 48), eight-grade students should understand that thermal energy "is in the disorderly motion of molecules." Explain how position as well as motion (i.e. potential energy as well as kinetic energy) contribute to thermal energy.

7.3 Normal Modes for a One-dimensional Chain

The matrix A is all zeros except for 2 on the diagonal and -2 on the superdiagonal. But this doesn't really help us solve the problem. The solution comes from physical insight, not mathematical trickery!

Dispersion relation:

$$\omega(k) = 2\sqrt{\frac{K}{m}}|\sin(\tfrac{1}{2}ka)| \tag{7.4}$$

Meaning of term "dispersion relation":

Start with an arbitrary wave packet, break it up into Fourier components.
Each such component moves at a particular speed.
After some time, find how all the components have moved, then sew them back together.
The wave packet will have changed shape (usually broadened... dispersed).

Remember that we haven't done any statistical mechanics in this section, nor even quantum mechanics. This has been classical mechanics!

7.4 Normal Modes in Three Dimensions

If you wanted to study heat flow, or how sound warms up a crystal, or how light warms up a crystal, you'd have to study these time-dependent dispersion effects. This is hard: the classical mechanics is hard (normal modes) and the quantum mechanics is hard. For the purposes of this book we need only examine static effects, and in particular we need only find the heat capacity at low temperatures.

7.5 Low-temperature Heat Capacity

If

$$G(\omega)\,d\omega = \text{ number of normal modes with frequencies from } \omega \text{ to } \omega + d\omega \tag{7.5}$$

then

$$E^{\text{crystal}} = \int_0^\infty G(\omega)e^{\text{SHO}}(\omega)\,d\omega \quad \text{and} \quad C_V^{\text{crystal}} = \int_0^\infty G(\omega)c_V^{\text{SHO}}(\omega)\,d\omega \tag{7.6}$$

and so forth.

Density of modes:

$$\begin{aligned} G(\omega)\,d\omega &= \sum_{\text{branches}} [\text{vol. of shell in } k\text{-space}](\text{density of modes in } k\text{-space}) \\ &= \sum_{\text{branches}} [4\pi(k_b(\omega))^2\,dk_b]\left(\frac{V}{8\pi^3}\right) \end{aligned} \tag{7.7}$$

This formula holds for any isotropic dispersion relation $k_b(\omega)$. For small values of ω the dispersion relation for each branch is linear (with sound speed c_b) so

$$k_b = \frac{\omega}{c_b} \quad \text{and} \quad dk_b = \frac{d\omega}{c_b}, \tag{7.8}$$

whence

$$\begin{aligned} G(\omega)\,d\omega &= \sum_{\text{branches}} \left[4\pi \left(\frac{\omega}{c_b} \right)^2 \frac{d\omega}{c_b} \right] \left(\frac{V}{8\pi^3} \right) \\ &= \frac{V}{2\pi^2} \left(\sum_{b=1}^{3} \frac{1}{c_b^3} \right) \omega^2\,d\omega. \end{aligned} \tag{7.9}$$

If we define the "average sound speed" c_s through the so-called "harmonic cubed average",

$$\frac{1}{c_s^3} \equiv \frac{1}{3} \sum_{b=1}^{3} \frac{1}{c_b^3}, \tag{7.10}$$

then we have the small-ω density of modes

$$G(\omega)\,d\omega = \frac{3V}{2\pi^2} \frac{\omega^2}{c_s^3}\,d\omega. \tag{7.11}$$

At any temperature,

$$C_V^{\text{crystal}} = \int_0^\infty G(\omega) c_V^{\text{SHO}}(\omega)\,d\omega. \tag{7.12}$$

Recall from equation (5.78) that

$$c_V^{\text{SHO}}(\omega) = k_B \left(\frac{\hbar\omega}{k_B T} \right)^2 \frac{e^{-\hbar\omega/k_B T}}{(1 - e^{-\hbar\omega/k_B T})^2}, \tag{7.13}$$

and using the small-ω result (7.11), we have the low-temperature result

$$C_V^{\text{crystal}} = \frac{3V}{2\pi^2} \frac{1}{c_s^3} k_B \int_0^\infty \omega^2\,d\omega \left(\frac{\hbar\omega}{k_B T} \right)^2 \frac{e^{-\hbar\omega/k_B T}}{(1 - e^{-\hbar\omega/k_B T})^2}. \tag{7.14}$$

For our first step, avoid despair — instead convert to the dimensionless variable

$$x = \frac{\hbar\omega}{k_B T}$$

and find

$$C_V^{\text{crystal}} = \frac{3V}{2\pi^2} \frac{1}{c_s^3} k_B \left(\frac{k_B T}{\hbar} \right)^3 \int_0^\infty \frac{x^4 e^{-x}}{(1 - e^{-x})^2}\,dx. \tag{7.15}$$

The integral is rather hard to do, but we don't *need* to do it — the integral is just a number. We have achieved our aim, namely to show that at low temperatures, $C_V \sim T^3$.

However, if you want to chase down the right numbers, after some fiddling you'll find that

$$\int_0^\infty \frac{x^4 e^{-x}}{(1-e^{-x})^2}\,dx = 4\Gamma(4)\zeta(4) = \frac{4}{15}\pi^4.$$

Thus, the low-temperature specific-heat of a solid due to lattice vibration is

$$C_V^{\text{crystal}} = k_B V \frac{2\pi^2}{5}\left(\frac{k_B T}{\hbar c_s}\right)^3. \tag{7.16}$$

7.3 **How far do the atoms vibrate?**
Consider a simplified classical Einstein model in which N atoms, each of mass m, move classically on a simple cubic lattice with nearest neighbor separation of a. Each atom is bound to its lattice site by a spring of spring constant K, and all the values of K are the same. At temperature T, what is the root mean square average distance of each atom from its equilibrium site? (Note: I am asking for an ensemble average, not a time average.)

7.6 More Realistic Models

7.4 **Debye frequency**
In the Debye model, a solid with average sound speed c_s has density of normal-mode frequencies

$$G(\omega) = \begin{cases} \dfrac{3V}{2\pi^2 c_s^3}\,\omega^2 & \text{for } \omega < \omega_D \\ 0 & \text{for } \omega > \omega_D. \end{cases} \tag{7.17}$$

Find a formula for $\omega_D(N, V, c_s)$, and write $G(\omega)$ in terms of ω_D.

7.5 **Debye model energy and heat capacity**
Find $E(T, V, N)$ and $C_V(T, V, N)$ for a harmonic solid in the Debye model, in terms of ω_D and the function

$$D(x) = \frac{3}{x^3}\int_0^x \frac{t^3}{e^t - 1}\,dt. \tag{7.18}$$

7.7 What is a Phonon?

7.8 Additional Problems

7.6 **Spin waves**
For harmonic lattice vibrations at low frequencies, $\omega = c_s k$. There are analogous excitations of ferromagnets called "spin waves" which, at low frequencies, satisfy $\omega = Ak^2$. Find the temperature dependence of the heat capacity of a ferromagnet at low temperatures. (Do not bother to evaluate constants…I am only looking for the functional form of the temperature dependence.)

7.7 **Comparison of models**

(This problem is stolen from a GRE Physics test.)

One feature common to both the Debye and Einstein models for the specific heat of a crystal composed of N identical atoms is that

a. The average energy of each atom is $3k_BT$.
b. The vibrational energy of the crystal is equivalent to the energy of $3N$ independent harmonic oscillators.
c. The crystal is assumed to be continuous for all elastic waves.
d. The speed of longitudinal elastic waves is less than the speed of transverse elastic waves.
e. The upper cutoff frequency of elastic waves is the same.

Chapter 8

Interacting Classical Fluids

8.1 Introduction

The subject of this chapter is also called "real gases", or "dense gases", or "non-ideal gases", or "imperfect gases", or "liquids and dense gases". The many names are a clue that the same problem has been approached by many different scientists from many different points of view, which in turn is a hint that the problem is one of enormous importance. And in this case the hints are correct. We have treated non-interacting classical atoms for long enough in this book. We know that this treatment leads to results in which all substances have the same equation of state (although they can sometimes be distinguished through their heat capacities) and in which there are no phase transitions, no crystals, no life, and very little of interest. It galls me that anyone ever called such a situation "ideal". The problem of interacting atoms is important for industrial and military applications, but it is just as important from the point of view of pure science. We are now going to see what happens when we allow the atoms to interact. Some call the methods and results "messy". I call them fascinating. I would not want to live in the "ideal" world.

To be specific, we will consider the model problem of:

- *Monatomic* atoms with no internal structure, interacting through spherically symmetric pair potentials.
- *Classical mechanics.*

Many undergraduate books state that this is an "important outstanding problem". That is no longer correct. In fact, the problem was solved (except near phase transitions) in the years 1980–85 by Lado, Ashcroft, Foiles, and Rosenfeld (see Talbot, Lebowitz, *et al.* "A comparison of MHNC and MC at high pressures", *J. Chem. Phys.* **85** (1986) 2187–2192, Y. Rosenfeld, "Variational MHNC", *J. Stat. Phys.* **42** (1986) 437–457). The solution is a technique called "modified hyper-netted chain". Unfortunately, I will not have time to tell you what the solution is or even what the words in the name mean. But I can tell you that it is an ingenious combination of perturbation and variational methods, and I will be telling you about these two techniques in this chapter. (The best references for this chapter are the books by Donald McQuarrie, *Statistical Mechanics*, and by J.P. Hansen and I.R. McDonald, *Theory of Simple Liquids.*)

Problems

8.1 **The Lennard-Jones potential**

The general Lennard-Jones potential is

$$u(r) = -\frac{a}{r^6} + \frac{b}{r^n}. \tag{8.1}$$

a. Given a and b, find $-\epsilon_m$, the minimum energy, and r_0, the distance of separation at that minimum. Write $u(r)$ in terms of the parameters ϵ_m and r_0 rather than the parameters a and b.

b. If σ is the separation at which $u(\sigma) = 0$, find σ in terms of r_0. Why is ϵ_m irrelevant here?

c. Note the simplifications in the above results if $n = 12$. For this case, write $u(r)$ using the parameters ϵ_m and σ.

8.2 **Negative compressibilities**

Look at figure 8.6.1 on page 307 of Reif. Notice that for temperatures below the critical temperature (T_4 in the figure), the van der Waals fluid can have negative values of κ_T. Suppose a fluid with negative compressibility existed, and I had a bottle of it on the table in front of me. What would happen if the volume of the bottle decreased slightly. . . say if I rapped my fingers on it? (This impossibility is a warning that the van der Waals equation is simply not applicable at temperatures in the vicinity of the critical temperature or below.)

8.3 **Entropy of a real gas**

A real gas obeys the equation of state

$$pV = Nk_BT \left[1 + B\frac{N}{V}\right], \tag{8.2}$$

where B is a positive constant.

a. In one sentence, describe the behavior of this gas in the limit that T and N are constant but $V \to \infty$. (Answers containing mathematical symbols are automatically disqualified.)

b. Using an appropriate Maxwell relation, calculate the difference in entropy between an ideal gas and this real gas when both have the same T, V, and N.

c. At a given T, V, and N, which entropy is larger? Is this consistent with "the entropy inequality"? Can you justify it with a qualitative argument? Is it possible for the constant B to be negative or zero?

8.2 Perturbation Theory

8.2.1 Fluids in the canonical ensemble

The partition function for a fluid is

$$Z(T,V,N)=\frac{1}{h^{3N}N!}\int d\Gamma e^{-\beta H(\Gamma)} \tag{8.3}$$

where

$$H(\Gamma)=\frac{1}{2m}\sum_{i=1}^{N}\mathbf{p}_i^2+U_N(\mathbf{r}_1,\ldots,\mathbf{r}_N). \tag{8.4}$$

The momentum integrals can be performed precisely as they were for the ideal gas, giving

$$Z(T,V,N)=\frac{1}{\lambda^{3N}(T)N!}\int d\mathbf{r}_1\cdots d\mathbf{r}_N e^{-\beta U_N(\mathbf{r}_1,\ldots,\mathbf{r}_N)}, \tag{8.5}$$

where $\lambda(T)$ is the thermal de Broglie wavelength. It is useful to define the "configurational partition function"

$$Q_N(T,V)=\frac{1}{N!}\int d\mathbf{r}_1\cdots d\mathbf{r}_N e^{-\beta U_N(\mathbf{r}_1,\ldots,\mathbf{r}_N)}. \tag{8.6}$$

For example, in a three-particle system with spherically symmetric pair potential $u(r)$, the configurational partition function is

$$Q_3(T,V)=\frac{1}{6}\int_V d\mathbf{r}_1\int_V d\mathbf{r}_2\int_V d\mathbf{r}_3 e^{-\beta[u(|\mathbf{r}_1-\mathbf{r}_2|)+u(|\mathbf{r}_1-\mathbf{r}_3|)+u(|\mathbf{r}_2-\mathbf{r}_3|)]}. \tag{8.7}$$

Every other time in this book that we have encountered a complicated partition function, like the one above, it has factorized into the product of many similar terms. (This happened even in our treatment of harmonic lattice vibrations, through the use of normal coordinates.) The expression above does not factorize in this neat way. With considerable diligence and patience, it is possible to evaluate $Q_N(T,V)$ for $N=3$. But you can see that doing it for cases of interest, such as $N=6.02\times 10^{23}$, is simply out of the question. Instead we attempt to use perturbation theory by expanding about an already solved problem, namely the ideal gas. Such an approximation will be a good one at low densities, where the gas is "nearly ideal". The obvious thing to do is to expand $Q_N(T,V)$ in the small parameter $\rho=N/V$, the number density. But how can we do that? The quantity ρ doesn't appear in these formulas!

8.2.2 The search for a small parameter

We cannot expand $Q_N(T,V)$ in terms of ρ, but we do know that at low densities all fluids behave like an ideal gas, and that for an ideal gas the chemical potential is

$$\mu=k_BT\ln\left(\frac{\rho}{1/\lambda^3(T)}\right), \tag{8.8}$$

so that as $\rho\to 0$, $\mu\to-\infty$ and $e^{\beta\mu}\to 0$. So here is a second small parameter. You might object that $e^{\beta\mu}$ doesn't appear in the partition function any more than ρ does, but it *does* appear in the grand canonical partition function!

8.2.3 Fluids in the grand canonical ensemble

The grand canonical partition function is

$$\begin{aligned}\Xi(T,V,\mu) &= \sum_{N=0}^{\infty} e^{\beta\mu N} Z(T,V,N) &(8.9)\\ &= \sum_{N=0}^{\infty}\left(\frac{e^{\beta\mu}}{\lambda^3(T)}\right)^N Q_N(T,V) &(8.10)\\ &= \sum_{N=0}^{\infty} z^N Q_N(T,V) &(8.11)\\ &= 1 + Q_1(T,V)z + Q_2(T,V)z^2 + Q_3(T,V)z^3 + \mathcal{O}(z^4), &(8.12)\end{aligned}$$

where we have defined the *activity*

$$z \equiv \frac{e^{\beta\mu}}{\lambda^3(T)}. \tag{8.13}$$

The activity is the small parameter upon which perturbation theory relies. (For an ideal gas, it is equal to the number density ρ.)

Note that in this approach we still have to calculate Q_N coefficients, but we will probably stop at $N = 4$ or 5 rather than $N = 6.02 \times 10^{23}$. I will write down the first two coefficients:

$$\begin{aligned}Q_1(T,V) &= \int_V d\mathbf{r}_1 e^{-\beta 0} = V\\ Q_2(T,V) &= \frac{1}{2}\int_V d\mathbf{r}_1 \int_V d\mathbf{r}_2 e^{-\beta u(|\mathbf{r}_1-\mathbf{r}_2|)}. &(8.14)\end{aligned}$$

Because the interactions are short-ranged, most of the time $u(|\mathbf{r}_1 - \mathbf{r}_2|)$ nearly vanishes, so Q_2 is pretty close to $V^2/2$. It is neither intensive nor extensive.

8.2.4 The Mayer expansion

Now we go from the partition function to an experimentally measurable master function, namely pressure:

$$\begin{aligned}\frac{p(T,z)}{k_BT} &= \frac{1}{V}\ln\Xi &(8.15)\\ &= \frac{1}{V}\ln[1 + Q_1z + Q_2z^2 + Q_3z^3 + \mathcal{O}(z^4)]. &(8.16)\end{aligned}$$

Employing

$$\ln(1+\epsilon) = \epsilon - \tfrac{1}{2}\epsilon^2 + \tfrac{1}{3}\epsilon^3 + \mathcal{O}(\epsilon^4) \tag{8.17}$$

we obtain

$$\begin{aligned}\frac{p(T,z)}{k_BT} &= \frac{1}{V}[Q_1z + Q_2z^2 + Q_3z^3 - \tfrac{1}{2}(Q_1z + Q_2z^2)^2 + \tfrac{1}{3}(Q_1z)^3 + \mathcal{O}(z^4)] &(8.18)\\ &= \frac{1}{V}Q_1z + \frac{1}{V}(Q_2 - \tfrac{1}{2}Q_1^2)z^2 + \frac{1}{V}(Q_3 - Q_1Q_2 + \tfrac{1}{3}Q_1^3)z^3 + \mathcal{O}(z^4) &(8.19)\\ &= \sum_{\ell=1}^{\infty} b_\ell z^\ell. &(8.20)\end{aligned}$$

The last line above defines the “Mayer expansion”. The expansion coefficients $b_\ell = b_\ell(T)$ are intensive functions of temperature (in contrast to the coefficients $Q_N(T,V)$).

Using equations (8.14) it is easy to show that $b_1 = 1$ and that

$$\begin{aligned} b_2 &= \frac{1}{2V}\left(\int_V d\mathbf{r}_1 \int_V d\mathbf{r}_2 e^{-\beta u(|\mathbf{r}_1-\mathbf{r}_2|)} - \int_V d\mathbf{r}_1 \int_V d\mathbf{r}_2 1\right) \\ &= \frac{1}{2V}\int_V d\mathbf{r}_1 \int_V d\mathbf{r}_2 (e^{-\beta u(|\mathbf{r}_1-\mathbf{r}_2|)} - 1). \end{aligned} \tag{8.21}$$

In contrast to the situation with equation (8.14), the integrand above is nearly always zero, which makes it much easier to work with. (The same is true for all the the Mayer coefficients.) Indeed, a little more work will show that

$$b_2 = 2\pi \int_0^\infty dr\, r^2 (e^{-u(r)/k_B T} - 1). \tag{8.22}$$

Specialists in the statistical mechanics of fluids spend a lot of time calculating b_ℓ coefficients for a given potential energy of interaction $u(r)$. We will instead emphasize what to do with the b_ℓs once they are calculated.

8.2.5 Expansion for the density

To obtain the number density $\rho = N/V$ from the Mayer expansion, use the thermodynamic connection between ρ and p:

$$\rho = \left.\frac{\partial p}{\partial \mu}\right)_T = \left.\frac{\partial z}{\partial \mu}\right)_T \left.\frac{\partial p}{\partial z}\right)_T = z \left.\frac{\partial(\beta p)}{\partial z}\right)_T . \tag{8.23}$$

Thus

$$\rho(T,z) = \sum_{\ell=1}^{\infty} \ell b_\ell z^\ell. \tag{8.24}$$

8.2.6 Eliminating the activity: the virial expansion

Now we have two expansions, (8.20) and (8.24), in terms of the activity:

$$\beta p(z) = z + b_2 z^2 + b_3 z^3 + \mathcal{O}(z^4) \tag{8.25}$$

$$\rho(z) = z + 2b_2 z^2 + 3b_3 z^3 + \mathcal{O}(z^4). \tag{8.26}$$

(The temperature dependence of p, ρ, and the b_ℓs is not shown explicitly.) What we would really like, however, would be the traditional (and experimentally accessible) equation of state, $p(\rho)$. In other words, we want to eliminate the zs between the two expansions above. To this end we will invert the expansion for $\rho(z)$ to find $z(\rho)$, and plug that expression into the expansion (8.25) for $p(z)$. In the appendix we perform the inversion to find, correct to third order,

$$z(\rho) = \rho - 2b_2\rho^2 + (8b_2^2 - 3b_3)\rho^3 + \mathcal{O}(\rho^4). \tag{8.27}$$

Plugging into (8.25) gives

$$\begin{aligned}
\beta p(\rho) &= z + b_2 z^2 + b_3 z^3 + \mathcal{O}(z^4) && (8.28)\\
&= [\rho - 2b_2\rho^2 + (8b_2^2 - 3b_3)\rho^3] + b_2[\rho - 2b_2\rho^2]^2 + b_3[\rho]^3 + \mathcal{O}(\rho^4) && (8.29)\\
&= [\rho - 2b_2\rho^2 + (8b_2^2 - 3b_3)\rho^3] + b_2[\rho^2 - 4b_2\rho^3] + b_3[\rho]^3 + \mathcal{O}(\rho^4) && (8.30)\\
&= \rho - b_2\rho^2 + (4b_2^2 - 2b_3)\rho^3 + \mathcal{O}(\rho^4). && (8.31)
\end{aligned}$$

This last expression is called the "virial expansion", and it is usually written (with the temperature dependence put back in) as

$$\frac{p(T,\rho)}{k_B T} = \rho + B_2(T)\rho^2 + B_3(T)\rho^3 + \mathcal{O}(\rho^4). \qquad (8.32)$$

8.2.7 Appendix: Inverting $\rho(z)$ to find $z(\rho)$

Begin with

$$\rho(z) = z + 2b_2 z^2 + 3b_3 z^3 + \mathcal{O}(z^4), \qquad (8.33)$$

then use

$$z = \rho + \mathcal{O}(z^2) \qquad \begin{aligned} z^2 &= (\rho + \mathcal{O}(z^2))(\rho + \mathcal{O}(z^2))\\ &= \rho^2 + 2\rho\mathcal{O}(z^2) + \mathcal{O}(z^4)\\ &= \rho^2 + \mathcal{O}(z^3)\end{aligned} \qquad \begin{aligned} z^3 &= (\rho^2 + \mathcal{O}(z^3))(\rho + \mathcal{O}(z^2))\\ &= \rho^3 + \mathcal{O}(z^4)\end{aligned}$$

$$z = \rho - 2b_2 z^2 + \mathcal{O}(z^3)$$

$$z = \rho - 2b_2\rho^2 + \mathcal{O}(z^3) \qquad \begin{aligned} z^2 &= (\rho - 2b_2\rho^2 + \mathcal{O}(z^3))(\rho - 2b_2\rho^2 + \mathcal{O}(z^3))\\ &= \rho^2 - 4b_2\rho^3 + 4b_2^2\rho^4 + \rho\mathcal{O}(z^3)\\ &= \rho^2 - 4b_2\rho^3 + \mathcal{O}(z^4)\end{aligned}$$

$$z = \rho - 2b_2 z^2 - 3b_3 z^3 + \mathcal{O}(z^4)$$

$$z = \rho - 2b_2[\rho^2 - 4b_2\rho^3 + \mathcal{O}(z^4)] - 3b_3[\rho^3 + \mathcal{O}(z^4)] + \mathcal{O}(z^4),$$

to find

$$z(\rho) = \rho - 2b_2\rho^2 + (8b_2^2 - 3b_3)\rho^3 + \mathcal{O}(\rho^4). \qquad (8.34)$$

Problems

8.4 **Virial expansion for the ideal gas**
Find Q_1, Q_2, Q_3, etc. for an ideal gas. Hence show that the virial equation of state for an ideal gas is $pV = Nk_BT$.

8.5 **General properties of expansion coefficients**

a. Show that $Q_1 = V$, whence $b_1 = 1$.

b. Show (informally) that the b_ℓ Mayer coefficients, as well as the $B_n(T)$ virial coefficients, are intensive.

8.3 Variational Methods

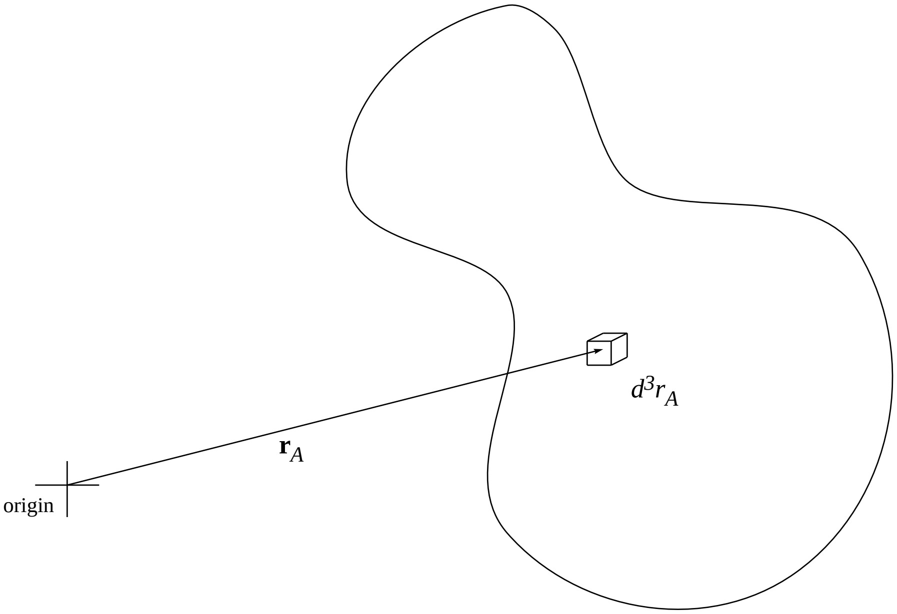
8.6 **Bogoliubov's contribution to the Gibbs-Bogoliubov inequality**

Show that the Gibbs-Bogoliubov inequality, which we derived in class for classical systems, also holds for quantal systems.

8.4 Distribution Functions

8.4.1 One-particle distribution functions

What is the mean number of particles in the box of volume d^3r_A about $\mathbf{r}_A$?



The probability that particle 1 is in d^3r_A about $\mathbf{r}_A$ is

$$\frac{d^3r_A \int d^3r_2 \int d^3r_3 \cdots \int d^3r_N \int d^3p_1 \cdots \int d^3p_N \, e^{-\beta H(\mathbf{r}_A,\mathbf{r}_2,\mathbf{r}_3,\ldots,\mathbf{r}_N,\mathbf{p}_1,\ldots,\mathbf{p}_N)}}{\int d^3r_1 \int d^3r_2 \int d^3r_3 \cdots \int d^3r_N \int d^3p_1 \cdots \int d^3p_N \, e^{-\beta H(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3,\ldots,\mathbf{r}_N,\mathbf{p}_1,\ldots,\mathbf{p}_N)}}. \tag{8.35}$$

The probability that particle 2 is in d^3r_A about $\mathbf{r}_A$ is

$$\frac{\int d^3r_1 \quad d^3r_A \int d^3r_3 \cdots \int d^3r_N \int d^3p_1 \cdots \int d^3p_N \, e^{-\beta H(\mathbf{r}_1,\mathbf{r}_A,\mathbf{r}_3,\ldots,\mathbf{r}_N,\mathbf{p}_1,\ldots,\mathbf{p}_N)}}{\int d^3r_1 \int d^3r_2 \int d^3r_3 \cdots \int d^3r_N \int d^3p_1 \cdots \int d^3p_N \, e^{-\beta H(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3,\ldots,\mathbf{r}_N,\mathbf{p}_1,\ldots,\mathbf{p}_N)}}. \tag{8.36}$$

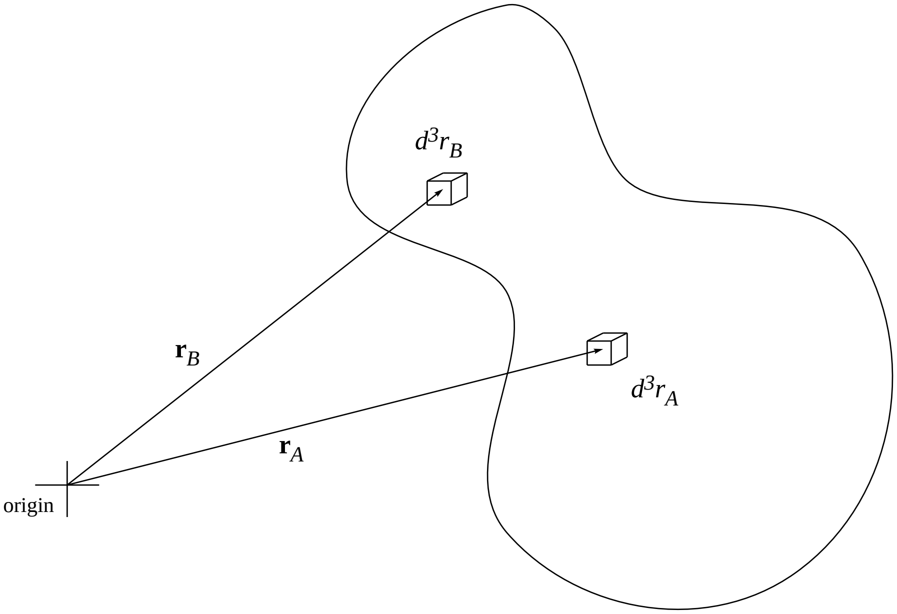
And so forth. I could write down N different integrals, but all of them would be equal.

Thus the mean number of particles in d^3r_A about $\mathbf{r}_A$ is

$$\begin{aligned}
&n_1(\mathbf{r}_A)\, d^3r_A \\
&\quad = N \frac{d^3r_A \int d^3r_2 \int d^3r_3 \cdots \int d^3r_N \int d^3p_1 \cdots \int d^3p_N \, e^{-\beta H(\mathbf{r}_A,\mathbf{r}_2,\mathbf{r}_3,\ldots,\mathbf{r}_N,\mathbf{p}_1,\ldots,\mathbf{p}_N)}}{\int d^3r_1 \int d^3r_2 \int d^3r_3 \cdots \int d^3r_N \int d^3p_1 \cdots \int d^3p_N \, e^{-\beta H(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3,\ldots,\mathbf{r}_N,\mathbf{p}_1,\ldots,\mathbf{p}_N)}} && (8.37) \\
&\quad = N \frac{d^3r_A \int d^3r_2 \int d^3r_3 \cdots \int d^3r_N \int d^3p_1 \cdots \int d^3p_N \, e^{-\beta H(\mathbf{r}_A,\mathbf{r}_2,\mathbf{r}_3,\ldots,\mathbf{r}_N,\mathbf{p}_1,\ldots,\mathbf{p}_N)}}{h^{3N} N! Z(T,V,N)} && (8.38) \\
&\quad = \frac{1}{(N-1)!} \frac{d^3r_A \int d^3r_2 \int d^3r_3 \cdots \int d^3r_N \, e^{-\beta U(\mathbf{r}_A,\mathbf{r}_2,\mathbf{r}_3,\ldots,\mathbf{r}_N)}}{Q(T,V,N)}. && (8.39)
\end{aligned}$$

8.4.2 Two-particle distribution functions

What is the mean number of pairs of particles, such that one member of the pair in a box of volume d^3r_A about $\mathbf{r}_A$ and the other member is in a box of volume d^3r_B about $\mathbf{r}_B$?



The probability that particle 1 is in d^3r_A about $\mathbf{r}_A$ and particle 2 is in d^3r_B about $\mathbf{r}_B$ is

$$\frac{d^3r_A \quad d^3r_B \int d^3r_3 \cdots \int d^3r_N \int d^3p_1 \cdots \int d^3p_N \, e^{-\beta H(\mathbf{r}_A,\mathbf{r}_B,\mathbf{r}_3,\ldots,\mathbf{r}_N,\mathbf{p}_1,\ldots,\mathbf{p}_N)}}{\int d^3r_1 \int d^3r_2 \int d^3r_3 \cdots \int d^3r_N \int d^3p_1 \cdots \int d^3p_N \, e^{-\beta H(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3,\ldots,\mathbf{r}_N,\mathbf{p}_1,\ldots,\mathbf{p}_N)}}. \tag{8.40}$$

The probability that particle 2 is in d^3r_A about $\mathbf{r}_A$ and particle 1 is in d^3r_B about $\mathbf{r}_B$ is

$$\frac{d^3r_B \quad d^3r_A \int d^3r_3 \cdots \int d^3r_N \int d^3p_1 \cdots \int d^3p_N \, e^{-\beta H(\mathbf{r}_B,\mathbf{r}_A,\mathbf{r}_3,\ldots,\mathbf{r}_N,\mathbf{p}_1,\ldots,\mathbf{p}_N)}}{\int d^3r_1 \int d^3r_2 \int d^3r_3 \cdots \int d^3r_N \int d^3p_1 \cdots \int d^3p_N \, e^{-\beta H(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3,\ldots,\mathbf{r}_N,\mathbf{p}_1,\ldots,\mathbf{p}_N)}}. \tag{8.41}$$

The probability that particle 3 is in d^3r_A about $\mathbf{r}_A$ and particle 1 is in d^3r_B about $\mathbf{r}_B$ is

$$\frac{d^3r_B \int d^3r_2 \quad d^3r_A \cdots \int d^3r_N \int d^3p_1 \cdots \int d^3p_N \, e^{-\beta H(\mathbf{r}_B,\mathbf{r}_2,\mathbf{r}_A,\ldots,\mathbf{r}_N,\mathbf{p}_1,\ldots,\mathbf{p}_N)}}{\int d^3r_1 \int d^3r_2 \int d^3r_3 \cdots \int d^3r_N \int d^3p_1 \cdots \int d^3p_N \, e^{-\beta H(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3,\ldots,\mathbf{r}_N,\mathbf{p}_1,\ldots,\mathbf{p}_N)}}. \tag{8.42}$$

And so forth. I could write down $N(N-1)$ different integrals, but all of them would be equal.

Thus the mean number of pairs with one particle in d^3r_A about $\mathbf{r}_A$ and the other in d^3r_B about r_B is

$$\begin{aligned} & n_2(\mathbf{r}_A,\mathbf{r}_B)\, d^3r_A d^3r_B \\ & \quad = N(N-1)\frac{d^3r_A \quad d^3r_B \int d^3r_3 \cdots \int d^3r_N \int d^3p_1 \cdots \int d^3p_N \, e^{-\beta H(\mathbf{r}_A,\mathbf{r}_B,\mathbf{r}_3,\ldots,\mathbf{r}_N,\mathbf{p}_1,\ldots,\mathbf{p}_N)}}{\int d^3r_1 \int d^3r_2 \int d^3r_3 \cdots \int d^3r_N \int d^3p_1 \cdots \int d^3p_N \, e^{-\beta H(\mathbf{r}_1,\mathbf{r}_2,\mathbf{r}_3,\ldots,\mathbf{r}_N,\mathbf{p}_1,\ldots,\mathbf{p}_N)}} && (8.43) \\ & \quad = \frac{1}{(N-2)!}\frac{d^3r_A d^3r_B \int d^3r_3 \cdots \int d^3r_N \, e^{-\beta U(\mathbf{r}_A,\mathbf{r}_B,\mathbf{r}_3,\ldots,\mathbf{r}_N)}}{Q(T,V,N)}. && (8.44) \end{aligned}$$

Problems

8.7 **Correlations of nearby particles**

Suppose that (as is usual) at small distances the interatomic potential $u(r)$ is highly repulsive. Argue that at small r,

$$g_2(r) \approx \text{ constant } e^{-u(r)/k_B T}. \tag{8.45}$$

Do not write down a long or elaborate derivation. . . I'm looking for a simple qualitative argument.

8.8 **Correlations between non-interacting identical quantal particles**

Guess the form of the pair correlation function $g_2(r)$ for ideal (non-interacting) fermions and bosons. Sketch your conjectures, and then compare them to the graphs presented by G. Baym in *Lectures on Quantum Mechanics* (W.A. Benjamin, Inc., Reading, Mass., 1969) pages 428 and 431.

8.9 **Correlation functions and structure factors**

A typical isotropic fluid, at temperatures above the critical temperature, has correlation functions that are complicated at short distances, but that fall off exponentially at long distances. In fact, the long-distance behavior is

$$g_2(r) = 1 + \frac{Ae^{-r/\xi}}{r} \tag{8.46}$$

where ξ, the so-called correlation length, depends on temperature and density. In contrast, at the critical temperature the correlation function falls off much more slowly, as

$$g_2(r) = 1 + \frac{A}{r^{1+\eta}}. \tag{8.47}$$

Find the structure factor

$$S(\mathbf{k}) = \int d^3r\, [g_2(\mathbf{r}) - 1] e^{-i\mathbf{k}\cdot\mathbf{r}} \tag{8.48}$$

associated with each of these correlation functions. Will your results match those of experiments at small values of k or at large values (i.e. at long or short wavelengths)?

8.10 **Long wavelength structure factor**

Show that, for an isotropic fluid, $\dfrac{dS(k)}{dk}$ vanishes at $k = 0$. Here $S(k)$ is the structure factor

$$S(\mathbf{k}) = 1 + \rho \int d^3r\, [g_2(\mathbf{r}) - 1] e^{i\mathbf{k}\cdot\mathbf{r}}. \tag{8.49}$$

8.11 **Correlations in a magnetic system**

In the Ising model for a magnet, described in problem 4.9, the (net) correlation function is defined by

$$G_i \equiv \langle s_0 s_i \rangle - \langle s_0 \rangle^2, \tag{8.50}$$

where the site $j = 0$ is some arbitrary "central spin". Using the results of problem 4.9, show that for a lattice of N sites,

$$\chi_T(T, H) = N \frac{m^2}{k_B T} \sum_i G_i. \tag{8.51}$$

8.5 Correlations and Scattering

8.6 The Hard Sphere Fluid

Consider a fluid in which each atom is modeled by a "hard sphere" of volume v_0. In this system the potential energy vanishes unless two spheres overlap, while if they do overlap it is infinite. The criterion for overlap is that the centers of the two spheres are separated by a distance of $2r_0$ or less, where $v_0 = \frac{4}{3}\pi r_0^3$. This model is certainly oversimplified in that it ignores the attractive part of the interatomic force, but it is an excellent starting point for perturbation theory, and it also has certain features of interest in its own right, as the problems below demonstrate. (The first problem below is required background for all of the others.)

8.12 **Scaling in the hard sphere fluid**

The canonical partition function for a fluid is

$$Z(T,V,N) = \frac{1}{\lambda^{3N}(T)N!}\int d^3r_1 \cdots \int d^3r_N \, e^{-\beta U_N(\mathbf{r}_1,\ldots,\mathbf{r}_N)}. \tag{8.52}$$

For an ideal gas, the integral over configuration space gives just V^N, so it makes sense to write

$$\begin{aligned} Z(T,V,N) &= \left(\frac{V^N/N!}{\lambda^{3N}(T)}\right)\left(\frac{1}{V^N}\int d^3r_1 \cdots \int d^3r_N \, e^{-\beta U_N(\mathbf{r}_1,\ldots,\mathbf{r}_N)}\right) \\ &\equiv Z_{\text{ideal}}(T,V,N)W(T,V,N), \end{aligned} \tag{8.53}$$

where the last line has defined W, the ratio of interacting to non-interacting ("ideal") configurational partition functions.

a. Argue that in the case of hard spheres W is independent of temperature. It does, however, depend on the mechanical parameter v_0, so we will write the ratio as $W(V,N,v_0)$.

b. Argue that $W(V,N,v_0) \leq 1$, where the equality holds only when $v_0 = 0$.

c. Show that the Helmholtz free energy for any fluid satisfies

$$\begin{aligned} F_{\text{HS}}(T,V,N,v_0) &= F_{\text{ideal}}(T,V,N) - k_BT\ln W(V,N,v_0) \\ &\equiv F_{\text{ideal}} + Nf_{\text{ex}}, \end{aligned} \tag{8.54}$$

where we have defined f_{ex}, the excess free energy per atom. Is the free energy of a hard sphere fluid greater than or less than the free energy of an ideal gas at the same T, V, and N?

d. Because f_{ex} is intensive, it cannot depend upon V and N separately, but only through their intensive quotient, the number density $\rho = N/V$. Use a similar argument to show that

$$W(V,N,v_0) = w(\rho,v_0)^N, \tag{8.55}$$

where w is a dimensionless, intensive quantity.

e. Use dimensional analysis to show that the hard sphere w (and hence f_{ex}) cannot depend upon ρ and v_0 separately, but only through their product: $w(\rho v_0)$.

This last result is of enormous importance. It implies that there is no need to perform elaborate computer simulations for a variety of densities and a variety of radii. It suffices to either simulate for a variety of densities at one fixed radius or vice versa. It also demonstrates that the quantity of importance in the statistical mechanics of hard spheres is the "scaled density" $\eta \equiv \rho v_0$.

f. Use thermodynamics to show that

$$p_{\text{HS}}(T, \rho, v_0) = p_{\text{ideal}}(T, \rho) + \rho \left[\eta \frac{\partial f_{\text{ex}}(\eta)}{\partial \eta} \right]_{\eta = \rho v_0} . \tag{8.56}$$

8.13 **The hard sphere phase transition**

a. Interpret the scaled density $\eta \equiv \rho v_0$ geometrically. Why is is sometimes called the "packing fraction"?

b. Is it possible to have a fluid with $\eta \geq 1$?

c. Show that if hard spheres are packed into a face-centered cubic lattice (which is probably the densest possible packing spheres, although no one has been able to prove it), $\eta = \pi\sqrt{2}/6 = 0.7405$.

In fact, at scaled densities η well below the limits mentioned above, the system undergoes a phase transition from a fluid to a solid. Computer simulations show that the transition occurs when the scaled density is $\eta_t \approx 0.496$. The conjecture $\eta_t = \frac{1}{2}$ is tempting, but apparently not correct. (On the other hand it is hard to do computer simulations near phase transitions, so the question is not completely closed!)

8.14 **The hard sphere fluid equation of state**

Many long and difficult hours of analytic calculation and computer simulation have gone into studying the hard sphere fluid. In 1964 Ree and Hoover[1] codified much of this work into the following empirical formula which is a good approximation for the hard sphere fluid equation of state:

$$p_{\text{HS}}(T, \rho, v_0) = k_B T \rho \left[1 + 4\eta \frac{1 + 0.25403\eta + 0.27726\eta^2}{1 - 2.2460\eta + 1.3010\eta^2} \right] \quad \text{where} \quad \eta = \rho v_0. \tag{8.57}$$

Only five years later, Carnahan and Starling[2] hit upon a much simpler yet still remarkably accurate equation of state, namely

$$p_{\text{HS}}(T, \rho, v_0) = k_B T \rho \frac{1 + \eta + \eta^2 - \eta^3}{(1 - \eta)^3} \quad \text{where} \quad \eta = \rho v_0. \tag{8.58}$$

Both of these formulas apply only to the fluid phase (see the previous problem) and neither one is exact. Answer the following questions for the Carnahan-Starling formula.

---

[1] F.H. Ree and W.G. Hoover, *J. Chem. Phys.*, **40** (1964) 939–950.

[2] N.F. Carnahan and K.E. Starling, *J. Chem. Phys.*, **51** (1969) 635–636.

a. As the density increases from zero, at what point does the formula become nonsense?

b. On which regions of the (T, ρ) plane does the hard sphere fluid exert a greater pressure than the ideal gas? Can you explain your answer through a simple physical argument?

c. Integrate equation (8.56) to show that for the hard sphere fluid,

$$f_{\text{ex}}(T, \eta) = k_B T\, \eta \frac{4 - 3\eta}{(1 - \eta)^2}. \tag{8.59}$$

Does this formula satisfy the inequality established in part (c.) of problem 8.12?

d. Find the difference between the entropy of the hard sphere fluid and that of an ideal gas. At a given T, V, and N, which entropy is larger? Can you justify this result with a qualitative argument?

8.15 **The hard sphere free energy**

Use the Gibbs-Bogoliubov inequality to show that

$$F_{\text{HS}}(T, V, N) \geq F_{\text{ideal}}(T, V, N). \tag{8.60}$$

Reason that $E_{\text{HS}}(T, V, N) = E_{\text{ideal}}(T, V, N)$, and conclude with a relation between entropies.

8.16 **Virial expansion for hard spheres**

Using the notation of problem 8.12, show that for a hard sphere fluid:

a. $Q_2 = \frac{1}{2} V(V - 8v_0)$.

b. $b_2 = -4v_0$.

c. $B_2(T) = 4v_0$.

d. Show that both the Ree-Hover and the Carnahan-Starling equations of state, introduced in problem 8.14, expand to give the correct first virial coefficient $B_2(T)$.

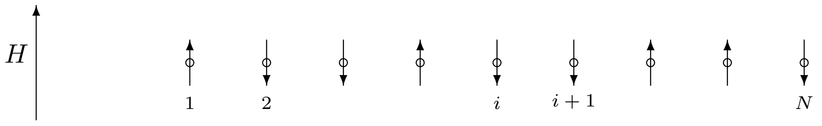
Chapter 9

Strongly Interacting Systems and Phase Transitions

9.1 Introduction to Magnetic Systems and Models

9.2 Free Energy of the One-Dimensional Ising Model

The N-spin one-dimensional Ising model consists of a horizontal chain of spins, s_1, s_2, …, s_N, where $s_i = \pm 1$.



A vertical magnetic field H is applied, and only nearest neighbor spins interact, so the Hamiltonian is

$$\mathcal{H}_N = -J \sum_{i=1}^{N-1} s_i s_{i+1} - mH \sum_{i=1}^{N} s_i. \tag{9.1}$$

For this system the partition function is

$$Z_N = \sum_{\text{states}} e^{-\beta \mathcal{H}_N} = \sum_{s_1=\pm 1} \sum_{s_2=\pm 1} \cdots \sum_{s_N=\pm 1} e^{K \sum_{i=1}^{N-1} s_i s_{i+1} + L \sum_{i=1}^{N} s_i}, \tag{9.2}$$

where

$$K \equiv \frac{J}{k_B T} \quad \text{and} \quad L \equiv \frac{mH}{k_B T}. \tag{9.3}$$

If $J = 0$, (the ideal paramagnet) the partition function factorizes, and the problem is easily solved using the "summing Hamiltonian yields factorizing partition function" theorem. If $H = 0$, the partition function nearly factorizes, and the problem is not too difficult. (See problem 9.3.) But in general, there is no factorization.

We will solve the problem using *induction on the size of the system.* If we add one more spin (spin number $N+1$), then the change in the system's energy depends only upon the state of the new spin and of the previous spin (spin number N). Define $Z_N^\uparrow$ as, not the sum over all states, but the sum over all states in which the last (i.e. Nth) spin is up, and define $Z_N^\downarrow$ as the sum over all states in which the last spin is down, so that

$$Z_N = Z_N^\uparrow + Z_N^\downarrow. \tag{9.4}$$

Now, if one more spin is added, the extra term in $e^{-\beta\mathcal{H}}$ results in a factor of

$$e^{Ks_Ns_{N+1}+Ls_{N+1}}. \tag{9.5}$$

From this, it is very easy to see that

$$\begin{aligned} Z_{N+1}^\uparrow &= Z_N^\uparrow e^{K+L} + Z_N^\downarrow e^{-K+L} & (9.6)\\ Z_{N+1}^\downarrow &= Z_N^\uparrow e^{-K-L} + Z_N^\downarrow e^{K-L}. & (9.7)\end{aligned}$$

This is really the end of the physics of this derivation. The rest is mathematics.

So put on your mathematical hats and look at the pair of equations above. What do you see? A matrix equation!

$$\begin{pmatrix} Z_{N+1}^\uparrow \\ Z_{N+1}^\downarrow \end{pmatrix} = \begin{pmatrix} e^{K+L} & e^{-K+L} \\ e^{-K-L} & e^{K-L} \end{pmatrix} \begin{pmatrix} Z_N^\uparrow \\ Z_N^\downarrow \end{pmatrix}. \tag{9.8}$$

We introduce the notation

$$\mathbf{w}_{N+1} = \mathsf{T}\mathbf{w}_N \tag{9.9}$$

for the matrix equation. The 2×2 matrix T, which acts to add one more spin to the chain, is called the *transfer matrix.* Of course, the entire chain can be built by applying T repeatedly to an initial chain of one site, i.e. that

$$\mathbf{w}_{N+1} = \mathsf{T}^N\mathbf{w}_1, \tag{9.10}$$

where

$$\mathbf{w}_1 = \begin{pmatrix} e^L \\ e^{-L} \end{pmatrix}. \tag{9.11}$$

The fact that we are raising a matrix to a power suggests that we should diagonalize it. The transfer matrix T has eigenvalues λ_A and λ_B (labeled so that $|\lambda_A| > |\lambda_B|$) and corresponding eigenvectors $\mathbf{x}_A$ and $\mathbf{x}_B$. Like any other vector, $\mathbf{w}_1$ can be expanded in terms of the eigenvectors

$$\mathbf{w}_1 = c_A\mathbf{x}_A + c_B\mathbf{x}_B \tag{9.12}$$

and in this form it is very easy to see what happens when $\mathbf{w}_1$ is multiplied by T N times:

$$\begin{aligned} \mathbf{w}_{N+1} = \mathsf{T}^N \mathbf{w}_1 &= c_A \mathsf{T}^N \mathbf{x}_A + c_B \mathsf{T}^N \mathbf{x}_B \\ &= c_A \lambda_A^N \mathbf{x}_A + c_B \lambda_B^N \mathbf{x}_B. \end{aligned} \tag{9.13}$$

So the partition function is

$$Z_{N+1} = Z_{N+1}^{\uparrow} + Z_{N+1}^{\downarrow} = c_A \lambda_A^N (x_A^{\uparrow} + x_A^{\downarrow}) + c_B \lambda_B^N (x_B^{\uparrow} + x_B^{\downarrow}). \tag{9.14}$$

By diagonalizing matrix T (that is, by finding both its eigenvalues and its eigenvectors) we could find every element in the right hand side of the above equation, and hence we could find the partition function Z_N for any N. But of course we are really interested only in the thermodynamic limit $N \to \infty$. Because $|\lambda_A| > |\lambda_B|$, λ_A^N dominates λ_B^N in the thermodynamic limit, and

$$Z_{N+1} \approx c_A \lambda_A^N (x_A^{\uparrow} + x_A^{\downarrow}), \tag{9.15}$$

provided that $c_A(x_A^{\uparrow} + x_A^{\downarrow}) \neq 0$. Now,

$$F_{N+1} = -k_B T \ln Z_{N+1} \approx -k_B T N \ln \lambda_A - k_B T \ln[c_A(x_A^{\uparrow} + x_A^{\downarrow})], \tag{9.16}$$

and this approximation becomes exact in the thermodynamic limit. Thus the free energy per spin is

$$f(K, L) = \lim_{N\to\infty} \frac{F_{N+1}(K, L)}{N+1} = -k_B T \ln \lambda_A. \tag{9.17}$$

So to find the free energy we only need to find the larger eigenvalue of T: we don't need to find the smaller eigenvalue, and we don't need to find the eigenvectors!

It is a simple matter to find the eigenvalues of our transfer matrix T. They are the two roots of

$$\det \begin{pmatrix} e^{K+L} - \lambda & e^{-K+L} \\ e^{-K-L} & e^{K-L} - \lambda \end{pmatrix} = 0 \tag{9.18}$$

$$(\lambda - e^{K+L})(\lambda - e^{K-L}) - e^{-2K} = 0 \tag{9.19}$$

$$\lambda^2 - 2e^K \cosh L \lambda + e^{2K} - e^{-2K} = 0, \tag{9.20}$$

which are

$$\lambda = e^K \left[\cosh L \pm \sqrt{\cosh^2 L - 1 + e^{-4K}} \right]. \tag{9.21}$$

It is clear that both eigenvalues are real, and that the larger one is positive, so

$$\lambda_A = e^K \left[\cosh L + \sqrt{\sinh^2 L + e^{-4K}} \right]. \tag{9.22}$$

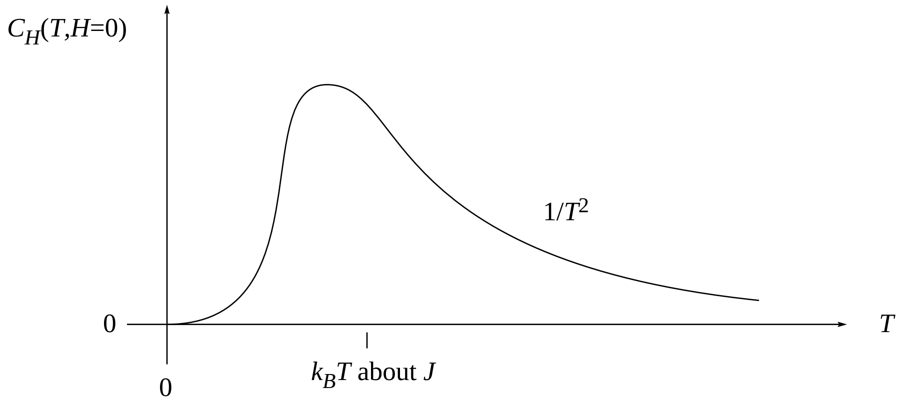
Finally, using equation (9.17), we find the free energy per spin

$$f(T, H) = -J - k_B T \ln \left[\cosh \frac{mH}{k_B T} + \sqrt{\sinh^2 \frac{mH}{k_B T} + e^{-4J/k_B T}} \right]. \tag{9.23}$$

Results

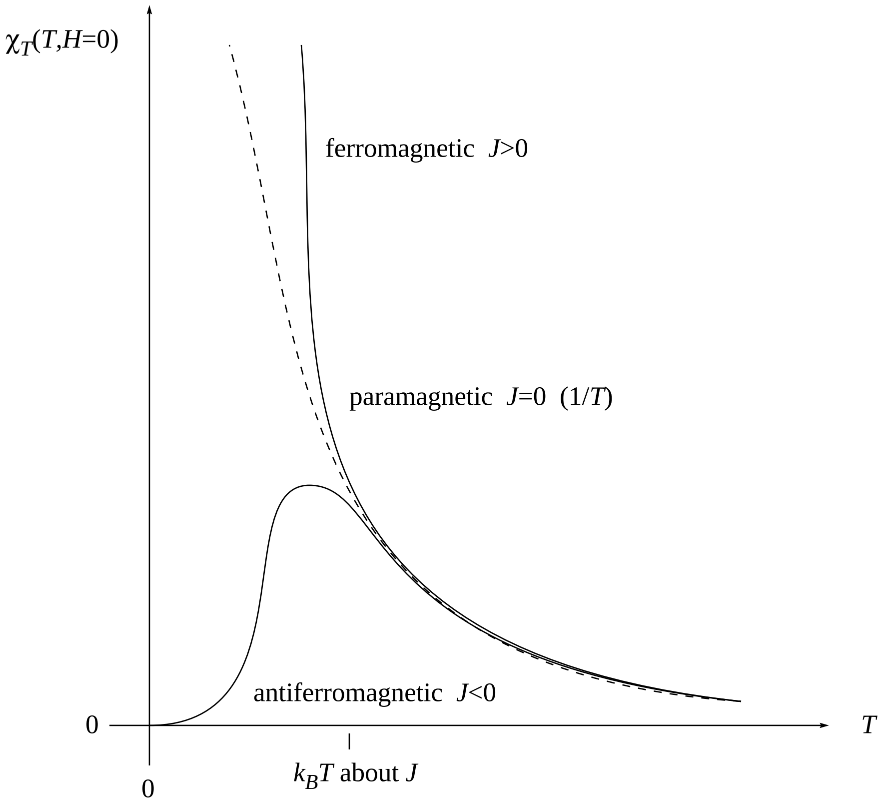
Knowing the free energy, we can take derivatives to find any thermodynamic quantity (see problem 9.2). Here I'll sketch and discuss the results obtained through those derivatives.

The heat capacity at constant, vanishing, magnetic field is sketched here:



Do you think an experimentalist needs a magnet to probe magnetic phenomena? This graph shows that a magnet is *not* required: The magnetic effects result in a bump in the heat capacity near $k_BT = J$, even when no magnetic field is applied.

The magnetic susceptibility is sketched here:



We have already seen that for independent spins (paramagnet, $J = 0$) the susceptibility falls like $1/T$ with temperature (the "Curie law"). Interacting spins at high temperature ($k_BT \gg J$) behave approximately the same way. But at low temperatures, the susceptibility for a ferromagnet *exceeds* the susceptibility for a paramagnet, while the susceptibility for a antiferromagnet *undershoots* the susceptibility for a paramagnet. This makes sense: For a paramagnet, the external magnetic field is inducing the spins to align. For a ferromagnet, both the external magnetic field and the tendency of neighboring spins to align are inducing the spins to align. For an antiferromagnet, the external magnetic field is inducing the spins to align, but the tendency of neighboring spins to antialign is opposing that inducement.

Aligning the spins in a paramagnet is like herding cats: the individual spins are independent and don't naturally take to pointing all in the same direction. Aligning the spins in a ferromagnet is like herding cows: the individual spins want to all go in the same direction and don't care which direction it is. Aligning the spins in an antiferromagnet is like herding siblings in a dysfunctional family, where each sibling says "I want to go to the opposite of wherever my brother/sister wants to go."

9.3 The Mean-Field Approximation

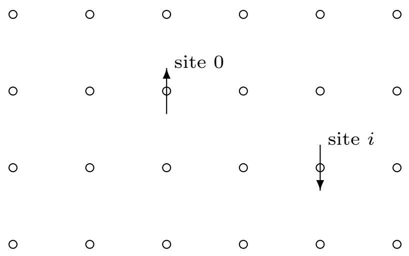
Many times, in this book, I have had occasion to make an approximation, but then I argued (sometimes rigorously and sometimes less rigorously) that this approximation would become "exact in the thermodynamic limit." So let me emphasize that the mean-field approximation is *not* exact in the thermodynamic limit. It is usually accurate at high temperatures. It is rarely accurate near phase transitions.

9.4 Correlation Functions in the Ising Model

9.4.1 Motivation and definition

How does a spin at one site influence a spin at another site? This is not a question of thermodynamics, but it's an interesting and useful question in statistical mechanics. The answer is given through correlation functions.

Consider an Ising model with spins $s_i = \pm 1$ on lattice sites i. The figure below shows part of a square lattice, although the discussion holds for any Bravais lattice in any dimension.



Choose a site at the center of the lattice and call it the origin, site 0. Your choice is quite arbitrary, because the lattice is infinite so *any* site is at the center. Now choose another site and call it site i. The product of these two spins is

$$s_0 s_i = \begin{cases} +1 & \text{if the spins point in the same direction} \\ -1 & \text{if the spins point in opposite directions.} \end{cases} \tag{9.24}$$

What is the average of this product over all the configurations in the ensemble? In general, this will be a difficult quantity to find, but in certain special cases we can hold reasonable expectations. For example if the system is ferromagnetic, then at low temperatures we expect that nearest neighbor spins will mostly be pointing in the same direction, whereas the opposite holds if the system is antiferromagnetic. Thus we expect that, if site i is adjacent to site 0,

$$\langle s_0 s_i \rangle \approx \begin{cases} +1 & \text{for ferromagnetic systems at low temperatures} \\ -1 & \text{for antiferromagnetic systems at low temperatures.} \end{cases} \tag{9.25}$$

Can you think of other expectations? (High temperatures? Next-nearest-neighbors at low temperatures?) Does the average of the product ever exceed 1 in any circumstances? Let me also point out a frequently-held expectation that is *not* correct. One might expect that $\langle s_0 s_i \rangle$ would vanish for sites very far apart. This is true under some circumstances, but not if an external magnetic field is applied, nor at zero field in a low-temperature ferromagnet, because in these situations all the spins in the sample (even those very far apart) tend to point in the same direction.

We have seen that the average of the product $\langle s_0 s_i \rangle$ is not trivial. In contrast the product of the averages $\langle s_0 \rangle \langle s_i \rangle$ is very easy, because all sites are equivalent whence $\langle s_i \rangle = \langle s_0 \rangle$ and

$$\langle s_0 \rangle \langle s_i \rangle = \langle s_0 \rangle^2. \tag{9.26}$$

In fact, $\langle s_0 s_i \rangle$ would be equal to $\langle s_0 \rangle^2$ if there were no correlations between spins…this is essentially the definition of "correlation". This motivates the definition of the *correlation function*

$$G_i(T, H) = \langle s_0 s_i \rangle - \langle s_0 \rangle^2. \tag{9.27}$$

The correlation function is essentially a measure of "peer pressure": How is the spin at site i influenced by the state of the spin at site 0? If there is a large magnetic field, for example, and if sites i and 0 are far apart, then both spins will tend to point up, but this is not because of peer pressure, it is because of "external pressure". (For example, two children in different cities might dress the same way, not because one imitates the other, but because both listen to the same advertisements.) The term $\langle s_0 \rangle^2$ measures external pressure, and we subtract it from $\langle s_0 s_i \rangle$ so that $G_i(T, H)$ will measure only peer pressure and not external pressure.

This definition doesn't say how the influence travels from site 0 to site i: If site 2 is two sites to the right of site 0, for example, then most of the influence will be due to site 0 influencing site 1 and then site 1 influencing site 2. But a little influence will travel up one site, over two sites, then down one site, and still smaller amounts will take even more circuitous routes.

Note that

$$\begin{array}{rrcl} \text{if } i = 0 \text{ then} & G_i(T, H) & = & 1 - \langle s_0 \rangle^2 \\ \text{if } i \text{ is far from 0 then} & G_i(T, H) & = & 0. \end{array} \tag{9.28}$$

I have three comments to make concerning the correlation function. First, realize that the correlation function gives information about the system beyond thermodynamic information. For most of this book we have been using microscopic information to calculate a partition function and then to find macroscopic (thermodynamic) information about the system. We did not use the partition function to ask any question that involved the distance between two spins (or two atoms). The correlation function enables us to probe more deeply into statistical mechanics and ask such important *microscopic* questions.

Second, the correlation function is a measurable quantity. I have produced the definition through conceptual motivations[1] that make it seem impossible to find except by examining individual spins…a conceptual nicety but experimental impossibility. But in fact the correlation function can be found experimentally through neutron scattering. This technique relies upon interference in the de Broglie waves of neutron waves scattered from nearby spins. It is not trivial: indeed two of the inventors of the technique were awarded the Nobel prize in physics for 1994. (It is also worth noting that the work of one of these two was based upon theoretical work done by Bob Weinstock in his Ph.D. thesis.) I will not have enough time to treat this interesting topic, but you should realize that what follows in this section is not mere theoretical fluff…it has been subjected to, and passed, the cold harsh probe of experimental test.

Third, although the definition given here applies only to Ising models on Bravais lattices, analogous definitions can be produced for other magnetic systems, for fluids, and for solids.

9.4.2 Susceptibility from the correlation function

I have emphasized above that the correlation function gives information beyond that given by thermodynamics. But the correlation function contains thermodynamic information as well. In this subsection we will prove that if the correlation function $G_i(T,H)$ is known for all sites in the lattice, then the susceptibility, a purely thermodynamic quantity, can be found through

$$\chi(T,H) = N\frac{m^2}{k_BT}\sum_i G_i(T,H), \tag{9.29}$$

where the sum is over all sites in the lattice (including the origin).

We begin with a few reminders. The microscopic magnetization for a single configuration is

$$\mathcal{M}(s_1,\ldots,s_N) = m\sum_i s_i \tag{9.30}$$

and the macroscopic (thermodynamic) magnetization is its ensemble average

$$M = \langle\mathcal{M}\rangle = mN\langle s_0\rangle. \tag{9.31}$$

The Ising Hamiltonian breaks into two pieces,

$$\begin{aligned} \mathcal{H} &= \mathcal{H}_0(s_1,\ldots,s_N) - mH\sum_i s_i & (9.32)\\ &= \mathcal{H}_0(s_1,\ldots,s_N) - H\mathcal{M}(s_1,\ldots,s_N), & (9.33) \end{aligned}$$

where $\mathcal{H}_0$ is independent of magnetic field. In the nearest-neighbor Ising model the field-independent part of the Hamiltonian is

$$\mathcal{H}_0(s_1,\ldots,s_N) = -J\sum_{<i,j>} s_is_j, \tag{9.34}$$

---

[1] Namely, by asking "Wouldn't it be nice to know how one spin is influenced by its neighbors?"

but we will not use this formula…the results of this section are true for spin-spin interactions of arbitrary complexity. Finally, the Boltzmann factor is

$$e^{-\beta\mathcal{H}} = e^{-\beta\mathcal{H}_0+\beta H\mathcal{M}}. \tag{9.35}$$

Now we can start the argument by examining the sum of the correlation function over all sites. In what follows, the notation $\sum_{\text{S}}$ means the "sum over states".

$$\begin{aligned}
\sum_i G_i &= \sum_i \langle s_0 s_i\rangle - \langle s_0\rangle^2 && (9.36)\\
&= \sum_i \left[\frac{\sum_{\text{S}} s_0 s_i e^{-\beta\mathcal{H}}}{Z} - \frac{\left(\sum_{\text{S}} s_0 e^{-\beta\mathcal{H}}\right)^2}{Z^2}\right] && (9.37)\\
&= \frac{\sum_{\text{S}} s_0(\mathcal{M}/m)e^{-\beta\mathcal{H}}}{Z} - N\frac{\left(\sum_{\text{S}} s_0 e^{-\beta\mathcal{H}}\right)^2}{Z^2} && (9.38)\\
&= \frac{Z\sum_{\text{S}} s_0(\mathcal{M}/m)e^{-\beta\mathcal{H}} - N\sum_{\text{S}} s_0 e^{-\beta\mathcal{H}}\sum_{\text{S}} s_0 e^{-\beta\mathcal{H}}}{Z^2} && (9.39)
\end{aligned}$$

Look at this last equation carefully. What do you see? The quotient rule! Do you remember our slick trick for finding dispersions? The $\mathcal{M}$ appearing in the leftmost summand can be gotten there by taking a derivative of equation (9.35) with respect to H:

$$\frac{\partial e^{-\beta\mathcal{H}}}{\partial H} = \beta\mathcal{M}e^{-\beta\mathcal{H}}. \tag{9.40}$$

Watch carefully:

$$\begin{aligned}
\frac{\partial}{\partial H}\left(\frac{\sum_{\text{S}} s_0 e^{-\beta\mathcal{H}}}{Z}\right) &= \frac{Z\sum_{\text{S}} s_0\beta\mathcal{M}e^{-\beta\mathcal{H}} - \sum_{\text{S}}\beta\mathcal{M}e^{-\beta\mathcal{H}}\sum_{\text{S}} s_0 e^{-\beta\mathcal{H}}}{Z^2} && (9.41)\\
&= \beta\left[\frac{Z\sum_{\text{S}} s_0\mathcal{M}e^{-\beta\mathcal{H}} - mN\sum_{\text{S}} s_0 e^{-\beta\mathcal{H}}\sum_{\text{S}} s_0 e^{-\beta\mathcal{H}}}{Z^2}\right] && (9.42)\\
& && (9.43)
\end{aligned}$$

But the quantity in square brackets is nothing more than m times equation (9.39), so

$$\frac{\partial}{\partial H}\left(\frac{\sum_{\text{S}} s_0 e^{-\beta\mathcal{H}}}{Z}\right) = \beta m\sum_i G_i. \tag{9.44}$$

But we also know that

$$\frac{\partial}{\partial H}\left(\frac{\sum_{\text{S}} s_0 e^{-\beta\mathcal{H}}}{Z}\right) = \frac{\partial\langle s_0\rangle}{\partial H} = \frac{\partial M/mN}{\partial H} = \frac{1}{mN}\chi \tag{9.45}$$

whence, finally

$$\chi(T,H) = N\frac{m^2}{k_BT}\sum_i G_i(T,H). \tag{9.46}$$

Whew!

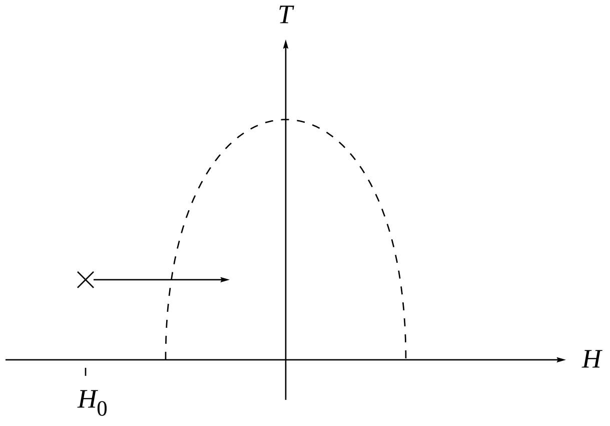
Now we can stop running and do our cool-down stretches. Does the above equation, procured at such expense, make sense? The left hand side is extensive. The right hand side has a factor of N and also a sum over all sites, and usually a sum over all sites is extensive. So at first glance the left hand side scales linearly with N while the right hand side scales with N^2, a sure sign of error! In fact, there is no error. The correlation function G_i vanishes except for sites very close to the origin. ("Distant sites are uncorrelated", see equation (9.28).) Thus the sum over all sites above has a summand that vanishes for most sites, and it is intensive rather than extensive.

9.4.3 All of thermodynamics from the susceptibility

The previous subsection shows us how to find one thermodynamic quantity, $\chi(T,H)$ at some particular values for temperature and field, by knowing the correlation function $G_i(T,H)$ for all sites i, at those same fixed values for temperature and field. In this subsection we will find how to calculate any thermodynamic quantity at all, at any value of T and H at all, by knowing $\chi(T,H)$ for all values of T and H. Thus knowing the correlation $G_i(T,H)$ as a function of all its arguments—i, T, and H—enables us to find any thermodynamic quantity at all.

To find any thermodynamic quantity it suffices to find the free energy $F(T,H)$, so the claim above reduces to saying that we can find $F(T,H)$ given $\chi(T,H)$. Now we can find $\chi(T,H)$ from $F(T,H)$ by simple differentiation, but going backwards requires some very careful integration. We will do so by looking at the difference between quantities for the Ising model and for the ideal paramagnet.

Remember that the thermodynamic state of an Ising magnet is specified by the two variables T and H, as indicated in the figure.



Over much of this diagram, namely the part outside the wavy line, the Ising magnet behaves very much as an ideal paramagnet does, because the typical thermal energy k_BT or the typical magnetic energy $m|H|$ overwhelms the typical spin-spin interaction energy $|J|$. Thus outside of the dashed line (e.g. at the ×) the Ising thermodynamic quantities are well-approximated by the paramagnetic thermodynamic quantities

$$\chi_P(T,H) \quad = \quad \left.\frac{\partial M}{\partial H}\right)_T = N\frac{m^2}{k_BT}\mathrm{sech}^2\frac{mH}{k_BT} \tag{9.47}$$

$$\begin{aligned} M_P(T,H) &= -\left.\frac{\partial F}{\partial H}\right)_T = mN\tanh^2\frac{mH}{k_BT} && (9.48)\\ F_P(T,H) &= -k_BTN\ln\left(2\cosh\frac{mH}{k_BT}\right), && (9.49)\end{aligned}$$

and this approximation becomes better and better as $T \to \infty$ or $H \to \pm\infty$.

The difference between the susceptibility for our Ising model and for the ideal paramagnet is

$$\chi(T,H) - \chi_P(T,H) = \left.\frac{\partial(M-M_P)}{\partial H}\right)_T. \qquad (9.50)$$

Integrate this equation along the path indicated in the figure to find

$$\begin{aligned} \int_{H_0}^{H} dH'\,[\chi(T,H') - \chi_P(T,H')] &= \int_{H_0}^{H} dH'\,\left.\frac{\partial(M-M_P)}{\partial H'}\right)_T && (9.51)\\ &= (M-M_P)|_{T,H} - (M-M_P)|_{T,H_0}. && (9.52)\end{aligned}$$

Then take the limit $H_0 \to -\infty$ so that $M(T,H_0) \to M_P(T,H_0)$ and

$$M(T,H) = M_P(T,H) + \int_{-\infty}^{H} dH'\,[\chi(T,H') - \chi_P(T,H')], \qquad (9.53)$$

where, remember, $M_P(T,H)$ and $\chi_P(T,H)$ are known functions.

We don't have to stop here. We can consider the difference

$$M(T,H) - M_P(T,H) = -\left.\frac{\partial(F-F_P)}{\partial H}\right)_T \qquad (9.54)$$

and then perform exactly the same manipulations that we performed above to find

$$F(T,H) = F_P(T,H) - \int_{-\infty}^{H} dH'\,[M(T,H') - M_P(T,H')]. \qquad (9.55)$$

Then we can combine equations (9.55) and (9.53) to obtain

$$F(T,H) = F_P(T,H) - \int_{-\infty}^{H} dH' \int_{-\infty}^{H'} dH''\,[\chi(T,H'') - \chi_P(T,H'')]. \qquad (9.56)$$

Using the known results for $F_P(T,H)$ and $\chi_P(T,H)$, as well as the correlation-susceptibility relation (9.46), this becomes

$$F(T,H) = -k_BTN\ln\left(2\cosh\frac{mH}{k_BT}\right) - N\frac{m^2}{k_BT}\int_{-\infty}^{H} dH' \int_{-\infty}^{H'} dH''\left(\sum_i G_i(T,H'') - \operatorname{sech}^2\frac{mH''}{k_BT}\right). \qquad (9.57)$$

Let me stress how remarkable this result is. You would think that to find the thermodynamic energy $E(T,H)$ of the Ising model you would need to know the spin-spin coupling constant J. But you don't: You can find $E(T,H)$ without knowing J, indeed without knowing the exact form of the spin-spin interaction Hamiltonian at all, if you do know the purely geometrical information contained within the correlation function.[2] This is one of the most amazing and useful facts in all of physics.

---

[2] This does not mean that the thermodynamic energy is independent of the spin-spin Hamiltonian, because the Hamiltonian influences the correlation function.

9.4.4 Parallel results for fluids

I cannot resist telling you how the results of this section change when applied to fluid rather than magnetic systems. In that case the correlation function $g_2(\mathbf{r}; T, V, N)$ depends upon the position $\mathbf{r}$ rather than the site index i. Just as the sum of G_i over all sites is related to the susceptibility χ, so the integral of $g_2(\mathbf{r})$ over all space is related to the compressibility κ_T. And just as the susceptibility can be integrated twice (carefully, through comparison to the ideal paramagnet) to give the magnetic free energy $F(T, H)$, so the compressibility can be integrated twice (carefully, through comparison to the ideal gas) to give the fluid free energy $F(T, V, N)$. And just as the magnetic thermodynamic quantities can be found from the correlation function without knowing the details of the spin-spin interaction Hamiltonian, so the fluid thermodynamic quantities can be found from the correlation function without knowing the details of the particle interaction forces. A question for you: How is it possible to get all this information knowing only the correlation function in space rather than the correlation function in phase space? In other words, why don't you need information about the velocities?

I should put in some references to experimental tests and to say who thought this up. Are these available in Joel's review article?

9.5 Computer Simulation

9.5.1 Basic strategy

If we're going to use a computer to solve problems in statistical mechanics, there are three basic strategies that we could take. I illustrate them here by showing how they would be applied to the Ising model.

1. Exhaustive enumeration. Just do it! List all the states (microstates, configurations), their associated probabilities, and average over them! Admittedly, there are a lot of states, but computers are fast, right? Let's see how many states there are. Consider a pretty small problem: a three dimensional Ising model on an $8 \times 8 \times 8$ cube. This system has 512 spins that can be oriented either "up" or "down", so there are $2^{512} \approx 10^{154}$ configurations. Suppose that our computer could generate and examine a million configurations per second…this is about as fast as is currently possible. Then an exhaustive enumeration would require 10^{148} seconds to do the job. By contrast, the universe is about 10^{18} seconds old. So for one computer to do the problem it would take 10^{130} times the age of the universe. Now this is impractical, but maybe we could do it by arranging computers in parallel. Well, there are about 10^{80} protons in the universe, and if every one were to turn into a spiffy Unix workstation, it would still require 10^{50} times the age of the universe to complete the list. And this is for a small problem! Sorry, computers aren't fast, and they never will be fast enough to solve the complete enumeration problem. It is not for nothing that this technique is called *exhaustive* enumeration.

2. Random sampling. Instead of trying to list the entire pool of possible configurations, we will dip into it at random and sample the configurations. This can be implemented by scanning through the lattice and orienting spins up with probability $\frac{1}{2}$ and down with probability $\frac{1}{2}$. The problem in this strategy is that all configurations are equally likely to be sampled, but because there are many more high energy configurations than low energy configurations, it is very unlikely to sample a low energy configuration (the "poker paradox" again). But in the Boltzmann distribution $e^{-\text{energy}/k_BT}$ the low energy configurations are in fact *more* likely to occur. So you could sample for a long time before encountering even one configuration with non-negligible probability. This strategy is considerably better than the first one, but it would still take about the age of the universe to implement.

3. Importance sampling. This strategy is to sample the pool of possible configurations not completely at random, but in such a way that the most likely configurations are most likely to be sampled. An enormously successful algorithm to perform importance sampling was developed by Nick Metropolis and his coworkers Arianna Rosenbluth, Marshall Rosenbluth, Augusta Teller, and Edward Teller (of hydrogen bomb fame) in 1953. ("Equation of state calculations by fast computing machines", *J. Chem. Phys.* **21** 1087–1092.) It is called "the Metropolis algorithm", or "the M(RT)^2 algorithm", or simply "the Monte Carlo algorithm". The next section treats this algorithm in detail.

An analogy to political polling is worth making here. Exhaustive enumeration corresponds to an election, random sampling corresponds to a random poll, and importance sampling corresponds to a poll which selects respondents according to the likelihood that they will vote.

9.5.2 The Metropolis algorithm

This algorithm builds a chain of configurations, each one modified (usually only slightly) from the one before. For example, if we number the configurations (say, for the $8 \times 8 \times 8$ Ising model, from 1 to 2^{512}) such a chain of configurations might be

$$C_{171} \to C_{49} \to C_{1294} \to C_{1294} \to C_{171} \to C_{190} \to \cdots .$$

Note that it is possible for two successive configurations in the chain to be identical.

To build any such chain, we need some transition probability rule $W(C_a \to C_b)$ giving the probability that configuration C_b will follow configuration C_a. And to be useful for importance sampling, the rule will have to build the chain in such a way that the probability of C_n appearing in the chain is $e^{-\beta E_n}/Z$.

So we need to produce a result of the form: if "rule" then "Boltzmann probability distribution". It is, however, very difficult to come up with such results. Instead we go the other way to produce a pool of plausible transition rules. . . plausible in that they are not obviously inconsistent with a Boltzmann probability distribution.

Consider a long chain of N_{configs} configurations, in which the probability of a configuration appearing is given by the Boltzmann distribution. The chain must be "at equilibrium" in that

$$\text{number of transitions}(C_a \to C_b) = \text{number of transitions}(C_b \to C_a). \tag{9.58}$$

But the number of C_as in the chain is $N_{\text{configs}}e^{-\beta E_a}/Z$, and similarly for the number of C_bs, so the equation above is

$$N_{\text{configs}}\frac{e^{-\beta E_a}}{Z}W(C_a \to C_b) = N_{\text{configs}}\frac{e^{-\beta E_b}}{Z}W(C_b \to C_a), \tag{9.59}$$

whence

$$\frac{W(C_a \to C_b)}{W(C_b \to C_a)} = e^{-\beta(E_b - E_a)}. \tag{9.60}$$

This condition, called "detailed balance", defines our pool of plausible transition probability rules. It is possible that a rule could satisfy detailed balance and still not sample according to the Boltzmann distribution, but any rule that does *not* satisfy detailed balance certainly *cannot* sample according to the Boltzmann distribution. In practice, all the rules that satisfy detailed balance seem to work.

Two transitions probability rules that do satisfy detailed balance, and the two rules most commonly used in practice, are

$$\begin{aligned} W(C_a \to C_b) &= [\text{normalization constant}]\left\{\frac{e^{-\beta\Delta E}}{1+e^{-\beta\Delta E}}\right\} && (9.61)\\ W(C_a \to C_b) &= [\text{normalization constant}]\left\{\begin{array}{cl} 1 & \text{if } \Delta E \le 0 \\ e^{-\beta\Delta E} & \text{if } \Delta E > 0 \end{array}\right\} && (9.62)\end{aligned}$$

where we have taken

$$\Delta E = E_b - E_a \tag{9.63}$$

and where the normalization constant is fixed so that

$$\sum_{C_b} W(C_a \to C_b) = 1. \tag{9.64}$$

If we had to calculate the normalization constant, then we would be back to performing an exhaustive enumeration, so we must find a way to work with unnormalized transition probabilities. To this end we define $w_{a\to b}$ as the factor for the transition probability aside from the normalization constant, i.e. the part in curly brackets in equations (9.61) and (9.62). Note that it is a positive number less than or equal to one:

$$0 < \{\quad\} \equiv w_{a\to b} \le 1. \tag{9.65}$$

Notice that for any rule satisfying detailed balance the transition probability must *increase* as the change in energy *decreases*, suggesting a simple physical interpretation: The chain of configurations is like a walker stepping from configuration to configuration on a "configuration landscape". If a step would decrease the walker's energy, he is likely to take it, whereas if it would increase his energy, he is likely to reject it. Thus the walker tends to go downhill on the configuration landscape, but it is not impossible for him to go uphill. This seems like a recipe for a constantly decreasing energy, but it is not, because more uphill steps than downhill steps are available to be taken.[3]

---

[3] This paragraph constitutes the most densely packed observation in this book. It looks backward to the poker paradox, to the definition of temperature, and to the "cash incentives" interpretation of the canonical ensemble. It looks forward to equilibration and to optimization by Monte Carlo simulated annealing. Why not read it again?

From these ingredients, Metropolis brews his algorithm:

```
Generate initial configuration [at random or otherwise]
Gather data concerning configuration [e.g. find $M := n_\uparrow - n_\downarrow$; $M_{\text{sum}} := M$]
DO Iconfig = 2, Nconfigs
    Generate candidate configuration [e.g. select a spin to flip]
    Compute $w_{a\to b}$ for transition to candidate
    With probability $w_{a\to b}$, make the transition
    Gather data concerning configuration [e.g. find $M := n_\uparrow - n_\downarrow$; $M_{\text{sum}} := M_{\text{sum}} + M$]
END DO
Summarize and print data [e.g. $M_{\text{ave}} := M_{\text{sum}}/$Nconfigs]
```

I'll make three comments concerning this algorithm. First of all, note that the step "With probability $w_{a\to b}$, make the transition" implies that sometimes the transition is not made, in which case two configurations adjacent in the chain will be identical. It is a common misconception that in this case the repeated configuration should be counted only once, but that's not correct: you must execute the "Gather data concerning `configuration`" step whether the previous candidate was accepted or rejected.

Secondly, I wish to detail how the step

```
With probability $w_{a\to b}$, make the transition
```

is implemented. It is done by expanding the step into the two substeps

```
Produce a random number $z$ [$0 \le z < 1$]
IF $z < w_{a\to b}$ THEN switch to candidate
    [i.e. configuration := candidate configuration]
```

Finally, I need to point out that this algorithm does not precisely implement either of the transition probability rules (9.61) or (9.62). For example, if the step "Generate `candidate configuration`" is done by selecting a single spin to flip, then the algorithm will never step from one configuration to a configuration three spin-flips away, regardless of the value of ΔE. Indeed, under such circumstances (and if there are N spins in the system), the transition probability rule is

$$W(C_a \to C_b) = \begin{cases} \frac{1}{N} w_{a\to b} & \text{if } C_a \text{ and } C_b \text{ differ by a single spin flip} \\ 0 & \text{if } C_a \text{ and } C_b \text{ differ by more than a single spin flip} \\ 1 - \sum_{C_b \neq C_a} W(C_a \to C_b) & \text{if } C_a = C_b. \end{cases} \tag{9.66}$$

It is easy to see that this transition probability rule satisfies detailed balance.

9.5.3 Implementing the Metropolis algorithm

It is not atypical to run a Monte Carlo program for about 10,000 Monte Carlo steps per site. As such, the program might run for hours or even days. This is considerably less than the age of the universe, but probably far longer than you are used to running programs. The following tips are useful for speeding up or otherwise improving programs implementing the Metropolis algorithm.

1. Use scaled quantities. The parameters J, m, H, and T do not enter in any possible combination, but only through two independent products. These are usually taken to be

$$\tilde{T} = \frac{k_B T}{J} \quad \text{and} \quad \tilde{H} = \frac{mH}{J}. \tag{9.67}$$

Thus the Boltzmann exponent for a given configuration is

$$-\frac{E}{k_B T} = \frac{1}{\tilde{T}} \left(\sum_{\langle i,j \rangle} s_i s_j + \tilde{H} \sum_i s_i \right), \tag{9.68}$$

where s_i is $+1$ if the spin at site i is up, -1 if it is down, and where $\langle i, j \rangle$ denotes a nearest neighbor pair.

2. Don't find total energies. To calculate $w_{a \to b}$ you must first know ΔE, and the obvious way to find ΔE is to find E_b and E_a (through equation (9.68)) and subtract. This way is obvious but terribly inefficient. Because the change in configuration is small (usually a single spin flip) the change in energy can be found from purely local considerations without finding the total energy of the entire system being simulated. Similarly, if you are finding the average (scaled) magnetization

$$M = n_\uparrow - n_\downarrow = \sum_i s_i \tag{9.69}$$

(as suggested by the square brackets in the algorithm on page 200) you don't need to scan the entire lattice to find it. Instead, just realize that it changes by ±2 with each spin flip.

3. Precompute Boltzmann factors. It is computationally expensive to find evaluate a exponential, yet we must know the value of $e^{-\beta \Delta E}$. However, usually there are only a few possible values of ΔE. (For example in the square lattice Ising model with nearest neighbor interactions and a field, a single spin flip gives rise to one of only ten possible values of the energy change.) It saves considerable computational time (and often makes the program clearer) to precalculate the corresponding values of $w_{a \to b}$ just once at the beginning of the program, and to store those values in an array for ready reference when they are needed.

4. Average "on the fly". The algorithm on page 200 finds the average (scaled) magnetization by summing the magnetization of each configuration in the chain and then dividing by the number of configurations. Because the chain is so long this raises the very real possibility of overflow in the value of M_{sum}. It is often better to keep a running tally of the average by tracking the "average so far" through

$$M_{\text{ave}} {:=} M_{\text{ave}}(\texttt{Iconfig} - 1)/\texttt{Iconfig} + M/\texttt{Iconfig} \tag{9.70}$$

or (identical mathematically, but preferable for numerical work)

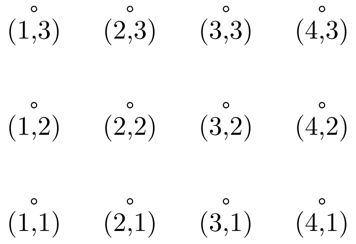
$$M_{\text{ave}} {:=} M_{\text{ave}} + (M - M_{\text{ave}})/\texttt{Iconfig}. \tag{9.71}$$

5. Finite size effects. Use periodic or skew-periodic boundary conditions.

6. Lattice data structures. Suppose we wish to simulate a two-dimensional Ising model on a 4×3 square grid. An obvious data structure to hold the configuration in the computer's memory is an integer-valued *two-dimensional array* declared through the code

```
INTEGER, PARAMETER ::  Nx = 4, Ny = 3
INTEGER ::  Spin (1:Nx, 1:Ny)
```

(I use the notation of Fortran 90. If you are familiar with some other computer language, the intent should nevertheless be clear.) If the spin at site (3,2) is up, then `Spin`$(3,2) = +1$, and if that spin is down, then `Spin`$(3,2) = -1$. The lattice sites are labeled as shown in this figure:



Although this representation is obvious, it suffers from a number of defects. First, it is difficult to generalize to other lattices, such as the triangular lattice in two dimensions or the face-centered cubic lattice in three dimensions. Second, finding the nearest neighbors of boundary sites using periodic or skew-periodic boundary conditions is complicated. And finally because the array is two-dimensional, any reference to an array element involves a multiplication,[4] which slows down the finding of data considerably.

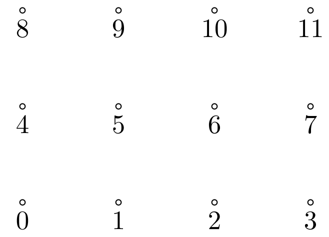
All of these defects are absent in the *folded array* representation of the lattice sites. In this representation the sites are stored as an integer-valued one-dimensional array declared through

```
INTEGER, PARAMETER ::  Nx = 4, Ny = 3, NSites = Nx*Ny
INTEGER ::  Spin (0:NSites-1)
```

Now the lattice sites are labeled as:

---

[4] In Fortran, the datum `Site(i,j)` is stored at memory location number `i + j*(Nx-1)`, whence the data are stored in the sequence (1,1), (2,1), (3,1), (4,1), (1,2), (2,2),. . . . In other computer languages the formula for finding the memory location is different, but in all languages it involves an integer multiply.



It is not hard to show that, with skew-periodic boundary conditions, the four neighbors of site number `l` (`l` for location) are

(`l` + 1) mod `NSites`, (`l` − 1) mod `NSites`, (`l` + `Nx`) mod `NSites`, (`l` − `Nx`) mod `NSites`.

Unfortunately, the Fortran `Mod` function was inanely chosen to differ from the mathematical mod function, so this arithmetic must be implemented through

```
Mod(l + 1, NSites)
Mod(l + (NSites - 1), NSites)
Mod(l + Nx, NSites)
Mod(l + (NSites - Nx), NSites)
```

7. Random number generators. It is hard to find an easy source of high-quality random numbers: this is a problem for physics, also for government and industry.

D.E. Knuth, *Seminumerical Algorithms* (Addison–Wesley, Reading, Massachusetts, 1981) chapter 3.

W.H. Press, S.A. Teukolsky, W.T. Vettering, and B.P. Flannery, *Numerical Recipes* chapter 7. (For a confession and a prize announcement, see also W.H. Press and S.A. Teukolsky, "Portable random number generators", *Computers in Physics* **6** (1992) 522–524.)

T.-W. Chiu and T.-S. Guu, "A shift-register sequence random number generator," *Computer Physics Communications* **47** (1987) 129–137. (See particularly figures 1 and 2.)

A.M. Ferrenberg, D.P. Landau, and Y.J. Wong, "Monte Carlo simulations: Hidden errors from 'good' random number generators," *Phys. Rev. Lett.* **69** (1992) 3382.

S.K. Park and K.W. Miller, "Random number generators: Good ones are hard to find," *Communications of the ACM* **31** (1988) 1192–1201.

Search the internet for "Mersenne Twister".

8. Initial configurations and equilibration. The Metropolis algorithm does not specify how to come up with the first configuration in the chain. Indeed, selecting this configuration is something of an art. If you are simulating at high temperatures, it is usually appropriate to begin with a configuration chosen at random, so that about half the spins will be up and half down. But if you are simulating at low temperatures (or at high fields) it might be better to start at the configuration with all spins up. Other possibilities are also possible. But however you select the initial configuration, it is highly unlikely that the one you pick will be "typical" of the configurations for the temperature and magnetic field at which you are simulating.

9. Low temperatures. At low temperatures, most candidate transitions are rejected. BLK algorithm. (A.B. Bortz, J.L. Lebowitz, and M.H. Kalos, "A new algorithm for Monte Carlo simulation of Ising spin systems," *J. Comput. Phys.* **17** (1975) 10–18.)

10. Critical temperatures. "Critical slowing down," response is cluster flipping. (U. Wolff, "Collective Monte Carlo updating for spin systems," *Phys. Rev. Lett.* **62** (1989) 361–364. See also Jian-Sheng Wang and R.H. Swendsen, "Cluster Monte Carlo algorithms," *Physica* A **167** (1990) 565–579.)

11. First-order transitions.

12. Molecular dynamics.

9.5.4 The Wolff algorithm

In 1989 Ulli Wolff proposed an algorithm for Monte Carlo simulation that is particularly effective near critical points. (U. Wolff, *Phys. Rev. Lett.*, **62** (1989) 361–364.) The next page presents the Wolff algorithm as applied to the zero-field ferromagnetic nearest-neighbor Ising model,

$$\mathcal{H} = -J \sum s_i s_j \quad \text{with} \quad s_i = \pm 1, \tag{9.72}$$

on a square lattice or a simple cubic lattice.

```
Generate initial configuration
Gather data concerning this configuration

DO Iconfig = 2, Nconfigs

    Select site j at random

    Flip spin at j
    Put j into cluster
    NFlippedThisGeneration = 1

    DO
    IF (NFlippedThisGeneration = 0) EXIT
        NFlippedPreviousGeneration = NFlippedThisGeneration
        NFlippedThisGeneration = 0

        FOR each previous generation member i of the cluster DO
            FOR each neighbor j of i DO
                IF (spin at j $\neq$ spin at i) THEN
                    with probability $P = 1 - \exp(-2J/k_BT)$
                        Flip spin at j
                        Put j into cluster
                        NFlippedThisGeneration = NFlippedThisGeneration + 1
                END IF
            END DO
        END DO

    END DO

    Gather data concerning this configuration
    Empty the cluster

END DO

Summarize and print out results
```

Template for example

configuration a								configuration b							
+	−	−	+	+	−	+	−	+	−	−	+	+	−	+	−
−	−	+	+	+	+	−	+	−	−	+	−	−	−	−	+
−	−	−	+	+	−	−	−	−	−	−	−	−	−	−	−
+	−	+	−	+	−	−	−	+	−	+	−	−	−	−	−
−	+	+	+	+	−	−	+	−	+	+	−	−	−	−	+
−	−	−	−	+	−	−	−	−	−	−	−	+	−	−	−
+	+	−	+	+	−	+	+	+	+	−	+	+	−	+	+
+	−	−	+	+	−	−	+	+	−	−	+	+	−	−	+

$w_{a\to b} = \frac{8}{N} P_J^7 (1-P^J)^5$

$w_{b\to a} = \frac{8}{N} P_J^7 (1-P^J)^{11}$

Demonstration of detailed balance. In these formulas,

$$P_J = 1 - e^{-2J/k_BT}. \tag{9.73}$$

The integer 8 is the number of sites in the cluster, 7 is the number of internal bonds in the skeleton, 5 is the number of external bonds leading to a + spin, and 11 is the number of external bonds leading to a − spin. The energy difference between configurations a and b depends only upon these last two integers. It is

$$\Delta E = +2J(5) - 2J(11) = -2J(11-5). \tag{9.74}$$

Thus

$$\frac{w_{a\to b}}{w_{b\to a}} = (1-P^J)^{5-11} = e^{-2J(5-11)/k_BT} = e^{-\Delta E/k_BT} \tag{9.75}$$

and detailed balance is insured.

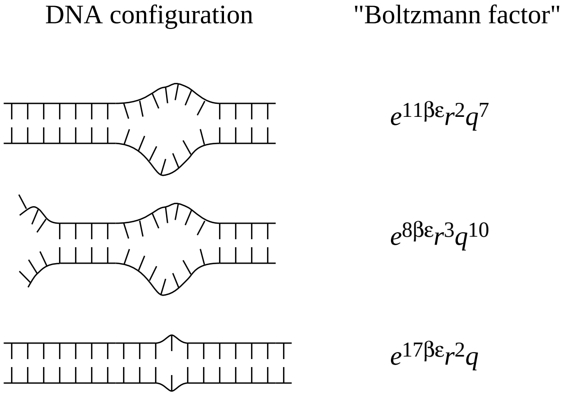
9.6 Additional Problems

9.1 **Denaturation of DNA**

(This problem is modified from one posed by M.E. Fisher. It deals with a research question born in the 1960s that is still of interest today: Douglas Poland and Harold A. Scheraga, “Occurrence of a phase transition in nucleic acid models,” *J. Chem. Phys.* **45** (1966) 1464–1469; M.E. Fisher, “Effect of excluded volume on phase transitions in biopolymers,” *J. Chem. Phys.* **45** (1966) 1469–1473; Yariv Kafri, David Mukamel, and Luca Peliti, “Why is the DNA denaturation transition first order?” *Phys. Rev. Lett.* **85** (2000) 4988–4991.)

The biological polymer DNA consists of two polymeric strands which, in their usual state, are twisted together to form a rather rigid double helix. However as the temperature is raised regions of the molecule may “melt”, breaking the weak bonds that hold the two strands together. In this case the two strands separate and coil randomly in the solution. If the entire molecule melts then the DNA is said to be “denatured”. A simple model to aid in understanding this phenomenon is the following.

Successive segments of the molecule are regarded as being in either the *helical state* or in the *melted state*. A segment in the helical state has a lower energy than one in the melted state ($-\epsilon$ *vs.* 0) but a segment in the melted state has q different possible orientations (due to coiling) whereas a segment in the helical state has only one. However, the first or last segment of a run of melted segments has a smaller number of configurations, rq, where r can be as small as 10^{-3}. (A melted segment that is both the first and last segment of a run is doubly restricted and has only r^2q configurations.) Sample DNA configurations and their associated "Boltzmann factors" are shown below.



a. Introduce a variable h_i for the ith segment such that

$$h_i = \begin{cases} 1 & \text{if the } i\text{th segment is helical} \\ 0 & \text{if the } i\text{th segment is melted.} \end{cases} \tag{9.76}$$

Show that the canonical partition function for a molecule of N segments is

$$Z_N(T,\epsilon,r) = \sum_{h_1=0}^{1}\sum_{h_2=0}^{1}\cdots\sum_{h_N=0}^{1}\prod_{i=1}^{N} e^{\beta\epsilon h_i} q^{(1-h_i)} r^{(h_i-h_{i-1})^2}. \tag{9.77}$$

b. If $F(T,\epsilon,r)$ is the Helmholtz free energy, show that the mean fraction of helical segments is

$$\theta(T) = -\frac{1}{N}\frac{\partial F}{\partial \epsilon} \tag{9.78}$$

while the mean number of junctions between melted and helical runs is

$$J(T) = -\frac{r}{k_BT}\frac{\partial F}{\partial r}. \tag{9.79}$$

c. By considering partial partition functions, Z_N^h and Z_N^m, for a molecule of N segments in which the last segment is in a helical or melted state, respectively, construct recursion relations from which the total partition function, Z_N, can be found.

d. Find the eigenvalues of the corresponding 2×2 matrix and conclude that the free energy per segment of a very long DNA molecule is

$$f(T, \epsilon, r) = -k_B T \ln \tfrac{1}{2} \left[1 + w + \sqrt{(1-w)^2 + 4wr^2} \right] - \epsilon, \tag{9.80}$$

where $w = qe^{-\beta\epsilon}$. Does this result take on the correct value at zero temperature?

e. In the limit that r vanishes show that the molecule undergoes a sharp melting transition at temperature

$$T_m = \frac{\epsilon}{k_B \ln q}. \tag{9.81}$$

Sketch the energy, entropy, and helical fraction $\theta(T)$ as a function of temperature and discuss the character of the transition.

f. If r is small but nonzero, sketch the behavior you expect for $\theta(T)$.

g. (Optional.) Show that when r is small but nonzero the sharp transition is "smeared out" over a temperature range of approximate width

$$\Delta T \approx \frac{4\epsilon r}{k_B \ln^2 q}. \tag{9.82}$$

h. (Optional.) Show that the number of junctions $J(T)$ defined in (b.) varies as Ar^α both at $T = T_m$ and at low temperatures. Find the values of A and α in each case.

9.2 Thermodynamics of the one-dimensional Ising model

The Helmholtz free energy of the one-dimensional, nearest-neighbor Ising magnet is

$$F(T, H) = -N \left\{ J + k_B T \ln \left[\cosh L + \sqrt{\sinh^2 L + e^{-4K}} \right] \right\}, \tag{9.83}$$

where

$$L = \frac{mH}{k_B T} \quad \text{and} \quad K = \frac{J}{k_B T}. \tag{9.84}$$

Use this result to show that

$$\begin{aligned}
E(T, H = 0) &= -JN \tanh K, & (9.85)\\
C_H(T, H = 0) &= k_B N \frac{K^2}{\cosh^2 K}, & (9.86)\\
M(T, H) &= mN \frac{\sinh L}{\sqrt{\sinh^2 L + e^{-4K}}}, & (9.87)\\
\chi_T(T, H = 0) &= N \frac{m^2}{k_B T} e^{2K}. & (9.88)
\end{aligned}$$

9.3 Zero-field one-dimensional Ising model

In class we found the free energy of a one-dimensional, nearest-neighbor Ising magnet with arbitrary magnetic field using the transfer matrix method. This problem finds the free energy in a much simpler way, which unfortunately works only in zero magnetic field.

a. Show that the partition function can be written as

$$Z_N = \sum_{s_1=\pm 1} \sum_{s_2=\pm 1} e^{Ks_1 s_2} \sum_{s_3=\pm 1} e^{Ks_2 s_3} \cdots \sum_{s_{N-1}=\pm 1} e^{Ks_{N-2} s_{N-1}} \sum_{s_N=\pm 1} e^{Ks_{N-1} s_N}. \tag{9.89}$$

b. Show that the last sum is

$$\sum_{s_N=\pm 1} e^{Ks_{N-1} s_N} = 2\cosh K, \tag{9.90}$$

regardless of the value of s_{N-1}.

c. Conclude that

$$Z_N = 2^N \cosh^{N-1} K \tag{9.91}$$

and that the zero-field Helmholtz free energy per site is

$$f(T) = -k_B T \ln\left(2\cosh \frac{J}{k_B T}\right). \tag{9.92}$$

d. Find the zero-field heat capacity, and show that it gives the expected behavior at very low temperatures.

9.4 **Magnetization near the critical point: mean field approximation**

Analyze the Ising model in the mean field approximation to show that the zero-field magnetization near the critical temperature is

$$M(T) = \begin{cases} mNa\left(\dfrac{T_c - T}{T_c}\right)^{1/2} & \text{for } T < T_c \\ 0 & \text{for } T > T_c. \end{cases} \tag{9.93}$$

Be sure to specify the value of the numerical constant a. (Hint: $\tanh x = x - \frac{1}{3}x^3 + \frac{2}{15}x^5 + \cdots$.) (Remark: Experiment shows that the magnetization is not precisely of the character predicted by mean field theory: While it does approach zero like $(T_c - T)^\beta$, the exponent β is not 1/2 — for two-dimensional systems $\beta = 1/8$, while for three-dimensional systems $\beta \approx 0.326$.)

9.5 **Correlation functions for paramagnets**

In a paramagnet (see problem 2.9) the spins are uncorrelated, i.e. the correlation function is

$$G_i(T, H) = 0 \quad \text{for} \quad i \neq 0. \tag{9.94}$$

Use this fact to verify the correlation sum rule

$$\chi_T(T, H) = N\frac{m^2}{k_B T}\sum_i G_i, \tag{9.95}$$

derived in problem 8.11.

9.6 **Lattice gas—Ising magnet**

In class we showed that for a lattice gas

$$\Xi(T, \mu) = \sum_{n_1=0}^{1} \sum_{n_2=0}^{1} \cdots \sum_{n_{\mathcal{N}}=0}^{1} \left(\frac{v_0}{\lambda^3(T)}\right)^N e^{\beta\mu \sum_i n_i + \beta\epsilon \sum_{\text{nn}} n_i n_j}, \tag{9.96}$$

whereas for an Ising magnet

$$Z(T,H) = \sum_{s_1=\pm1} \sum_{s_2=\pm1} \cdots \sum_{s_\mathcal{N}=\pm1} e^{\beta mH \sum_i s_i + \beta J \sum_{\text{nn}} s_i s_j}, \tag{9.97}$$

and we concluded that the lattice gas and Ising magnet were more-or-less equivalent, with chemical potential and magnetic field playing sort of analogous roles. These conclusions are indeed correct, but this problem renders them precise.

a. Show that an up spin is associated with an occupied site, and a down spin with a vacant site, through

$$n_i = \tfrac{1}{2}(s_i + 1). \tag{9.98}$$

b. Write out the sum for $\Xi(T,\mu)$ in terms of the variables s_i, and show that the correspondence

$$\begin{aligned} \epsilon &= 4J && (9.99) \\ \mu &= 2mH - k_B T \ln(v_0/\lambda^3(T)) - 4qJ && (9.100) \end{aligned}$$

(where q is the number of nearest neighbors for each site on the lattice) leads to

$$p(T,\mu)v_0 = mH - \tfrac{3}{2}qJ - f(T,H), \tag{9.101}$$

where $p(T,\mu)$ is the pressure of the gas and $f(T,H)$ is the free energy per spin of the magnet.

c. Interpret equation (9.100) using the phrase "escaping tendency". (Is this a sensible question?)

d. (Hard.) Take derivatives of equation (9.101) to show that

$$\begin{aligned} \rho(T,\mu)v_0 &= \tfrac{1}{2}[1 + M(T,H)/m\mathcal{N}], && (9.102) \\ 4\rho^2\kappa_T(T,\mu)v_0 &= \chi(T,H)/m^2\mathcal{N}, && (9.103) \\ S_{\text{gas}} - k_B N[\ln(v_0/\lambda^3(T)) + \tfrac{3}{2}] &= S_{\text{mag}}, && (9.104) \\ C_V - \tfrac{3}{2}k_B N &= C_M. && (9.105) \end{aligned}$$

9.7 **Estimates concerning exhaustive enumeration**

Consider an Ising model with 6.02×10^{23} sites. How many distinct configurations can this system take on? Estimate the mass of paper and ink required to write out a single character. What mass would be required to write out this number of configurations in decimal notation? Compare your estimate to the mass of the earth.

9.8 **Fluctuations in Monte Carlo simulation**

When the mean energy of a system is determined through Monte Carlo simulation, the result will necessarily have an uncertainty due to the statistical character of the simulation. (The same is true of any other measured quantity.) So if mean energy is plotted as a function of temperature, the data points will not fall on a sharp line but instead within a broad band. Using a fluctuation-susceptibility relation, show that the width of the band depends on its slope. Will steep bands be wide or narrow?

9.9 **The folded array representation**

Implement the folded array representation of a triangular lattice subject to skew-periodic boundary conditions. Clue: The piece of lattice under study will be a parallelogram.

9.10 **Monte Carlo project**

Perform a Monte Carlo simulation on the Ising model. The precise form and direction of the simulation is up to you: here are some suggestions that you are free to use, combine, extend, or ignore.

a. Draw movies showing the spin configuration of a two-dimensional Ising model as the simulation proceeds. Discuss the qualitative character of the model at high temperatures, low temperatures, and near the critical temperature (which is known, from Onsager's exact solution, to be $k_BT_c/J = -2/\ln(\sqrt{2}-1)$).

b. Simulate the one-dimensional Ising model and compare your results to the analytic solution obtained in class. Consider using the BKL algorithm[5] at low temperatures.

c. Simulate the DNA denaturation model of problem 9.1, and compare your results to the analytic results of that problem. You will need to modify the Metropolis algorithm.

d. Simulate a two- or three-dimensional Ising ferromagnet at zero field, using an initial configuration of all spins up. Monitor the magnetization for a number of temperatures ranging from $k_BT \approx 5J$ down to $k_BT = 0$. Record both the equilibrium magnetization and the number of steps required to reach equilibrium, and plot these as a function of temperature. Can you locate the critical temperature?

e. Monitor both the mean energy (or magnetization) and the fluctuations in energy (or magnetization). Use a fluctuation-susceptibility relation to find the heat capacity (or susceptibility). In particular, show how a simulation at zero magnetic field can still give information about the magnetic susceptibility.

f. Verify the relation discussed in problem 9.8.

g. Implement the Wolff algorithm[6] for improved simulation near the critical point.

h. Use finite size scaling[7] to obtain accurate results near the critical point.

i. Compare the BKL and Wolff algorithms at low temperature.

j. Find the correlation function

$$G_i = \langle s_0 s_i \rangle - \langle s_0 \rangle^2 \tag{9.106}$$

for a few values of T and H. How does it behave as the critical point is approached?

k. (Very ambitious.) Verify the correlation-susceptibility relation (9.46).

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[5] A.B. Bortz, J.L. Lebowitz, and M.H. Kalos, *J. Comput. Phys.*, **17** (1975) 10–18.

[6] U. Wolff, *Phys. Rev. Lett.* **62** (1989) 361–364. J.-S. Wang and R.H. Swendsen, *Physica* A **167** (1990) 565–579.

[7] H. Gould and J. Tobochnik, *An Introduction to Computer Simulation Methods: Applications to Physical Systems*, part I (Addison-Wesley, Reading, Mass., 1988) sections 12.4 and 16.5

Appendix A

Series and Integrals

$$\frac{1}{1-x} = 1 + x + x^2 + x^3 + x^4 + \cdots \quad \text{for } |x| < 1 \quad \text{(the “geometric series”)} \tag{A.1}$$

$$e^x = 1 + x + \frac{1}{2!}x^2 + \frac{1}{3!}x^3 + \frac{1}{4!}x^4 + \cdots \tag{A.2}$$

$$\ln(1+x) = x - \frac{1}{2}x^2 + \frac{1}{3}x^3 - \frac{1}{4}x^4 + \cdots \quad \text{for } |x| < 1 \tag{A.3}$$

$$\int_{-\infty}^{+\infty} e^{-ax^2+bx}\, dx = \sqrt{\frac{\pi}{a}} e^{b^2/4a} \quad \text{for } a > 0 \quad \text{(the “Gaussian integral”)} \tag{A.4}$$

Appendix B

Evaluating the Gaussian Integral

The integral

$$\int_{-\infty}^{+\infty} e^{-x^2}\, dx, \tag{B.1}$$

called the Gaussian integral, does not fall to any of the methods of attack that you learned in elementary calculus. But it can be evaluated quite simply using the following trick.

Define the value of the integral to be A. Then

$$A^2 = \int_{-\infty}^{+\infty} e^{-x^2}\, dx \int_{-\infty}^{+\infty} e^{-y^2}\, dy = \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} dx\, dy\, e^{-(x^2+y^2)}. \tag{B.2}$$

At the last step we have written A^2 as a two-variable integral over the entire plane. This seems perverse, because most of the times we work hard to reduce two-dimensional integrals to one-dimensional integrals, whereas here we are going in reverse. But look at the integrand again. When regarded as an integral on the plane, it is clear that we can regard $x^2 + y^2$ as just r^2, and this suggests we should convert the integral from Cartesian (x, y) to polar (r, θ) coordinates:

$$A^2 = \int_0^{\infty} dr \int_0^{2\pi} r\, d\theta\, e^{-r^2} = 2\pi \int_0^{\infty} re^{-r^2}\, dr. \tag{B.3}$$

The last integral immediately suggests the substitution $u = r^2$, giving

$$A^2 = \pi \int_0^{\infty} e^{-u}\, du = -\pi\; e^{-u}\big|_0^{\infty} = \pi. \tag{B.4}$$

We conclude that

$$\int_{-\infty}^{+\infty} e^{-x^2}\, dx = \sqrt{\pi}. \tag{B.5}$$

B.1 (I) **Problem: Another integral**

Show that

$$\int_0^{\infty} \frac{e^{-x}}{\sqrt{x}}\, dx = \sqrt{\pi}. \tag{B.6}$$

(Clue: Use the substitution $y = \sqrt{x}$.)

Appendix C

Clinic on the Gamma Function

The gamma function $\Gamma(s)$ is defined, for $s > 0$, by

$$\Gamma(s) = \int_0^\infty x^{s-1} e^{-x}\, dx. \tag{C.1}$$

Upon seeing any integral, your first thought is to evaluate it. Stay calm…first make sure that the integral exists. A quick check shows that the integral above converges when $s > 0$.

There is no simple formula for the gamma function for arbitrary s. But for $s = 1$,

$$\Gamma(1) = \int_0^\infty e^{-x}\, dx = -e^{-x}\Big|_0^\infty = 1. \tag{C.2}$$

For $s > 1$ we may integrate by parts,

$$\int_0^\infty x^{s-1} e^{-x}\, dx = -x^{s-1} e^{-x}\Big|_0^\infty + (s-1)\int_0^\infty x^{s-2} e^{-x}\, dx, \tag{C.3}$$

giving

$$\Gamma(s) = (s-1)\Gamma(s-1) \quad \text{for } s > 1. \tag{C.4}$$

Apply equation (C.4) repeatedly for n a positive integer,

$$\Gamma(n) = (n-1)\Gamma(n-1) = (n-1)(n-2)\Gamma(n-2) = (n-1)(n-2)\cdots 2\cdot 1\cdot \Gamma(1) = (n-1)!, \tag{C.5}$$

to find a relation between the gamma function and the factorial function. Thus the gamma function generalizes the factorial function to non-integer values, and can be used to define the factorial function through

$$x! = \Gamma(x+1) \quad \text{for any } x > -1. \tag{C.6}$$

In particular,

$$0! = \Gamma(1) = 1. \tag{C.7}$$

(It is a deep and non-obvious result that the gamma function is in fact the simplest generalization of the factorial function.)

The gamma function can be simplified for half-integral arguments. For example

$$\Gamma(\tfrac{1}{2}) = \int_0^\infty x^{-1/2} e^{-x}\, dx = \int_0^\infty y^{-1} e^{-y^2} (2y\, dy) = \int_{-\infty}^\infty e^{-y^2}\, dy = \sqrt{\pi} \tag{C.8}$$

where we used the substitution $y = \sqrt{x}$. Thus

$$\Gamma(\tfrac{3}{2}) = \tfrac{1}{2}\Gamma(\tfrac{1}{2}) = \frac{\sqrt{\pi}}{2} = (\tfrac{1}{2})!, \tag{C.9}$$

$$\Gamma(\tfrac{5}{2}) = \tfrac{3}{2}\Gamma(\tfrac{3}{2}) = \tfrac{3}{4}\sqrt{\pi}, \tag{C.10}$$

and so forth.

Appendix D

Volume of a Sphere in d Dimensions

I will call the volume of a d-dimensional sphere, as a function of radius, $V_d(r)$. You know, of course, that

$$V_2(r) = \pi r^2 \tag{D.1}$$

(two-dimensional volume is commonly called "area") and that

$$V_3(r) = \tfrac{4}{3}\pi r^3. \tag{D.2}$$

But what is the formula for arbitrary d? There are a number of ways to find it. I will use induction on dimensionality d. That is, I will use the formula for $d = 2$ to find the formula for $d = 3$, the formula for $d = 3$ to find the formula for $d = 4$, and in general use the formula for d to find the formula for $d + 1$. This is not the most rigorous formal method to derive the formula, but it is very appealing and has much to recommend it.

To illustrate the process, I will begin with a well-known and easily visualized stage, namely deriving $V_3(r)$ from $V_2(r)$. Think of a 3-dimensional sphere (of radius r) as a stack of pancakes of various radii, but each with infinitesimal thickness dz. The pancake on the very bottom of the stack ($z = -r$) has zero radius. The one above it is slightly broader. They get broader and broader until we get to the middle of the stack ($z = 0$), where the pancake has radius r. The pancakes stacked still higher become smaller and smaller, until they vanish again at the top of the stack ($z = +r$). Because the equation for the sphere is

$$x^2 + y^2 + z^2 = r^2, \tag{D.3}$$

the radius of the pancake at height z_0 is

$$\sqrt{r^2 - z_0^2}. \tag{D.4}$$

This whole process shows that

$$V_3(r) = \int_{-r}^{+r} dz\, V_2(\sqrt{r^2 - z^2}). \tag{D.5}$$

It is easy to check this integral against the known result for $V_3(r)$:

$$\begin{aligned} V_3(r) &= \int_{-r}^{+r} dz\, \pi(r^2 - z^2) && \text{(D.6)} \\ &= \pi \left[r^2 z - \tfrac{1}{3} z^3\right]_{-r}^{+r} && \text{(D.7)} \\ &= \pi \left[2r^3 - \tfrac{2}{3} r^3\right] && \text{(D.8)} \\ &= \tfrac{4}{3}\pi r^3. && \text{(D.9)} \end{aligned}$$

So we haven't gone wrong yet.

Now, how to derive $V_4(r)$ from $V_3(r)$? This requires a more vivid imagination. Last time we started with a two-dimensional disk of radius r_0 in (x, y) space and thickened it a bit into the third dimension (z) to form a pancake of three-dimensional volume $dz\, V_2(r_0)$. Stacking an infinite number of such pancakes in the z direction, from $z = -r$ to $z = +r$, gave us a three-dimensional sphere. Now we begin with a three-dimensional sphere of radius r_0 in (w, x, y) space and thicken it a bit into the fourth dimension (z) to form a thin four-dimensional pancake of four-dimensional volume $dz\, V_3(r_0)$. Stacking an infinite number of such pancakes in the z direction, from $z = -r$ to $z = +r$, gives a four-dimensional sphere. Because the equation for the four-sphere is

$$w^2 + x^2 + y^2 + z^2 = r^2, \tag{D.10}$$

the radius of the three-dimensional sphere at height z_0 is

$$\sqrt{r^2 - z_0^2}, \tag{D.11}$$

and the volume of the four-sphere is

$$V_4(r) = \int_{-r}^{+r} dz\, V_3(\sqrt{r^2 - z^2}). \tag{D.12}$$

In general, the volume of a $(d+1)$-sphere is

$$V_{d+1}(r) = \int_{-r}^{+r} dz\, V_d(\sqrt{r^2 - z^2}). \tag{D.13}$$

If we guess that the formula for $V_d(r)$ takes the form

$$V_d(r) = C_d r^d \tag{D.14}$$

(which is certainly true for two and three dimensions, and which is reasonable from dimensional analysis), then

$$\begin{aligned} V_{d+1}(r) &= \int_{-r}^{+r} dz\, C_d (r^2 - z^2)^{d/2} && \text{(D.15)} \\ &= \int_{-1}^{+1} r\, du\, C_d (r^2 - r^2 u^2)^{d/2} && \text{(D.16)} \\ &= r^{d+1} C_d \int_{-1}^{+1} du\, (1 - u^2)^{d/2}. && \text{(D.17)} \end{aligned}$$

This proves our guess and gives us a recursive formula for C_d:

$$C_{d+1} = C_d \int_{-1}^{+1} du\,(1-u^2)^{d/2}. \tag{D.18}$$

The problem below shows how to build this recursive chain up from $C_2 = \pi$ to

$$C_d = \frac{\pi^{d/2}}{\Gamma(\frac{d}{2}+1)} = \frac{\pi^{d/2}}{(d/2)!}. \tag{D.19}$$

Thus the volume of a d-dimensional sphere of radius r is

$$V_d(r) = \frac{\pi^{d/2}}{(d/2)!} r^d. \tag{D.20}$$

D.1 (I) **Problem: Volume of a d-dimensional sphere**

Before attempting this problem, you should read the material concerning beta functions in an applied mathematics textbook, such as George Arfken's *Mathematical Methods for Physicists* or Mary Boas's *Mathematical Methods in the Physical Sciences.* (Or in the Digital Library of Mathematical Functions.)

a. Show that

$$\int_{-1}^{+1} (1-u^2)^{d/2}\,du = B(\tfrac{1}{2}, \tfrac{d}{2}+1). \tag{D.21}$$

b. Use

$$B(p,q) = \frac{\Gamma(p)\Gamma(q)}{\Gamma(p+q)} \tag{D.22}$$

and $C_2 = \pi$ to conclude that

$$C_d = \frac{\pi^{d/2}}{\Gamma(\frac{d}{2}+1)}. \tag{D.23}$$

D.2 (I) **Problem: Volume of a d-dimensional ellipse**

Show that the volume of the d-dimensional ellipse described by the equation

$$\left(\frac{x_1}{a_1}\right)^2 + \left(\frac{x_2}{a_2}\right)^2 + \left(\frac{x_3}{a_3}\right)^2 + \cdots + \left(\frac{x_d}{a_d}\right)^2 = 1 \tag{D.24}$$

is

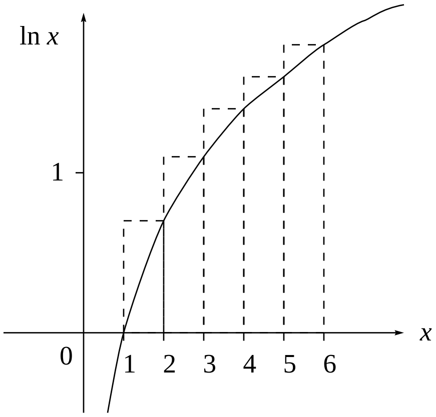
$$V_d(r) = \frac{\pi^{d/2}}{(d/2)!} a_1 a_2 a_3 \cdots a_d. \tag{D.25}$$

Appendix E

Stirling's Approximation

The Stirling formula is an approximation for $n!$ that is good at large values of n.

$$\begin{aligned} n! &= 1 \cdot 2 \cdot 3 \cdots (n-1) \cdot n && \text{(E.1)} \\ \ln(n!) &= \underbrace{\ln 1}_{0} + \ln 2 + \ln 3 + \cdots + \ln(n-1) + \ln(n) && \text{(E.2)} \end{aligned}$$



Note that the function $\ln x$ is nearly flat for large values of x. For example, $\ln 10^{23}$ is about equal to 23.

From the figure

$$\ln(6!) = \text{area under the staircase} > \int_1^6 \ln x \, dx, \tag{E.3}$$

and in general

$$\ln(n!) > \int_1^n \ln x \, dx = \Big[x \ln x - x \Big]_1^n = n \ln n - n + 1. \tag{E.4}$$

For large values of n, where the $\ln n$ function is nearly flat, the two expressions above become quite close. Also, the 1 becomes negligible. We conclude that

$$\ln(n!) \approx n \ln n - n \qquad \text{for } n \gg 1. \tag{E.5}$$

This is Stirling's formula. For corrections to the formula, see M. Boas, *Mathematical Methods in the Physical Sciences*, sections 9-10 and 9-11.

You know that

$$A^n \tag{E.6}$$

increases rapidly with n for positive A, but

$$n! \approx \left(\frac{n}{e}\right)^n \tag{E.7}$$

increases a bit more rapidly still.

E.1 Problem: An upper bound for the factorial function

Stirling's approximation gives a rigorous lower bound for $n!$.

a. Use the general ideas presented in the derivation of that lower bound to show that

$$\int_1^n \ln(x+1)\,dx > \ln n!. \tag{E.8}$$

b. Conclude that

$$(n+1)\ln(n+1) - n + 1 - 2\ln 2 > \ln n! > n \ln n - n + 1. \tag{E.9}$$

Appendix F

The Euler-MacLaurin Formula and Asymptotic Series

You know that a sum can be approximated by an integral. How accurate is that approximation? The *Euler-MacLaurin formula* gives the corrections.

$$\begin{aligned}\sum_{k=0}^{n-1} f(k) \quad &\approx \quad \int_0^n f(x)\,dx \\ &-\frac{1}{2}[f(n)-f(0)]+\frac{1}{12}[f'(n)-f'(0)]-\frac{1}{720}[f'''(n)-f'''(0)]+\frac{1}{30\,240}[f^{(\mathrm{v})}(n)-f^{(\mathrm{v})}(0)]-\frac{1}{1\,209\,600}[f^{(\mathrm{vii})}(n)-\end{aligned}$$

This series is asymptotic. If the series is truncated at any point, it can give a highly accurate approximation. But the series may be either convergent or divergent, so adding additional terms to the truncated series might give rise to a poorer approximation. The Stirling approximation is a truncation of an asymptotic series.

References

C.M. Bender and S.A. Orszag, *Advanced Mathematical Methods for Scientists and Engineers*, (McGraw-Hill, New York, 1978).

M. Abramowitz and I. Stegum, *Handbook of Mathematical Functions*, (National Bureau of Standards, Washington, D.C., 1964).

Appendix G

Ramblings on the Riemann Zeta Function

The function

$$\zeta(s) = \sum_{n=1}^{\infty} \frac{1}{n^s} \quad \text{for} \quad s > 1,$$

called the Riemann zeta function, has applications to number theory, statistical mechanics, and quantal chaos.

History

From Simmons:

> No great mind of the past has exerted a deeper influence on the mathematics of the twentieth century than Bernhard Riemann (1826–1866), the son of a poor country minister in northern Germany. He studied the works of Euler and Legendre while he was still in secondary school, and it is said that he mastered Legendre's treatise on the theory of numbers in less than a week. But he was shy and modest, with little awareness of his own extraordinary abilities, so at the age of nineteen he went to the University of Göttingen with the aim of pleasing his father by studying theology and becoming a minister himself.

Instead he became a mathematician. He made contributions to the theory of complex variables ("Cauchy-Riemann equations", "Riemann sheet", "Riemann sphere"), to Fourier series, to analysis ("Riemann integral"), to hypergeometric functions, to convergence of infinite sums ("Riemann rearrangement theorem"), to geometry ("Riemannian curved space"), and to classical mechanics, the theory of fields and other areas of physics. In his thirties he became interested in the prime number theorem.

The first few prime numbers are 2, 3, 5, 7, 11, 13, 17, 19, 23, 29, 31, 37, 41, 43,…. It is clear that the primes are distributed among all the positive integers in a rather irregular way; for as we move out, they seem to occur less and less frequently, and yet there are many adjoining pairs separated by a single even number ["twin primes"]. … Many attempts have been made to find simple formulas for the nth prime and for the exact number of primes among the first n positive integers. All such efforts have failed, and real progress was achieved only when mathematicians started instead to look for information about the average distribution of the primes among the positive integers. It is customary to denote by $\pi(x)$ the number of primes less than or equal to a positive number x. Thus $\pi(1) = 0$, $\pi(2) = 1$, $\pi(3) = 2$, $\pi(\pi) = 2$, $\pi(4) = 2$, and so on. In his early youth Gauss studied $\pi(x)$ empirically, with the aim of finding a simple function that seems to approximate it with a small relative error for large x. On the basis of his observations he conjectured (perhaps at the age of fourteen or fifteen) that $x/\log x$ is a good approximating function, in the sense that

$$\lim_{x\to\infty} \frac{\pi(x)}{x/\log x} = 1.$$

This statement is the famous *prime number theorem*; and as far as anyone knows, Gauss was never able to support his guess with even a fragment of proof.

Chebyshev, unaware of Gauss's conjecture, was the first mathematician to establish any firm conclusions about this question. In 1848 and 1850 he proved that

$$0.9213\ldots < \frac{\pi(x)}{x/\log x} < 1.1055\ldots$$

for all sufficiently large x, and also that if the limit exists, then its value must be 1. (The numbers in the inequality are $A = \log 2^{1/2}3^{1/3}5^{1/5}30^{-1/30}$ on the left, and $\frac{6}{5}A$ on the right.) …

In 1859 Riemann published his only work on the theory of numbers, a brief but exceedingly profound paper of less than 10 pages devoted to the prime number theorem. … His starting point was a remarkable identity discovered by Euler over a century earlier: if s is a real number greater than 1, then

$$\sum_{n=1}^{\infty} \frac{1}{n^s} = \prod_p \frac{1}{1-(1/p^s)},$$

where the expression on the right denotes the product of the numbers $(1-p^{-s})^{-1}$ for all primes p. To understand how this identity arises, we note that $1/(1-x) = 1 + x + x^2 + \cdots$ for $|x| < 1$, so for each p we have

$$\frac{1}{1-(1/p^s)} = 1 + \frac{1}{p^s} + \frac{1}{p^{2s}} + \cdots.$$

On multiplying these series for all primes p and recalling that each integer $n > 1$ is uniquely expressible as a product of powers of different primes, we see that

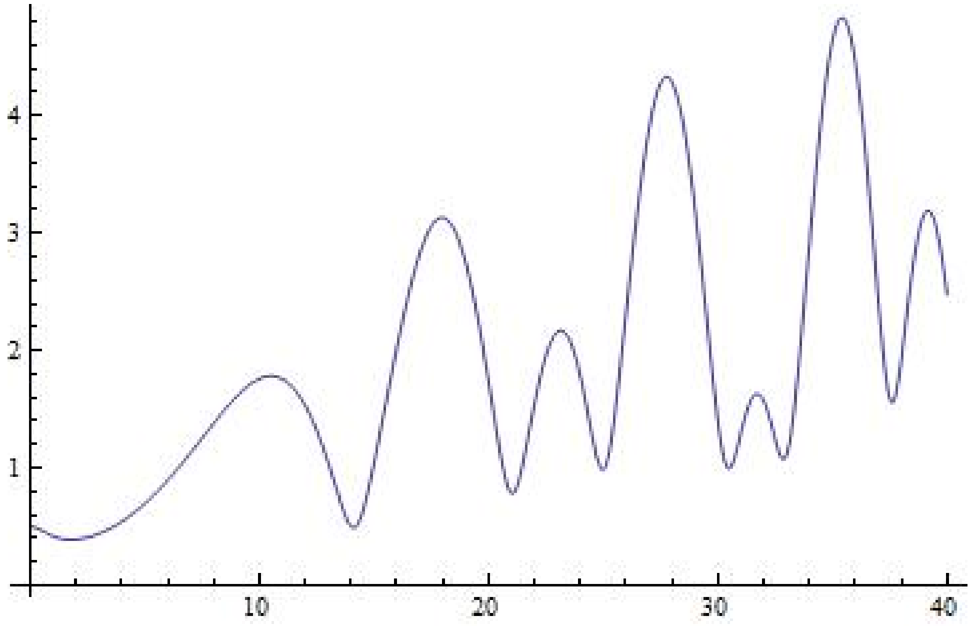
$$\begin{aligned} \prod_p \frac{1}{1-(1/p^s)} &= \prod_p \left(1 + \frac{1}{p^s} + \frac{1}{p^{2s}} + \cdots\right) \\ &= 1 + \frac{1}{2^s} + \frac{1}{3^s} + \cdots + \frac{1}{n^s} + \cdots \end{aligned}$$

$$= \sum_{n=1}^{\infty} \frac{1}{n^s},$$

> which is the desired identity. The sum of this series is evidently a function of the real variable $s > 1$, and the identity establishes a connection between the behavior of this function and properties of the primes. Euler himself exploited this connection in several ways, but Riemann perceived that access to the deeper features of the distribution of primes can only be gained by allowing s to be a complex variable. … In his paper he proved several important properties of this function, and in a sovereign way simply stated a number of others without proof. During the century since his death, many of the finest mathematicians in the world have exerted their strongest efforts and created rich new branches of analysis in attempts to prove these statements. The first success was achieved in 1893 by J. Hadamard, and with one exception every statement has since been settled in the sense Riemann expected. (Hadamard's work led him to his 1896 proof of the prime number theorem.) The one exception is the famous Riemann hypothesis: that all the zeros of $\zeta(s)$ in the strip $0 \leq \Re e\{s\} \leq 1$ lie on the central line $\Re e\{s\} = \frac{1}{2}$. It stands today as the most important unsolved problem in mathematics, and is probably the most difficult problem that the mind of man has ever conceived. In a fragmentary note found among his posthumous papers, Riemann wrote that these theorems "follow from an expression for the function $\zeta(s)$ which I have not yet simplified enough to publish". …
>
> At the age of thirty-nine Riemann died of tuberculosis in Italy, on the last of several trips he undertook in order to avoid the cold, wet climate of northern Germany.

General character of the zeta function

It is easy to see that $\zeta(s)$ diverges at $s = 1$ and that it decreases monotonically to 1 as s increases from 1. As the historical note suggests, its behavior for complex values of s is much more elaborate.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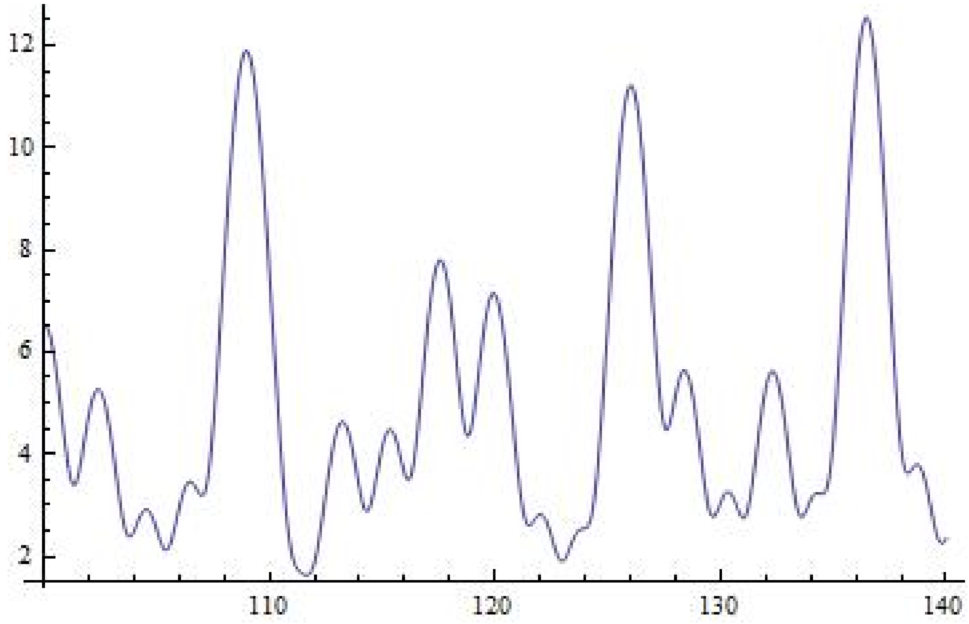
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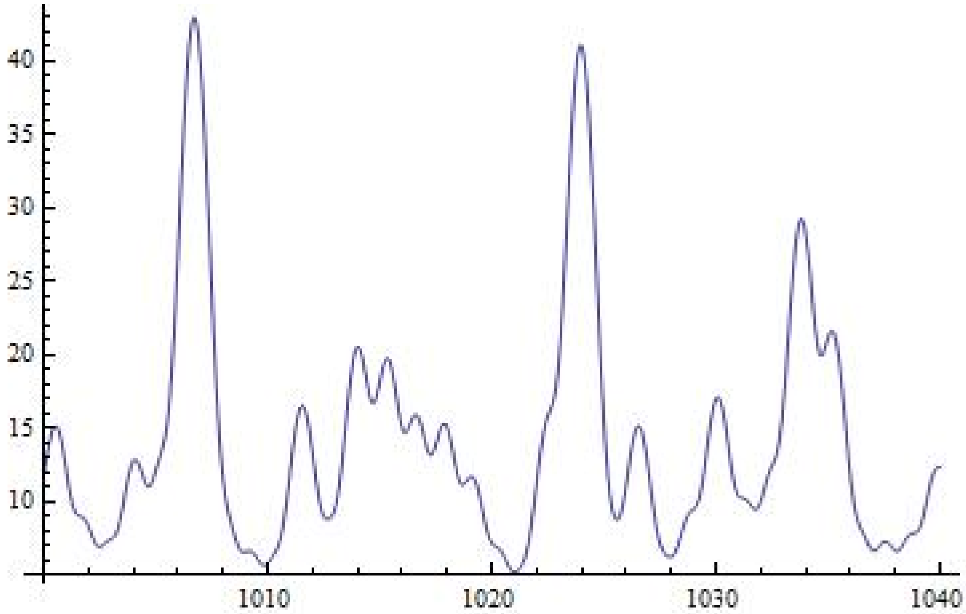


These graphs were made using *Mathematica* commands like

```
Plot[Abs[Zeta[I*y]], {y, 100, 140}].
```

It's fun to try them with other values of the range.

Exact values for the zeta function

The zeta function can be evaluated exactly for positive even integer arguments:

$$\zeta(m) = \frac{(2\pi)^m |B_m|}{2m!} \quad \text{for} \quad m = 2, 4, 6, \ldots.$$

Here the B_m are the Bernoulli numbers, defined through

$$\frac{x}{e^x - 1} = \sum_{m=0}^{\infty} \frac{B_m}{m!} x^m.$$

The first few Bernoulli numbers are

$$B_0 = 1, \quad B_1 = -\tfrac{1}{2}, \quad B_2 = \tfrac{1}{6}, \quad B_4 = -\tfrac{1}{30}, \quad B_6 = \tfrac{1}{42}, \quad B_8 = -\tfrac{1}{30}, \quad B_{10} = \tfrac{5}{66}, \quad B_{12} = -\tfrac{691}{2730}$$

whence

$$\zeta(2) = \frac{\pi^2}{6}, \quad \zeta(4) = \frac{\pi^4}{90}, \quad \zeta(6) = \frac{\pi^6}{945}, \quad \zeta(8) = \frac{\pi^8}{9450}.$$

The zeta function near $s = 1$

The zeta function diverges with a simple pole at $s = 1$. In the vicinity of the divergence it is approximately equal to

$$\zeta(s) \approx C + \frac{1}{s-1}$$

where C is Euler's constant, 0.5772.... (The rest of this section is stolen from Bender and Orszag.)

When s is near 1, the defining series

$$\zeta(s) = \sum_{n=1}^{\infty} \frac{1}{n^s}$$

is *very* slowly converging. About 10^{20} terms are needed to compute $\zeta(1.1)$ accurate to 1 percent!

Fortunately, there is an expression for the difference between $\zeta(s)$ and the Nth partial sum:

$$\zeta(s) = \sum_{n=0}^{N} \frac{1}{s^n} + \frac{1}{\Gamma(s)} \int_0^{\infty} \frac{u^{s-1} e^{-Nu}}{e^u - 1} \, du.$$

The integral cannot be evaluated analytically but it can be expanded in an asymptotic series, giving

$$\zeta(s) \approx \sum_{n=0}^{N} \frac{1}{s^n} + \frac{1}{(s-1)N^{s-1}} - \frac{1}{2N^s} + \frac{B_2 s}{N^{s+1}} + \frac{B_4 s(s+1)(s+2)}{2N^{s+3}} + \cdots$$

where the B_m are again the Bernoulli numbers.

Truncating this formula can give extremely accurate results. For example, using $N = 9$, only 38 terms of the series are needed to find $\zeta(1.1)$ accurate to 26 decimal places.

References

G.F. Simmons, *Differential Equations with Applications and Historical Notes*, (McGraw-Hill, New York, 1972) pp. 210–211, 214–218.

C.M. Bender and S.A. Orszag, *Advanced Mathematical Methods for Scientists and Engineers*, (McGraw-Hill, New York, 1978) p. 379.

Jahnke, Emde, and Lösch, *Tables of Higher Functions*, 6th ed. (McGraw-Hill, New York, 1960) chap. IV. (Note particularly the beautiful relief plot of $|\zeta(s)|$ for complex values of s.)

J. Spanier and K. Oldham, *An Atlas of Functions*, (Hemisphere Publishing, Washington, D.C., 1987) chap. 3. (Presents an algorithm purporting to find $\zeta(s)$ accurately for any real s.)

M. Abramowitz and I. Stegum, *Handbook of Mathematical Functions*, (National Bureau of Standards, Washington, D.C., 1964) chap. 23.

M.C. Gutzwiller, *Chaos in Classical and Quantum Mechanics*, (Springer-Verlag, New York, 1990) section 17.9.

Appendix H

Tutorial on Matrix Diagonalization

You know from as far back as your introductory mechanics course that some problems are difficult given one choice of coordinate axes and easy or even trivial given another. (For example, the famous "monkey and hunter" problem is difficult using a horizontal axis, but easy using an axis stretching from the hunter to the monkey.) The mathematical field of linear algebra is devoted, in large part, to systematic techniques for finding coordinate systems that make problems easy. This tutorial introduces the most valuable of these techniques. It assumes that you are familiar with matrix multiplication and with the ideas of the inverse, the transpose, and the determinant of a square matrix. It is also useful to have a nodding acquaintance with the inertia tensor.

This presentation is intentionally non-rigorous. A rigorous, formal treatment of matrix diagonalization can be found in any linear algebra textbook,[1] and there is no need to duplicate that function here. What is provided here instead is a heuristic picture of what's going on in matrix diagonalization, how it works, and why anyone would want to do such a thing anyway. Thus this presentation complements, rather than replaces, the logically impeccable ("bulletproof") arguments of the mathematics texts.

Essential problems in this tutorial are marked by asterisks (*).

Warning: This tutorial is still in **draft** form.

H.1 What's in a name?

There is a difference between an entity and its name. For example, a tree is made of wood, whereas its name "tree" made of ink. One way to see this is to note that in German, the name for a tree is "Baum", so the name changes upon translation, but the tree itself does not change. (Throughout this tutorial, the term "translate" is used as in "translate from one language to another" rather than as in "translate by moving in a straight line".)

The same holds for mathematical entities. Suppose a length is represented by the number “2” because it is two feet long. Then the same length is represented by the number “24” because it is twenty-four inches long. The same length is represented by two different numbers, just as the same tree has two different names. The representation of a length as a number depends not only upon the length, but also upon the coordinate system used to measure the length.

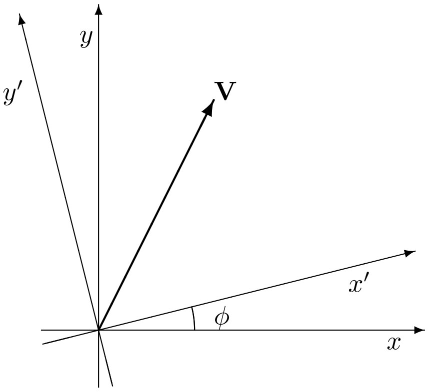
H.2 Vectors in two dimensions

One way of describing a two-dimensional vector **V** is by giving its x and y components in the form of a 2×1 column matrix

$$\begin{pmatrix} V_x \\ V_y \end{pmatrix}. \tag{H.1}$$

Indeed it is sometimes said that the vector **V** is *equal* to the column matrix (H.1). This is not precisely correct—it is better to say that the vector is *described by* the column matrix or *represented by* the column matrix or that its *name* is the column matrix. This is because if you describe the vector using a different set of coordinate axes you will come up with a different column matrix to describe the same vector. For example, in the situation shown below the descriptions in terms of the two different coordinate systems are related through the matrix equation

$$\begin{pmatrix} V_{x'} \\ V_{y'} \end{pmatrix} = \begin{pmatrix} \cos\phi & \sin\phi \\ -\sin\phi & \cos\phi \end{pmatrix} \begin{pmatrix} V_x \\ V_y \end{pmatrix}. \tag{H.2}$$



The 2×2 matrix above is called the “rotation matrix” and is usually denoted by $\mathsf{R}(\phi)$:

$$\mathsf{R}(\phi) \equiv \begin{pmatrix} \cos\phi & \sin\phi \\ -\sin\phi & \cos\phi \end{pmatrix}. \tag{H.3}$$

One interesting property of the rotation matrix is that it is always invertible, and that its inverse is equal to its transpose. Such matrices are called *orthogonal*.[1] You could prove this by working a matrix multiplication, but it is easier to simply realize that the inverse of a rotation by ϕ is simply a rotation by $-\phi$, and noting that

$$\mathsf{R}^{-1}(\phi) = \mathsf{R}(-\phi) = \mathsf{R}^{\dagger}(\phi). \tag{H.4}$$

(The dagger represents matrix transposition.)

There are, of course, an infinite number of column matrix representations for any vector, corresponding to the infinite number of coordinate axis rotations with ϕ from 0 to 2π. But one of these representations is special: It is the one in which the x'-axis lines up with the vector, so the column matrix representation is just

$$\begin{pmatrix} V \\ 0 \end{pmatrix}, \tag{H.5}$$

where $V = |\mathbf{V}| = \sqrt{V_x^2 + V_y^2}$ is the magnitude of the vector. This set of coordinates is the preferred (or "canonical") set for dealing with this vector: one of the two components is zero, the easiest number to deal with, and the other component is a physically important number. You might wonder how I can claim that this representation has full information about the vector: The initial representation (H.1) contains two independent numbers, whereas the preferred representation (H.5) contains only one. The answer is that the preferred representation contains one number (the magnitude of the vector) explicitly while another number (the polar angle of the vector relative to the initial x-axis) is contained implicitly in the rotation needed to produce the preferred coordinate system.

H.1 Problem: Right angle rotations

Verify equation (H.2) in the special cases $\phi = 90°$, $\phi = 180°$, $\phi = 270°$, and $\phi = 360°$.

H.2 Problem: The rotation matrix

a. Derive equation (H.2) through purely geometrical arguments.

b. Express $\hat{\mathbf{i}}'$ and $\hat{\mathbf{j}}'$, the unit vectors of the (x', y') coordinate system, as linear combinations of $\hat{\mathbf{i}}$ and $\hat{\mathbf{j}}$. Then use

$$V_{x'} = \mathbf{V}\cdot\hat{\mathbf{i}}' \quad \text{and} \quad V_{y'} = \mathbf{V}\cdot\hat{\mathbf{j}}' \tag{H.6}$$

to derive equation (H.2).

c. Which derivation do you find easier?

H.3 Problem: Rotation to the preferred coordinate system*

In the preferred coordinate system, $V_{y'} = 0$. Use this requirement to show that the preferred system is rotated from the initial system by an angle ϕ with

$$\tan\phi = \frac{V_y}{V_x}. \tag{H.7}$$

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[1] Although all rotation matrices are orthogonal, there are orthogonal matrices that are not rotation matrices: see problem H.4.

For any value of V_y/V_x, there are *two* angles that satisfy this equation. What is the representation of **V** in each of these two coordinate systems?

H.4 **Problem: A non-rotation orthogonal transformation**
In one coordinate system the y-axis is vertical and the x-axis points to the right. In another the y'-axis is vertical and the x'-axis points to the left. Find the matrix that translates vector coordinates from one system to the other. Show that this matrix is orthogonal but not a rotation matrix.

H.5 **Problem: Other changes of coordinate***
Suppose vertical distances (distances in the y direction) are measured in feet while horizontal distances (distances in the x direction) are measured in miles. (This system is not perverse. It is used in nearly all American road maps.) Find the matrix that changes the representation of a vector in this coordinate system to the representation of a vector in a system where all distances are measured in feet. Find the matrix that translates back. Are these matrices orthogonal?

H.6 **Problem: Other special representations**
At equation (H.5) we mentioned one "special" (or "canonical") representation of a vector. There are three others, namely

$$\begin{pmatrix} 0 \\ -V \end{pmatrix}, \quad \begin{pmatrix} -V \\ 0 \end{pmatrix}, \quad \begin{pmatrix} 0 \\ V \end{pmatrix}. \tag{H.8}$$

If coordinate-system rotation angle ϕ brings the vector representation into the form (H.5), then what rotation angle will result in these three representations?

H.3 Tensors in two dimensions

A tensor, like a vector, is a geometrical entity that may be described ("named") through components, but a d-dimensional tensor requires d^2 rather than d components. Tensors are less familiar and more difficult to visualize than vectors, but they are neither less important nor "less physical". We will introduce tensors through the concrete example of the inertia tensor of classical mechanics (see, for example, reference [2]), but the results we present will be perfectly general.

Just as the two components of a two-dimensional vector are most easily kept track of through a 2×1 matrix, so the four components of two-dimensional tensor are most conveniently written in the form of a 2×2 matrix. For example, the inertia tensor **T** of a point particle with mass m located[2] at (x, y) has components

$$\mathsf{T} = \begin{pmatrix} my^2 & -mxy \\ -mxy & mx^2 \end{pmatrix}. \tag{H.9}$$

(Note the distinction between the tensor **T** and its matrix of components, its "name", T.) As with vector components, the tensor components are different in different coordinate systems, although the tensor itself

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[2] Or, to be absolutely precise, the particle located at the point represented by the vector with components (x, y).

does not change. For example, in the primed coordinate system of the figure on page 229, the tensor components are of course

$$\mathsf{T}' = \begin{pmatrix} my'^2 & -mx'y' \\ -mx'y' & mx'^2 \end{pmatrix}. \tag{H.10}$$

A little calculation shows that the components of the inertia tensor in two different coordinate systems are related through

$$\mathsf{T}' = \mathsf{R}(\phi)\mathsf{T}\mathsf{R}^{-1}(\phi). \tag{H.11}$$

This relation holds for *any* tensor, not just the inertia tensor. (In fact, one way to define "tensor" is as an entity with four components that satisfy the above relation under rotation.) If the matrix representing a tensor is symmetric (i.e. the matrix is equal to its transpose) in one coordinate system, then it is symmetric in all coordinate systems (see problem H.7). Therefore the symmetry is a property of the tensor, not of its matrix representation, and we may speak of "a symmetric tensor" rather than just "a tensor represented by a symmetric matrix".

As with vectors, one of the many matrix representations of a given tensor is considered special (or "canonical"): It is the one in which the lower left component is zero. Furthermore if the tensor is symmetric (as the inertia tensor is) then in this preferred coordinate system the upper right component will be zero also, so the matrix will be all zeros except for the diagonal elements. Such a matrix is called a "diagonal matrix" and the process of finding the rotation that renders the matrix representation of a symmetric tensor diagonal is called "diagonalization".[3] We may do an "accounting of information" for this preferred coordinate system just as we did with vectors. In the initial coordinate system, the symmetric tensor had three independent components. In the preferred system, it has two independent components manifestly visible in the diagonal matrix representation, and one number hidden through the specification of the rotation.

H.7 **Problem: Representations of symmetric tensors***

Show that if the matrix S representing a tensor is symmetric, and if B is any orthogonal matrix, then all of the representations

$$\mathsf{B}\mathsf{S}\mathsf{B}^{\dagger} \tag{H.12}$$

are symmetric. (Clue: If you try to solve this problem for rotations in two dimensions using the explicit rotation matrix (H.3), you will find it solvable but messy. The clue is that this problem asks you do prove the result in any number of dimensions, and for any orthogonal matrix B, not just rotation matrices. This more general problem is considerably easier to solve.)

H.8 **Problem: Diagonal inertia tensor**

The matrix (H.9) represents the inertia tensor of a point particle with mass m located a distance r from the origin. Show that the matrix is diagonal in four different coordinate systems: one in which the x'-axis points directly toward the particle, one in which the y'-axis points directly away from the particle, one in which the x'-axis points directly away from the particle, and one in which the y'-axis

---

[3] An efficient algorithm for diagonalization is discussed in section H.8. For the moment, we are more interested in knowing that a diagonal matrix representation must exist than in knowing how to most easily find that preferred coordinate system.

points directly toward the particle. Find the matrix representation in each of these four coordinate systems.

H.9 **Problem: Representations of a certain tensor**

Show that a tensor represented in one coordinate system by a diagonal matrix with equal elements, namely

$$\begin{pmatrix} d_0 & 0 \\ 0 & d_0 \end{pmatrix}, \tag{H.13}$$

has the same representation in *all* orthogonal coordinate systems.

H.10 **Problem: Rotation to the preferred coordinate system***

A tensor is represented in the initial coordinate system by

$$\begin{pmatrix} a & b \\ b & c \end{pmatrix}. \tag{H.14}$$

Show that the tensor is diagonal in a preferred coordinate system which is rotated from the initial system by an angle ϕ with

$$\tan(2\phi) = \frac{2b}{a-c}. \tag{H.15}$$

This equation has four solutions. Find the rotation matrix for $\phi = 90°$, then show how the four different diagonal representations are related. You do not need to find any of the diagonal representations in terms of a, b and c. . . just show what the other three are given that one of them is

$$\begin{pmatrix} d_1 & 0 \\ 0 & d_2 \end{pmatrix}. \tag{H.16}$$

H.11 **Problem: Inertia tensor in outer product notation**

The discussion in this section has emphasized the tensor's matrix representation ("name") T rather than the tensor $\mathbf{T}$ itself.

a. Define the "identity tensor" **1** as the tensor represented in some coordinate system by

$$\mathsf{1} = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}. \tag{H.17}$$

Show that this tensor has the same representation in any coordinate system.

b. Show that the inner product between two vectors results in a scalar: Namely

$$\text{if vector } bfa \text{ is represented by } \begin{pmatrix} a_x \\ a_y \end{pmatrix} \text{ and vector } bfb \text{ is represented by } \begin{pmatrix} b_x \\ b_y \end{pmatrix}$$

then the inner product $\mathbf{a} \cdot \mathbf{b}$ is given through

$$\begin{pmatrix} a_x & a_y \end{pmatrix} \begin{pmatrix} b_x \\ b_y \end{pmatrix} = a_x b_x + a_y b_y,$$

and this inner product is a scalar. (A 1×2 matrix times a 2×1 matrix is a 1×1 matrix.) That is, the vector $\mathbf{a}$ is represented by different coordinates in different coordinate systems, and the vector $\mathbf{b}$ is represented by different coordinates in different coordinate systems, but the inner product $\mathbf{a} \cdot \mathbf{b}$ is the same in all coordinate systems.

c. In contrast, show that the outer product of two vectors is a tensor: Namely

$$\mathbf{ab} \doteq \begin{pmatrix} a_x \\ a_y \end{pmatrix} \begin{pmatrix} b_x & b_y \end{pmatrix} = \begin{pmatrix} a_x b_x & a_x b_y \\ a_y b_x & a_y b_y \end{pmatrix}.$$

(A 2×1 matrix times a 1×2 matrix is a 2×2 matrix.) That is, show that the representation of $\mathbf{ab}$ transforms from one coordinate system to another as specified through (H.11).

d. Show that the inertia tensor for a single particle of mass m located at position $\mathbf{r}$ can be written in coordinate-independent fashion as

$$\mathbf{T} = m\mathbf{1}r^2 - m\mathbf{rr}. \tag{H.18}$$

H.4 Tensors in three dimensions

A three-dimensional tensor is represented in component form by a 3×3 matrix with nine entries. If the tensor is symmetric, there are six independent elements. . . three on the diagonal and three off-diagonal. The components of a tensor in three dimensions change with coordinate system according to

$$\mathsf{T}' = \mathsf{R}\mathsf{T}\mathsf{R}^\dagger, \tag{H.19}$$

where R is the 3×3 rotation matrix.

A rotation in two dimension is described completely by giving a single angle. In three dimensions more information is required. Specifically, we need not only the amount of the rotation, but we must also know the plane in which the rotation takes place. We can specify the plane by giving the unit vector perpendicular to that plane. Specifying an arbitrary vector in three dimensions requires three numbers, but specifying a unit vector in three dimensions requires only two numbers because the magnitude is already fixed at unity. Thus three numbers are required to specify a rotation in three dimensions: two to specify the rotation's plane, one to specify the rotation's size. (One particularly convenient way to specify a three-dimensional rotation is through the three *Euler angles.* Reference [3] defines these angles and shows how to write the 3×3 rotation matrix in terms of these variables. For the purposes of this tutorial, however, we will not need an explicit rotation matrix. . . all we need is to know is the number of angles required to specify a rotation.)

In two dimensions, any symmetric tensor (which has three independent elements), could be represented by a diagonal tensor (with two independent elements) plus a rotation (one angle). We were able to back up this claim with an explicit expression for the angle.

In three dimensions it seems reasonable that any symmetric tensor (six independent elements) can be represented by a diagonal tensor (three independent elements) plus a rotation (three angles). The three angles just have to be selected carefully enough to make sure that they cause the off-diagonal elements to vanish. This supposition is indeed correct, although we will not pause for long enough to prove it by producing explicit formulas for the three angles.

H.5 Tensors in d dimensions

A d-dimensional tensor is represented by a $d \times d$ matrix with d^2 entries. If the tensor is symmetric, there are d independent on-diagonal elements and $d(d-1)/2$ independent off-diagonal elements. The tensor components will change with coordinate system in the now-familiar form

$$\mathsf{T}' = \mathsf{R}\mathsf{T}\mathsf{R}^\dagger, \tag{H.20}$$

where R is the $d \times d$ rotation matrix.

How many angles does it take to specify a rotation in d dimensions? Remember how we went from two dimensions to three: The three dimensional rotation took place "in a plane", i.e. in a two-dimensional subspace. It required two (i.e. $d-1$) angles to specify the orientation of the plane plus one to specify the rotation within the plane... a total of three angles.

A rotation in four dimensions takes place within a three-dimensional subspace. It requires $3 = d-1$ angles to specify the orientation of the three-dimensional subspace, plus, as we found above, three angles to specify the rotation within the three-dimensional subspace... a total of six angles.

A rotation in five dimensions requires $4 = d-1$ angles to specify the four-dimensional subspace in which the rotation occurs, plus the six angles that we have just found specify a rotation within that subspace... a total of ten angles.

In general, the number of angles needed to specify a rotation in d dimensions is

$$A_d = d - 1 + A_{d-1} = d(d-1)/2. \tag{H.21}$$

This is exactly the number of independent off-diagonal elements in a symmetric tensor. It seems reasonable that we can choose the angles to ensure that, in the resulting coordinate system, all the off-diagonal elements vanish. The proof of this result is difficult and proceeds in a very different manner from the plausibility argument sketched here. (The proof involves concepts like eigenvectors and eigenvalues, and it gives an explicit recipe for constructing the rotation matrix. It has the advantage of rigor and the disadvantage of being so technical that it's easy to lose track of the fact that that all you're doing is choosing a coordinate system.)

H.12 **Problem: Non-symmetric tensors***

Argue that a non-symmetric tensor can be brought into a "triangular" representation in which all the elements below the diagonal are equal to zero and all the elements on and above the diagonal are independent. (This is indeed the case, although in general some of the non-zero elements remaining will be complex-valued, and some of the angles will involve rotations into complex-valued vectors.)

H.6 Linear transformations in two dimensions

Section H.3 considered 2×2 matrices as representations of tensors. This section gains additional insight by considering 2×2 matrices as representations of linear transformations. It demonstrates how diagonalization can be useful and gives a clue to an efficient algorithm for diagonalization.

A linear transformation is a function from vectors to vectors that can be represented in any given coordinate system as

$$\begin{pmatrix} u \\ v \end{pmatrix} = \begin{pmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{pmatrix} \begin{pmatrix} x \\ y \end{pmatrix}. \tag{H.22}$$

If the equation above represents ("names") the transformation in one coordinate system, what is its representation in some other coordinate system? We assume that the two coordinate systems are related through an orthogonal matrix B such that

$$\begin{pmatrix} u' \\ v' \end{pmatrix} = \mathsf{B} \begin{pmatrix} u \\ v \end{pmatrix} \quad \text{and} \quad \begin{pmatrix} x' \\ y' \end{pmatrix} = \mathsf{B} \begin{pmatrix} x \\ y \end{pmatrix}. \tag{H.23}$$

(For example, if the new coordinate system is the primed coordinate system of the figure on page 229, then the matrix B that translates from the original to the new coordinates is the rotation matrix $\mathsf{R}(\phi)$.) Given this "translation dictionary", we have

$$\begin{pmatrix} u' \\ v' \end{pmatrix} = \mathsf{B} \begin{pmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{pmatrix} \begin{pmatrix} x \\ y \end{pmatrix}. \tag{H.24}$$

But B is invertible, so

$$\begin{pmatrix} x \\ y \end{pmatrix} = \mathsf{B}^{-1} \begin{pmatrix} x' \\ y' \end{pmatrix} \tag{H.25}$$

whence

$$\begin{pmatrix} u' \\ v' \end{pmatrix} = \mathsf{B} \begin{pmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{pmatrix} \mathsf{B}^{-1} \begin{pmatrix} x' \\ y' \end{pmatrix}. \tag{H.26}$$

Thus the representation of the transformation in the primed coordinate system is

$$\mathsf{B} \begin{pmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{pmatrix} \mathsf{B}^{-1} \tag{H.27}$$

(compare equation H.11). This equation has a very direct physical meaning. Remember that the matrix B translates from the old (x, y) coordinates to the new (x', y') coordinates, while the matrix B^{-1} translates in the opposite direction. Thus the equation above says that the representation of a transformation in the new coordinates is given by translating from new to old coordinates (through the matrix B^{-1}), then applying the old representation (the "a matrix") to those old coordinates, and finally translating back from old to new coordinates (through the matrix B).

The rest of this section considers only transformations represented by symmetric matrices, which we will denote by

$$\begin{pmatrix} u \\ v \end{pmatrix} = \begin{pmatrix} a & b \\ b & c \end{pmatrix} \begin{pmatrix} x \\ y \end{pmatrix}. \tag{H.28}$$

Let's try to understand this transformation as something more than a jumble of symbols awaiting a plunge into the calculator. First of all, suppose the vector **V** maps to the vector **W**. Then the vector 5**V** will be mapped to vector 5**W**. In short, if we know how the transformation acts on vectors with magnitude unity, we will be able to see immediately how it acts on vectors with other magnitudes. Thus we focus our attention on vectors on the unit circle:

$$x^2 + y^2 = 1. \tag{H.29}$$

A brief calculation shows that the length of the output vector is then

$$\sqrt{u^2+v^2} = \sqrt{a^2x^2 + b^2 + c^2y^2 + 2b(a+c)xy}, \tag{H.30}$$

which isn't very helpful. Another brief calculation shows that if the input vector has polar angle θ, then the output vector has polar angle φ with

$$\tan\varphi = \frac{b + c\tan\theta}{a + b\tan\theta}, \tag{H.31}$$

which is similarly opaque and messy.

Instead of trying to understand the transformation in its initial coordinate system, let's instead convert (rotate) to the special coordinate system in which the transformation is represented by a diagonal matrix. In this system,

$$\begin{pmatrix} u' \\ v' \end{pmatrix} = \begin{pmatrix} d_1 & 0 \\ 0 & d_2 \end{pmatrix} \begin{pmatrix} x' \\ y' \end{pmatrix} = \begin{pmatrix} d_1x' \\ d_2y' \end{pmatrix}. \tag{H.32}$$

The unit circle is still

$$x'^2 + y'^2 = 1, \tag{H.33}$$

so the image of the unit circle is

$$\left(\frac{u'}{d_1}\right)^2 + \left(\frac{v'}{d_2}\right)^2 = 1, \tag{H.34}$$

namely an ellipse! This result is transparent in the special coordinate system, but almost impossible to see in the original one.

Note particularly what happens to a vector pointing along the x' coordinate axis. For example, the unit vector in this direction transforms to

$$\begin{pmatrix} d_1 \\ 0 \end{pmatrix} = \begin{pmatrix} d_1 & 0 \\ 0 & d_2 \end{pmatrix} \begin{pmatrix} 1 \\ 0 \end{pmatrix}. \tag{H.35}$$

In other words, the when the vector is transformed it changes in magnitude, but *not* in direction. Vectors with this property are called *eigenvectors*. It is easy to see that any vector on either the x' or y' coordinate axes are eigenvectors.

H.7 What does "eigen" mean?

If a vector **x** is acted upon by a linear transformation B, then the output vector

$$\mathbf{x}' = \mathsf{B}\mathbf{x} \tag{H.36}$$

will usually be skew to the original vector $\mathbf{x}$. However, for some very special vectors it might just happen that $\mathbf{x}'$ is parallel to $\mathbf{x}$. Such vectors are called "eigenvectors". (This is a terrible name because (1) it gives no idea of what eigenvectors are or why they're so important and (2) it sounds gross. However, that's what they're called.) We have already seen, in the previous section, that eigenvectors are related to coordinate systems in which the transformation is particularly easy to understand.

If $\mathbf{x}$ is an eigenvector, then

$$\mathsf{B}\mathbf{x} = \lambda\mathbf{x}, \tag{H.37}$$

where λ is a scalar called "the eigenvalue associated with eigenvector $\mathbf{x}$". If $\mathbf{x}$ is an eigenvector, then any vector parallel to $\mathbf{x}$ is also an eigenvector with the same eigenvalue. (That is, any vector of the form $c\mathbf{x}$, where c is any scalar, is also an eigenvector with the same eigenvalue.) Sometimes we speak of a "line of eigenvectors".

The vector $\mathbf{x} = \mathbf{0}$ is never considered an eigenvector, because

$$\mathsf{B}\mathbf{0} = \lambda\mathbf{0}, \tag{H.38}$$

for any value of λ for any linear transformation. On the other hand, if

$$\mathsf{B}\mathbf{x} = 0\mathbf{x} = \mathbf{0} \tag{H.39}$$

for some non-zero vector $\mathbf{x}$, then $\mathbf{x}$ is an eigenvector with eigenvalue $\lambda = 0$.

H.13 **Problem: Plane of eigenvectors**

Suppose $\mathbf{x}$ and $\mathbf{y}$ are two non-parallel vectors with the same eigenvalue. (In this case the eigenvalue is said to be "degenerate", which sounds like an aspersion cast upon the morals of the eigenvalue but which is really just poor choice of terminology again.) Show that any vector of the form $c_1\mathbf{x} + c_2\mathbf{y}$ is an eigenvector with the same eigenvalue.

H.8 How to diagonalize a symmetric matrix

We saw in section H.3 that for any 2×2 symmetric matrix, represented in its initial basis by, say,

$$\begin{pmatrix} a & b \\ b & c \end{pmatrix}, \tag{H.40}$$

a simple rotation of axes would produce a new coordinate system in which the matrix representation is diagonal:

$$\begin{pmatrix} d_1 & 0 \\ 0 & d_2 \end{pmatrix}. \tag{H.41}$$

These two matrices are related through

$$\begin{pmatrix} d_1 & 0 \\ 0 & d_2 \end{pmatrix} = \mathsf{R}(\phi) \begin{pmatrix} a & b \\ b & c \end{pmatrix} \mathsf{R}^{-1}(\phi), \tag{H.42}$$

where $\mathsf{R}(\phi)$ is the rotation matrix (H.3). Problem H.10 gave a direct way to find the desired rotation. However this direct technique is cumbersome and doesn't generalize readily to higher dimensions. This section presents a different technique, which relies on eigenvalues and eigenvectors, that is more efficient and that generalizes readily to complex-valued matrices and to matrices in any dimension, but that is somewhat sneaky and conceptually roundabout.

We begin by noting that any vector lying along the x'-axis (of the preferred coordinate system) is an eigenvector. For example, the vector $5\hat{\mathbf{i}}'$ is represented (in the preferred coordinate system) by

$$\begin{pmatrix} 5 \\ 0 \end{pmatrix}. \tag{H.43}$$

Multiplying this vector by the matrix in question gives

$$\begin{pmatrix} d_1 & 0 \\ 0 & d_2 \end{pmatrix}\begin{pmatrix} 5 \\ 0 \end{pmatrix} = d_1\begin{pmatrix} 5 \\ 0 \end{pmatrix}, \tag{H.44}$$

so $5\hat{\mathbf{i}}'$ is an eigenvector with eigenvalue d_1. The same holds for any scalar multiple of $\hat{\mathbf{i}}'$, whether positive or negative. Similarly, any scalar multiple of $\hat{\mathbf{j}}'$ is an eigenvector with eigenvalue d_2. In short, the two elements on the diagonal in the preferred (diagonal) representation are the two eigenvalues, and the two unit vectors $\hat{\mathbf{i}}'$ and $\hat{\mathbf{j}}'$ of the preferred coordinate system are two of the eigenvectors.

Thus finding the eigenvectors and eigenvalues of a matrix gives you the information needed to diagonalize that matrix. The unit vectors $\hat{\mathbf{i}}'$ and $\hat{\mathbf{j}}'$ constitute an "orthonormal basis of eigenvectors". The eigenvectors even give the rotation matrix directly, as described in the next paragraph.

Let's call the rotation matrix

$$\mathsf{B} = \begin{pmatrix} b_{11} & b_{12} \\ b_{21} & b_{22} \end{pmatrix}, \tag{H.45}$$

so that the inverse (transpose) matrix is

$$\mathsf{B}^{-1} = \mathsf{B}^{\dagger} = \begin{pmatrix} b_{11} & b_{21} \\ b_{12} & b_{22} \end{pmatrix}. \tag{H.46}$$

The representation of $\hat{\mathbf{i}}'$ in the preferred basis is

$$\begin{pmatrix} 1 \\ 0 \end{pmatrix}, \tag{H.47}$$

so its representation in the initial basis is (see equation H.2)

$$\mathsf{B}^{\dagger}\begin{pmatrix} 1 \\ 0 \end{pmatrix} = \begin{pmatrix} b_{11} & b_{21} \\ b_{12} & b_{22} \end{pmatrix}\begin{pmatrix} 1 \\ 0 \end{pmatrix} = \begin{pmatrix} b_{11} \\ b_{12} \end{pmatrix}. \tag{H.48}$$

Similarly, the representation of $\hat{\mathbf{j}}'$ in the initial basis is

$$\mathsf{B}^{\dagger}\begin{pmatrix} 0 \\ 1 \end{pmatrix} = \begin{pmatrix} b_{11} & b_{21} \\ b_{12} & b_{22} \end{pmatrix}\begin{pmatrix} 0 \\ 1 \end{pmatrix} = \begin{pmatrix} b_{21} \\ b_{22} \end{pmatrix}. \tag{H.49}$$

Thus the rotation matrix is

$$\mathsf{B} = \begin{pmatrix} \text{initial rep. of } \hat{\mathbf{i}}', \text{ on its side} \\ \text{initial rep. of } \hat{\mathbf{j}}', \text{ on its side} \end{pmatrix}. \tag{H.50}$$

Example

Suppose we need to find a diagonal representation for the matrix

$$\mathsf{T} = \begin{pmatrix} 7 & 3 \\ 3 & 7 \end{pmatrix}. \tag{H.51}$$

First we search for the special vectors—the eigenvectors—such that

$$\begin{pmatrix} 7 & 3 \\ 3 & 7 \end{pmatrix} \begin{pmatrix} x \\ y \end{pmatrix} = \lambda \begin{pmatrix} x \\ y \end{pmatrix}. \tag{H.52}$$

At the moment, we don't know either the eigenvalue λ or the associated eigenvector (x, y). Thus it seems that (bad news) we are trying to solve two equations for three unknowns:

$$\begin{aligned} 7x + 3y &= \lambda x \\ 3x + 7y &= \lambda y \end{aligned} \tag{H.53}$$

Remember, however, that there is not one *single* eigenvector: any multiple of an eigenvector is also an eigenvector. (Alternatively, any vector on the line that extends the eigenvector is another eigenvector.) We only need one of these eigenvectors, so let's take the one that has $x = 1$ (i.e. the vector on the extension line where it intersects the vertical line $x = 1$). (This technique will fail if we have the bad luck that our actual eigenvector is vertical and hence never passes through the line $x = 1$.) So we really have two equations in two unknowns:

$$\begin{aligned} 7 + 3y &= \lambda \\ 3 + 7y &= \lambda y \end{aligned}$$

but note that they are not *linear* equations…the damnable product λy in the lower right corner means that all our techniques for solving linear equations go right out the window. We *can* solve these two equations for λ and y, but there's an easier, if somewhat roundabout, approach.

Finding eigenvalues

Let's go back to equation (H.52) and write it as

$$\begin{pmatrix} 7 & 3 \\ 3 & 7 \end{pmatrix} \begin{pmatrix} x \\ y \end{pmatrix} - \lambda \begin{pmatrix} x \\ y \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix}. \tag{H.54}$$

Then

$$\begin{pmatrix} 7 & 3 \\ 3 & 7 \end{pmatrix}\begin{pmatrix} x \\ y \end{pmatrix} - \lambda \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}\begin{pmatrix} x \\ y \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix} \tag{H.55}$$

or

$$\begin{pmatrix} 7-\lambda & 3 \\ 3 & 7-\lambda \end{pmatrix}\begin{pmatrix} x \\ y \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix}. \tag{H.56}$$

Let's think about this. It says that for some matrix $\mathsf{M} = \mathsf{T} - \lambda\mathsf{1}$, we have

$$\mathsf{M}\begin{pmatrix} x \\ y \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix}. \tag{H.57}$$

You know right away one vector (x, y) that satisfies this equation, namely $(x, y) = (0, 0)$. And most of the time, this is the *only* vector that satisfies the equation, because

$$\begin{pmatrix} x \\ y \end{pmatrix} = \mathsf{M}^{-1}\begin{pmatrix} 0 \\ 0 \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix}. \tag{H.58}$$

We appear to have reached a dead end. The solution is $(x, y) = (0, 0)$, but the zero vector is not, by definition, considered an eigenvector of any transformation. (Because it always gives eigenvalue zero for any transformation.)

However, if the matrix M is *not invertible*, then there will be other solutions to

$$\mathsf{M}\begin{pmatrix} x \\ y \end{pmatrix} = \begin{pmatrix} 0 \\ 0 \end{pmatrix}. \tag{H.59}$$

in addition to the trivial solution $(x, y) = (0, 0)$. Thus we must look for those special values of λ such that the so-called *characteristic matrix* M is not invertible. These values come if and only if the determinant of M vanishes. For this example, we have to find values of λ such that

$$\det\begin{pmatrix} 7-\lambda & 3 \\ 3 & 7-\lambda \end{pmatrix} = 0. \tag{H.60}$$

This is a quadratic equation in λ

$$(7-\lambda)^2 - 3^2 = 0 \tag{H.61}$$

called the *characteristic equation.* Its two solutions are

$$7 - \lambda = \pm 3 \tag{H.62}$$

or

$$\lambda = 7 \pm 3 = 10 \text{ or } 4. \tag{H.63}$$

We have found the two eigenvalues of our matrix!

Finding eigenvectors

Let's look now for the eigenvector associated with $\lambda = 4$. Equation (H.53)

$$\begin{aligned} 7x + 3y &= \lambda x \\ 3x + 7y &= \lambda y \end{aligned}$$

still holds, but no longer does it look like two equations in three unknowns, because we are now interested in the case $\lambda = 4$:

$$\begin{aligned} 7x + 3y &= 4x \\ 3x + 7y &= 4y \end{aligned}$$

Following our nose gives

$$\begin{aligned} 3x + 3y &= 0 \\ 3x + 3y &= 0 \end{aligned}$$

and when we see this our heart skips a beat or two… a degenerate system of equations! Relax and rest your heart. This system has an infinite number of solutions and it's supposed to have an infinite number of solutions, because any multiple of an eigenvector is also an eigenvector. The eigenvectors associated with $\lambda = 4$ are any multiple of

$$\begin{pmatrix} 1 \\ -1 \end{pmatrix}. \tag{H.64}$$

An entirely analogous search for the eigenvectors associated with $\lambda = 10$ finds any multiple of

$$\begin{pmatrix} 1 \\ 1 \end{pmatrix}. \tag{H.65}$$

Tidying up

We have the two sets of eigenvectors, but which shall we call $\hat{\mathbf{i}}'$ and which $\hat{\mathbf{j}}'$? This is a matter of individual choice, but my choice is usually to make the transformation be a rotation (without reflection) through a small positive angle. Our new, preferred coordinate system is related to the original coordinates by a simple rotation of 45° if we choose

$$\hat{\mathbf{i}}' = \tfrac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ 1 \end{pmatrix} \quad \text{and} \quad \hat{\mathbf{j}}' = \tfrac{1}{\sqrt{2}} \begin{pmatrix} -1 \\ 1 \end{pmatrix}. \tag{H.66}$$

(Note that we have also "normalized the basis", i.e. selected the basis vectors to have magnitude unity.) Given this choice, the orthogonal rotation matrix that changes coordinates from the original to the preferred system is (see equation H.50)

$$\mathsf{B} = \tfrac{1}{\sqrt{2}} \begin{pmatrix} 1 & 1 \\ -1 & 1 \end{pmatrix} \tag{H.67}$$

and the diagonalized matrix (or, more properly, the representation of the matrix in the preferred coordinate system) is

$$\begin{pmatrix} 10 & 0 \\ 0 & 4 \end{pmatrix}. \tag{H.68}$$

You don't believe me? Then multiply out

$$\mathsf{B}\begin{pmatrix} 7 & 3 \\ 3 & 7 \end{pmatrix}\mathsf{B}^\dagger \tag{H.69}$$

and see for yourself.

Problems

H.14 **Problem: Diagonalize a 2×2 matrix***

Diagonalize the matrix

$$\begin{pmatrix} 26 & 12 \\ 12 & 19 \end{pmatrix}. \tag{H.70}$$

a. Find its eigenvalues.

b. Find its eigenvectors, and verify that they are orthogonal.

c. Sketch the eigenvectors, and determine the signs and sequence most convenient for assigning axes. (That is, should the first eigenvector you found be called $\hat{\mathbf{i}}'$, $-\hat{\mathbf{i}}'$, or $\hat{\mathbf{j}}'$?)

d. Find the matrix that translates from the initial basis to the basis of eigenvectors produced in part (c.).

e. Verify that the matrix produced in part (d.) is orthogonal.

f. Verify that the representation of the matrix above in the basis of eigenvectors is diagonal.

g. (Optional.) What is the rotation angle?

H.15 **Problem: Eigenvalues of a 2×2 matrix**

Show that the eigenvalues of

$$\begin{pmatrix} a & b \\ b & c \end{pmatrix} \tag{H.71}$$

are

$$\lambda = \tfrac{1}{2}\left[(a+c) \pm \sqrt{(a-c)^2 + 4b^2}\right]. \tag{H.72}$$

Under what circumstances is an eigenvalue complex valued? Under what circumstances are the two eigenvalues the same?

H.16 **Problem: Diagonalize a 3×3 matrix**

Diagonalize the matrix

$$\frac{1}{625}\begin{pmatrix} 1182 & -924 & 540 \\ -924 & 643 & 720 \\ 540 & 720 & -575 \end{pmatrix}. \tag{H.73}$$

a. Find its eigenvalues by showing that the characteristic equation is

$$\lambda^3 - 2\lambda^2 - 5\lambda + 6 = (\lambda - 3)(\lambda + 2)(\lambda - 1) = 0. \tag{H.74}$$

b. Find its eigenvectors, and verify that they are orthogonal.

c. Show that the translation matrix can be chosen to be

$$\mathsf{B} = \frac{1}{25}\begin{pmatrix} 20 & -15 & 0 \\ 9 & 12 & -20 \\ 12 & 16 & 15 \end{pmatrix}. \tag{H.75}$$

Why did I use the phrase “the translation matrix can be chosen to be” rather then “the translation matrix is”?

H.17 **Problem: A 3×3 matrix eigenproblem**

Find the eigenvalues and associated eigenvectors for the matrix

$$\begin{pmatrix} 1 & 2 & 3 \\ 2 & 3 & 4 \\ 3 & 4 & 5 \end{pmatrix}. \tag{H.76}$$

H.9 A glance at computer algorithms

Anyone who has worked even one of the problems in section H.8 knows that diagonalizing a matrix is no picnic: there’s a lot of mundane arithmetic involved and it’s very easy to make mistakes. This is a problem ripe for computer solution. One’s first thought is to program a computer to solve the problem using the same technique that we used to solve it on paper: first find the eigenvalues through the characteristic equation, then find the eigenvectors through a degenerate set of linear equations.

This turns out to be a very poor algorithm for automatic computation. The effective algorithm is to choose a matrix B such that the off-diagonal elements of

$$\mathsf{B}\mathsf{A}\mathsf{B}^{-1} \tag{H.77}$$

are smaller than the off-diagonal elements of A. Then choose another, and another. Go through this process again and again until the off-diagonal elements have been ground down to machine zero. There are many strategies for choosing the series of B matrices. These are well-described in any edition of *Numerical Recipes*.[4]

When you need to diagonalize matrices numerically, I urge you to look at *Numerical Recipes* to see what’s going on, but I urge you *not* to code these algorithms yourself. These algorithms rely in an essential way on the fact that computer arithmetic is approximate rather than exact, and hence they are quite tricky to implement. Instead of coding the algorithms yourself, I recommend that you use the implementations in either LAPACK[5] (the Linear Algebra PACKage) or EISPACK.[6] These packages are probably the finest computer software ever written, and they are free. They can be obtained through the “Guide to Available Mathematical Software” (GAMS) at http://gams.nist.gov.

H.10 A glance at non-symmetric matrices and the Jordan form

Many of the matrices that arise in applications are symmetric and hence the results of the previous sections are the only ones needed. But every once in a while you do encounter a non-symmetric matrix and this section gives you a guide to treating them. It is just an introduction and treats only 2 × 2 matrices.

Given a non-symmetric matrix, the first thing to do is rotate the axes to make the matrix representation triangular, as discussed in problem H.12:

$$\begin{pmatrix} a & b \\ 0 & c \end{pmatrix}. \tag{H.78}$$

Note that $b \neq 0$ because otherwise the matrix would be symmetric and we would already be done. In this case vectors on the x-axis are eigenvectors because

$$\begin{pmatrix} a & b \\ 0 & c \end{pmatrix}\begin{pmatrix} 1 \\ 0 \end{pmatrix} = a\begin{pmatrix} 1 \\ 0 \end{pmatrix}. \tag{H.79}$$

Are there any other eigenvectors? The equation

$$\begin{pmatrix} a & b \\ 0 & c \end{pmatrix}\begin{pmatrix} x \\ y \end{pmatrix} = \lambda\begin{pmatrix} x \\ y \end{pmatrix} \tag{H.80}$$

tells us that

$$\begin{aligned} ax + by &= \lambda x \\ cy &= \lambda y \end{aligned}$$

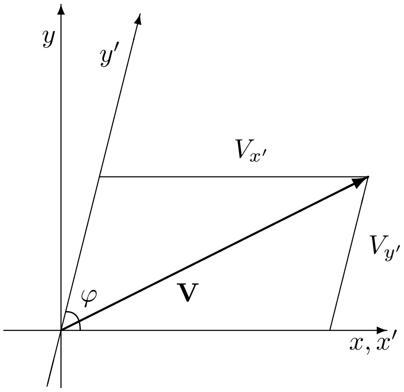
whence $\lambda = c$ and the eigenvector has polar angle θ where

$$\tan\theta = \frac{c-a}{b}. \tag{H.81}$$

Note that if $c = a$ (the "degenerate" case: both eigenvalues are the same) then $\theta = 0$ or $\theta = \pi$. In this case *all* of the eigenvectors are on the x-axis.

Diagonal form

We already know that that a rotation of orthogonal (Cartesian) coordinates will not diagonalize this matrix. We must instead transform to a skew coordinate system in which the axes are not perpendicular.



Note that in with oblique axes, the coordinates are given by

$$\mathbf{V} = V_{x'}\hat{\mathbf{i}}' + V_{y'}\hat{\mathbf{j}}' \tag{H.82}$$

but, because $\hat{\mathbf{i}}'$ and $\hat{\mathbf{j}}'$ are not perpendicular, it is *not true* that

$$V_{x'} = \mathbf{V} \cdot \hat{\mathbf{i}}'. \qquad \textbf{NO!} \tag{H.83}$$

A little bit of geometry will convince you that the name of the vector $\mathbf{V}$ changes according to

$$\begin{pmatrix} V_{x'} \\ V_{y'} \end{pmatrix} = \mathsf{B} \begin{pmatrix} V_x \\ V_y \end{pmatrix}, \tag{H.84}$$

where

$$\mathsf{B} = \frac{1}{\sin\varphi} \begin{pmatrix} \sin\varphi & -\cos\varphi \\ 0 & 1 \end{pmatrix}. \tag{H.85}$$

This matrix is *not* orthogonal. In fact its inverse is

$$\mathsf{B}^{-1} = \begin{pmatrix} 1 & \cos\varphi \\ 0 & \sin\varphi \end{pmatrix}. \tag{H.86}$$

Finally, note that we cannot have $\varphi = 0$ or $\varphi = \pi$, because then both $V_{x'}$ and $V_{y'}$ would give information about the horizontal component of the vector, and there would be no information about the vertical component of the vector.

What does this say about the representations of tensors (or, equivalently, of linear transformations)? The "name translation" argument of equation (H.27) still applies, so

$$\mathsf{T}' = \mathsf{B}\mathsf{T}\mathsf{B}^{-1}. \tag{H.87}$$

Using the explicit matrices already given, this says

$$\mathsf{T}' = \frac{1}{\sin\varphi}\begin{pmatrix} \sin\varphi & -\cos\varphi \\ 0 & 1 \end{pmatrix}\begin{pmatrix} a & b \\ 0 & c \end{pmatrix}\begin{pmatrix} 1 & \cos\varphi \\ 0 & \sin\varphi \end{pmatrix} = \begin{pmatrix} a & (a-c)\cos\varphi + b\sin\varphi \\ 0 & c \end{pmatrix}. \tag{H.88}$$

To make this diagonal, we need only choose a skew coordinate system where the angle φ gives

$$(a-c)\cos\varphi + b\sin\varphi = 0, \tag{H.89}$$

that is, one with

$$\tan\varphi = \frac{c-a}{b}. \tag{H.90}$$

Comparison with equation (H.81) shows that this simply means that the skew coordinate system should have its axes pointing along two eigenvectors. We have once again found an intimate connection between diagonal representations and eigenvectors, a connection which is exploited fully in abstract mathematical treatments of matrix diagonalization.

Once again we can do an accounting of information. In the initial coordinate system, the four elements of the matrix contain four independent pieces of information. In the diagonalizing coordinate system, two of those pieces are explicit in the matrix, and two are implicit in the two axis rotation angles needed to implement the diagonalization.

This procedure works almost all the time. But, if $a = c$, then it would involve $\varphi = 0$ or $\varphi = \pi$, and we have already seen that this is not an acceptable change of coordinates.

Degenerate case

Suppose our matrix has equal eigenvalues, $a = c$, so that it reads

$$\begin{pmatrix} a & b \\ 0 & a \end{pmatrix}. \tag{H.91}$$

If $b = 0$, then the matrix is already diagonal. (Indeed, in this case *all* vectors are eigenvectors with eigenvalue a, and the linear transformation is simply multiplication of each vector by a).

But if $b \neq 0$, then, as we have seen, the only eigenvectors are on the x-axis, and it is impossible to make a basis of eigenvectors. Only one thing can be done to make the matrix representation simpler than it stands in equation (H.91), and that is a shift in the scale used to measure the y-axis.

For example, suppose that in the (x, y) coordinate system, the y-axis is calibrated in inches. We wish to switch to the (x', y') system in which the y'-axis is calibrated in feet. There is no change in axis orientation or in the x-axis. It is easy to see that the two sets of coordinates are related through

$$\begin{pmatrix} x' \\ y' \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 0 & 1/12 \end{pmatrix}\begin{pmatrix} x \\ y \end{pmatrix} \quad \text{and} \quad \begin{pmatrix} x \\ y \end{pmatrix} = \begin{pmatrix} 1 & 0 \\ 0 & 12 \end{pmatrix}\begin{pmatrix} x' \\ y' \end{pmatrix} \tag{H.92}$$

This process is sometimes called a “stretching” or a “scaling” of the y-axis.

The transformation represented by matrix (H.91) in the initial coordinate system is represented in the new coordinate system by

$$\begin{pmatrix} 1 & 0 \\ 0 & 1/12 \end{pmatrix} \begin{pmatrix} a & b \\ 0 & a \end{pmatrix} \begin{pmatrix} 1 & 0 \\ 0 & 12 \end{pmatrix} = \begin{pmatrix} a & 12b \\ 0 & a \end{pmatrix}. \tag{H.93}$$

The choice of what to do now is clear. Instead of scaling the y-axis by a factor of 12, we can scale it by a factor of $1/b$, and produce a new matrix representation of the form

$$\begin{pmatrix} a & 1 \\ 0 & a \end{pmatrix}. \tag{H.94}$$

Where is the information in this case? In the initial coordinate system, the four elements of the matrix contain four independent pieces of information. In the new coordinate system, two of those pieces are explicit in the matrix, one is implicit in the rotation angle needed to implement the initial triangularization, and one is implicit in the y-axis scale transformation.

The Jordan form

Remarkably, the situation discussed above for 2×2 matrices covers all the possible cases for $n \times n$ matrices. That is, in n dimensional space, the proper combination of rotations, skews, and stretches of coordinate axes will bring the matrix representation (the "name") of any tensor or linear transformation into a form where every element is zero except on the diagonal and on the superdiagonal. The elements on the diagonal are eigenvalues, and each element on the superdiagonal is either zero or one: zero if the two adjacent eigenvalues differ, either zero or one if they are the same. The warning of problem H.12 applies here as well: The eigenvalues on the diagonal may well be complex valued, and the same applies for the elements of the new basis vectors.

References

[1] For example, Kenneth Hoffman and Ray Kunze, *Linear Algebra*, second edition (Prentice-Hall, Englewood Cliffs, New Jersey, 1971).

[2] For example, Jerry Marion and Stephen Thorton, *Classical Dynamics of Particles and Systems*, fourth edition (Saunders College Publishing, Fort Worth, Texas, 1995) section 11.2.

[3] For example, Jerry Marion and Stephen Thorton, *Classical Dynamics of Particles and Systems*, fourth edition (Saunders College Publishing, Fort Worth, Texas, 1995) section 11.7.

[4] W.H. Press, S.A. Teukolsky, W.T. Vetterling, B.P. Flannery, *Numerical Recipes* (Cambridge University Press, Cambridge, U.K., 1992).

[5] E. Anderson, *et al.*, *LAPACK Users' Guide* (SIAM, Philadelphia, 1992).

[6] B.T. Smith, *et al.*, *Matrix Eigensystem Routines—EISPACK Guide* (Springer-Verlag, Berlin, 1976).

Appendix I

Catalog of Misconceptions

Effective teaching does not simply teach students what is correct—it also insures that students do not believe what is incorrect. There are a number of prevalent misconceptions in statistical mechanics. For example, an excellent history of statistical mechanics is titled *The Kind of Motion We Call Heat.* This title is wonderfully memorable and historically justifiable, but it embodies no fewer than three different physics misconceptions: heat is confused with thermal energy; thermal energy is confused with kinetic energy; and kinetic energy is confused with motion. Below is a list of misconceptions that are explicitly mentioned in this book, together with the page number where that misconception is pointed out and corrected.

Appendix J

Thermodynamic Master Equations

$E(S,V,N)$

$$dE = T\,dS - p\,dV + \mu\,dN$$

$F(T,V,N) = E - TS$

$$dF = -S\,dT - p\,dV + \mu\,dN$$

$H(S,p,N) = E + pV$

$$dH = T\,dS + V\,dp + \mu\,dN$$

$G(T,p,N) = F + pV$

$$dG = -S\,dT + V\,dp + \mu\,dN$$

$\Pi(T,V,\mu) = F - \mu N = -pV$

$$d\Pi = -S\,dT - p\,dV - N\,d\mu$$

$p(T,\mu)$ [intensive quantities only]

$$dp = \mathcal{S}\,dT + \rho\,d\mu \qquad [\mathcal{S} = S/V, \quad \rho = N/V]$$

Appendix K

Useful Formulas

Isothermal compressibility:

$$\kappa_T = -\frac{1}{V}\left.\frac{\partial V}{\partial p}\right)_{T,N} = \frac{1}{\rho}\left.\frac{\partial \rho}{\partial p}\right)_{T} = \frac{1}{\rho^2}\left.\frac{\partial^2 p}{\partial \mu^2}\right)_{T}$$

Master thermodynamic equation:

$$dF = -S\,dT - p\,dV - M\,dH + \sum_i \mu_i\,dN_i$$

Gibbs-Helmholtz equation:

$$E(T,V,N) = \left.\frac{\partial(F/T)}{\partial(1/T)}\right)_{V,N} = -\left.\frac{\partial \ln Z}{\partial \beta}\right)_{V,N}$$

Free energy from partition function:

$$F(T,V,N) = -k_BT\ln Z(T,V,N)$$

Classical pure point-particle partition function:

$$Z(T,V,N) = \frac{1}{h^{3N}N!}\int d^{3N}p\int d^{3N}r\,e^{-H(r,p)/k_BT}$$

$$Z(T,V,N) = \frac{1}{\lambda^{3N}(T)}\int d^{3N}r\,e^{-U(r)/k_BT} \qquad \text{where} \qquad \lambda(T) = \frac{h}{\sqrt{2\pi m k_B T}}$$

Quantal ideal gases (+ for fermions, − for bosons):

$$\Xi(\beta,\mu) = \prod_{r=1}^{M}[1 \pm e^{-\beta(\epsilon_r-\mu)}]^{\pm 1}$$

$$\langle n_r\rangle = \frac{1}{e^{\beta(\epsilon_r-\mu)} \pm 1}$$

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