Contents

Chapter 1

From Microscopic to Macroscopic Behavior

The goal of this introductory chapter is to explore the fundamental differences between microscopic and macroscopic systems and the connections between classical mechanics and statistical mechanics. We note that bouncing balls come to rest and hot objects cool, and discuss how the behavior of macroscopic objects is related to the behavior of their microscopic constituents. Computer simulations will be introduced to demonstrate the relation of microscopic and macroscopic behavior.

1.1   Introduction

Our goal is to understand the properties of *macroscopic* systems, that is, systems of many electrons, atoms, molecules, photons, or other constituents. Examples of familiar macroscopic objects include systems such as the air in your room, a glass of water, a copper coin, and a rubber band (examples of a gas, liquid, solid, and polymer, respectively). Less familiar macroscopic systems are superconductors, cell membranes, the brain, the stock market, and the galaxies.

We will find that the type of questions we ask about macroscopic systems differ in important ways from the questions we ask about systems that we treat microscopically. For example, you might wondered about the nature of a successful free throw in basketball. Although the basketball consists of many particles, we are interested in this context only in the trajectory of its center of mass. In contrast, have you ever wondered about the trajectory of a particular molecule in the air of your room? Why not? Is it relevant that these molecules are not visible to the eye? Examples of questions that we ask about macroscopic systems include the following:

1. How does the pressure of a gas depend on the temperature and the volume of its container?

2. How does a refrigerator work? What is its maximum efficiency?

3. How much energy do we need to add to a kettle of water to change it to steam?

4. Why are the properties of water different from those of steam, even though water and steam consist of the same type of molecules?

5. How are the molecules arranged in a liquid?

6. How and why does water freeze into a particular crystalline structure?

7. Why does helium condense into a superfluid phase at very low temperatures? Why do some materials exhibit zero resistance to electrical current at sufficiently low temperatures? In general, how do the properties of a system emerge from its constituents?

8. How fast does a river current have to be before its flow changes from laminar to turbulent?

9. What will the weather be tomorrow?

The above questions can be roughly classified into three groups. Questions 1–3 are concerned with macroscopic properties such as pressure, volume, and temperature and questions related to heating and work. These questions are relevant to *thermodynamics* which provides a framework for relating the macroscopic properties of a system to one another. Thermodynamics is concerned only with macroscopic quantities and ignores the microscopic variables that characterize individual molecules. For example, we will find that understanding the maximum efficiency of a refrigerator does not require a knowledge of the particular liquid used as the coolant. Many of the applications of thermodynamics are to thermal engines, for example, the internal combustion engine and the steam turbine.

Questions 4–7 relate to understanding the behavior of macroscopic systems starting from the atomic nature of matter. For example, we know that water consists of molecules of hydrogen and oxygen. We also know that the laws of classical and quantum mechanics determine the behavior of molecules at the microscopic level. The goal of *statistical mechanics* is to begin with the microscopic laws of physics that govern the behavior of the constituents of the system and deduce the properties of the system as a whole. Statistical mechanics is the bridge between the microscopic and macroscopic worlds.

Thermodynamics and statistical mechanics assume that the macroscopic properties of the system do not change with time on the average. Thermodynamics describes the change of a macroscopic system from one equilibrium state to another. Questions 8 and 9 concern macroscopic phenomena that change with time. Related areas are *nonequilibrium thermodynamics* and *fluid mechanics* from the macroscopic point of view and *nonequilibrium statistical mechanics* from the microscopic point of view. Although there has been progress in our understanding of nonequilibrium phenomena such as turbulent flow and hurricanes, our understanding of nonequilibrium phenomena is much less advanced than our understanding of equilibrium systems. Because understanding the properties of macroscopic systems that are independent of time is easier, we will focus our attention on equilibrium systems and consider questions such as those in Questions 1–7.

1.2 Some Qualitative Observations

We begin our discussion of macroscopic systems by considering a glass of water. We know that if we place a glass of hot water into a cool room, the hot water cools until its temperature equals that of the room. This simple observation illustrates two important properties associated with macroscopic systems – the importance of *temperature* and the *arrow of time*. Temperature is familiar because it is associated with the physiological sensation of hot and cold and is important in our everyday experience. We will find that temperature is a subtle concept.

The direction or arrow of time is an even more subtle concept. Have you ever observed a glass of water at room temperature spontaneously become hotter? Why not? What other phenomena exhibit a direction of time? Time has a direction as is expressed by the nursery rhyme:

> *Humpty Dumpty sat on a wall*
> *Humpty Dumpty had a great fall*
> *All the king's horses and all the king's men*
> *Couldn't put Humpty Dumpty back together again.*

Is there a direction of time for a single particle? Newton's second law for a single particle, $\mathbf{F} = d\mathbf{p}/dt$, implies that the motion of particles is *time reversal invariant*, that is, Newton's second law looks the same if the time t is replaced by $-t$ and the momentum $\mathbf{p}$ by $-\mathbf{p}$. There is no direction of time at the microscopic level. Yet if we drop a basketball onto a floor, we know that it will bounce and eventually come to rest. Nobody has observed a ball at rest spontaneously begin to bounce, and then bounce higher and higher. So based on simple everyday observations, we can conclude that the behavior of macroscopic bodies and single particles is very different.

Unlike generations of about a century or so ago, we know that macroscopic systems such as a glass of water and a basketball consist of many molecules. Although the intermolecular forces in water produce a complicated trajectory for each molecule, the observable properties of water are easy to describe. Moreover, if we prepare two glasses of water under similar conditions, we would find that the observable properties of the water in each glass are indistinguishable, even though the motion of the individual particles in the two glasses would be very different.

Because the macroscopic behavior of water must be related in some way to the trajectories of its constituent molecules, we conclude that there must be a relation between the notion of temperature and mechanics. For this reason, as we discuss the behavior of the macroscopic properties of a glass of water and a basketball, it will be useful to discuss the relation of these properties to the motion of their constituent molecules.

For example, if we take into account that the bouncing ball and the floor consist of molecules, then we know that the total energy of the ball and the floor is conserved as the ball bounces and eventually comes to rest. What is the cause of the ball eventually coming to rest? You might be tempted to say the cause is "friction," but friction is just a name for an effective or phenomenological force. At the microscopic level we know that the fundamental forces associated with mass, charge, and the nucleus conserve the total energy. So if we take into account the molecules of the ball and the floor, their total energy is conserved. Conservation of energy does not explain why the inverse process does not occur, because such a process also would conserve the total energy. So a more fundamental explanation is that the ball comes to rest consistent with conservation of the total energy and consistent with some other principle of physics. We will learn

that this principle is associated with an increase in the *entropy* of the system. For now, entropy is only a name, and it is important only to understand that energy conservation is not sufficient to understand the behavior of macroscopic systems. (As for most concepts in physics, the meaning of entropy in the context of thermodynamics and statistical mechanics is very different than the way entropy is used by nonscientists.)

For now, the nature of entropy is vague, because we do not have an entropy meter like we do for energy and temperature. What is important at this stage is to understand why the concept of energy is not sufficient to describe the behavior of macroscopic systems.

By thinking about the constituent molecules, we can gain some insight into the nature of entropy. Let us consider the ball bouncing on the floor again. Initially, the energy of the ball is associated with the motion of its center of mass, that is, the energy is associated with one degree of freedom. However, after some time, the energy becomes associated with many degrees of freedom associated with the individual molecules of the ball and the floor. If we were to bounce the ball on the floor many times, the ball and the floor would each feel warm to our hands. So we can hypothesize that energy has been transferred from one degree of freedom to many degrees of freedom at the same time that the total energy has been conserved. Hence, we conclude that the entropy is a measure of how the energy is distributed over the degrees of freedom.

What other quantities are associated with macroscopic systems besides temperature, energy, and entropy? We are already familiar with some of these quantities. For example, we can measure the air *pressure* in a basketball and its *volume*. More complicated quantities are the *thermal conductivity* of a solid and the *viscosity* of oil. How are these macroscopic quantities related to each other and to the motion of the individual constituent molecules? The answers to questions such as these and the meaning of temperature and entropy will take us through many chapters.

1.3 Doing Work

We already have observed that hot objects cool, and cool objects do not spontaneously become hot; bouncing balls come to rest, and a stationary ball does not spontaneously begin to bounce. And although the total energy must be conserved in any process, the *distribution* of energy changes in an irreversible manner. We also have concluded that a new concept, the entropy, needs to be introduced to explain the direction of change of the distribution of energy.

Now let us take a purely macroscopic viewpoint and discuss how we can arrive at a similar qualitative conclusion about the asymmetry of nature. This viewpoint was especially important historically because of the lack of a microscopic theory of matter in the 19th century when the laws of thermodynamics were being developed.

Consider the conversion of stored energy into heating a house or a glass of water. The stored energy could be in the form of wood, coal, or animal and vegetable oils for example. We know that this conversion is easy to do using simple methods, for example, an open fireplace. We also know that if we rub our hands together, they will become warmer. In fact, there is no theoretical limit[1] to the efficiency at which we can convert stored energy to energy used for heating an object.

What about the process of converting stored energy into work? Work like many of the other concepts that we have mentioned is difficult to define. For now let us say that doing work is

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[1]Of course, the efficiency cannot exceed 100%.

equivalent to the raising of a weight (see Problem 1.22). To be useful, we need to do this conversion in a controlled manner and indefinitely. A single conversion of stored energy into work such as the explosion of a bomb might do useful work, such as demolishing an unwanted football stadium, but a bomb is not a useful device that can be recycled and used again. It is much more difficult to convert stored energy into work and the discovery of ways to do this conversion led to the industrial revolution. In contrast to the primitiveness of the open hearth, we have to build an *engine* to do this conversion.

Can we convert stored energy into work with 100% efficiency? On the basis of macroscopic arguments alone, we cannot answer this question and have to appeal to observations. We know that some forms of stored energy are more useful than others. For example, why do we bother to burn coal and oil in power plants even though the atmosphere and the oceans are vast reservoirs of energy? Can we mitigate global warming by extracting energy from the atmosphere to run a power plant? From the work of Kelvin, Clausius, Carnot and others, we know that we cannot convert stored energy into work with 100% efficiency, and we must necessarily "waste" some of the energy. At this point, it is easier to understand the reason for this necessary inefficiency by microscopic arguments. For example, the energy in the gasoline of the fuel tank of an automobile is associated with many molecules. The job of the automobile engine is to transform this energy so that it is associated with only a few degrees of freedom, that is, the rolling tires and gears. It is plausible that it is inefficient to transfer energy from many degrees of freedom to only a few. In contrast, transferring energy from a few degrees of freedom (the firewood) to many degrees of freedom (the air in your room) is relatively easy.

The importance of entropy, the direction of time, and the inefficiency of converting stored energy into work are summarized in the various statements of the *second law of thermodynamics*. It is interesting that historically, the second law of thermodynamics was conceived before the first law. As we will learn in Chapter 2, the first law is a statement of conservation of energy.

1.4 Quality of Energy

Because the total energy is conserved (if all energy transfers are taken into account), why do we speak of an "energy shortage"? The reason is that energy comes in many forms and some forms are more useful than others. In the context of thermodynamics, the usefulness of energy is determined by its ability to do work.

Suppose that we take some firewood and use it to "heat" a sealed room. Because of energy conservation, the energy in the room plus the firewood is the same before and after the firewood has been converted to ash. But which form of the energy is more capable of doing work? You probably realize that the firewood is a more useful form of energy than the "hot air" that exists after the firewood is burned. Originally the energy was stored in the form of chemical (potential) energy. Afterward the energy is mostly associated with the motion of the molecules in the air. What has changed is not the total energy, but its ability to do work. We will learn that an increase in entropy is associated with a loss of ability to do work. We have an entropy problem, not an energy shortage.

1.5   Some Simple Simulations

So far we have discussed the behavior of macroscopic systems by appealing to everyday experience and simple observations. We now discuss some simple ways that we can *simulate* the behavior of macroscopic systems, which consist of the order of 10^{23} particles. Although we cannot simulate such a large system on a computer, we will find that even relatively small systems of the order of a hundred particles are sufficient to illustrate the qualitative behavior of macroscopic systems.

Consider a macroscopic system consisting of particles whose internal structure can be ignored. In particular, imagine a system of N particles in a closed container of volume V and suppose that the container is far from the influence of external forces such as gravity. We will usually consider two-dimensional systems so that we can easily visualize the motion of the particles.

For simplicity, we assume that the motion of the particles is given by classical mechanics, that is, by Newton's second law. If the resultant equations of motion are combined with initial conditions for the positions and velocities of each particle, we can calculate, in principle, the trajectory of each particle and the evolution of the system. To compute the total force on each particle we have to specify the nature of the interaction between the particles. We will assume that the force between any pair of particles depends only on the distance between them. This simplifying assumption is applicable to simple liquids such as liquid argon, but not to water. We will also assume that the particles are not charged. The force between any two particles must be repulsive when their separation is small and weakly attractive when they are reasonably far apart. For simplicity, we will usually assume that the interaction is given by the Lennard-Jones potential, whose form is given by

$$u(r) = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right]. \tag{1.1}$$

A plot of the Lennard-Jones potential is shown in Figure 1.1. The r^{-12} form of the repulsive part of the interaction is chosen for convenience only and has no fundamental significance. However, the attractive $1/r^6$ behavior at large r is the van der Waals interaction.[2] The force between any two particles is given by $f(r) = -du/dr$.

Usually we want to simulate a gas or liquid in the bulk. In such systems the fraction of particles near the walls of the container is negligibly small. However, the number of particles that can be studied in a simulation is typically 10^3–10^6. For these relatively small systems, the fraction of particles near the walls of the container would be significant, and hence the behavior of such a system would be dominated by surface effects. The most common way of minimizing surface effects and to simulate more closely the properties of a bulk system is to use what are known as toroidal boundary conditions. These boundary conditions are familiar to computer game players. For example, a particle that exits the right edge of the "box," re-enters the box from the left side. In one dimension, this boundary condition is equivalent to taking a piece of wire and making it into a loop. In this way a particle moving on the wire never reaches the end.

Given the form of the interparticle potential, we can determine the total force on each particle due to all the other particles in the system. Given this force, we find the acceleration of each particle from Newton's second law of motion. Because the acceleration is the second derivative

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[2]The van der Waals interaction arises from an induced dipole-dipole effect. It is present in all molecules, but is important only for the heavier noble gas atoms. See <en.wikipedia.org/wiki/Van_der_Waals_force> or John J. Brehm and William J. Mullin, *Introduction to the Structure of Matter*, John Wiley & Sons (1989).
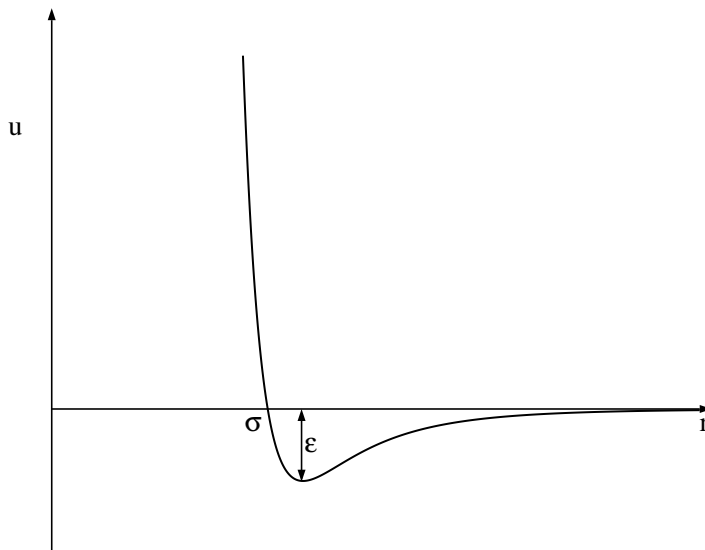
Figure 1.1: Plot of the Lennard-Jones potential $u(r)$, where r is the distance between the particles. Note that the potential is characterized by a length σ and an energy ϵ.

of the position, we need to solve a second-order differential equation for each particle (for each direction). (For a two-dimensional system of N particles, we would have to solve $2N$ differential equations.) These differential equations are coupled because the acceleration of a given particle depends on the positions of all the other particles. Obviously, we cannot solve the resultant set of coupled differential equations analytically. However, we can use relatively straightforward numerical methods to solve these equations to a good approximation. This way of simulating dense gases, liquids, solids, and biomolecules is called *molecular dynamics*.[3]

Approach to equilibrium. In the following we will explore some of the qualitative properties of macroscopic systems by doing some simple simulations. Before you actually do the simulations, think about what you believe the results will be. In many cases, the most valuable part of the simulation is not the simulation itself, but the act of thinking about a concrete model and its behavior. The simulations can be run as applications on your computer by downloading the Launcher from `<stp.clarku.edu/simulations/>`. The Launcher conveniently packages all the simulations (and a few more) discussed in these notes into a single file. Alternatively, you can run each simulation as an applet using a browser.

Problem 1.1. Approach to equilibrium

Suppose that we divide a box into three equal parts and place N particles at random in the middle third of the box.[4] The velocity of each particle is assigned at random and then the velocity of the center of mass is set to zero. At $t = 0$, we remove the "barriers" between the three parts and

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[3]The nature of molecular dynamics is discussed in Chapter 8 of Gould, Tobochnik, and Christian.

[4]We have divided the box into three parts so that the effects of the toroidal boundary conditions will not be as apparent as if we had initially confined the particles to one half of the box. The particles are placed at random
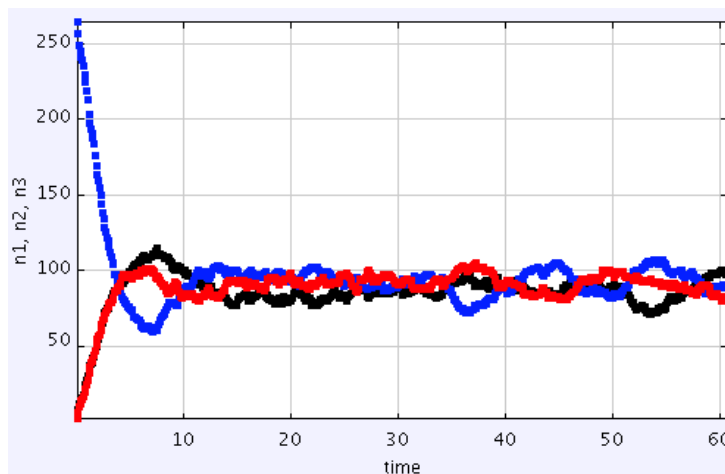
Figure 1.2: Evolution of the number of particles in each third of the box for $N = 270$. The particles were initially restricted to the middle third of the box. Toroidal boundary conditions are used in both directions. The initial velocities were assigned at random from a distribution corresponding to temperature $T = 5$.

watch the particles move according to Newton's equations of motion. We say that the removal of the barrier corresponds to the removal of an internal constraint. What do you think will happen? The applet/application at <stp.clarku.edu/simulations/approachtoequilibrium/md3.html> implements this simulation. (The initial density $\rho = N/A$ is $\rho = 0.2$.) Give your answers to the following questions before you do the simulation.

(a) Start the simulation with $N = 3$ particles. Does the system appear to show a direction of time?

(b) Choose $N = 27$ corresponding to $n_1 = 0$, $n_2 = N$, and $n_3 = 0$. What is the qualitative behavior of n_1, n_2, and n_3, the number of particles in each third of the box, as a function of the time t? Does the system appear to show a direction of time? Choose various values of N that are multiples of three up to $N = 270$. Is the direction of time better defined for larger N?

(c) Run the simulation for a sufficiently long time so that the mean number of particles in each cell is approximately equal. (For $N = 270$ this time is about $t \gtrsim 15$. It is possible to make a video of the motion of the particles (choose Video Capture under the Tools menu). Would you be able to tell if the video were played forward or backward for the various values of N? Does your conclusion about the direction of time become more certain as N increases?

The results of the simulations in Problem 1.1 might not seem very surprising until you start to think about them. Why does the system as a whole exhibit a direction of time when the motion

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with the constraint that no two particles can be closer than the length σ. This constraint prevents the initial force between any two particles from being too big, which would lead to the breakdown of the numerical method used to solve the differential equations.

of each particle is time reversible? Do the particles fill up the available space simply because the system becomes less dense?

To gain some more insight into these questions, we consider a simpler simulation. Imagine a closed box that is divided into two parts of equal volume. The left half initially contains N identical particles and the right half is empty. We then make a small hole in the partition between the two halves. What happens? Instead of simulating this system by solving Newton's equations for each particle, we adopt a simpler approach based on a probabilistic model. We assume that the system is so dilute that the particles do not interact with one another. Hence, the probability per unit time that a particle goes through the hole in the partition is the same for all particles regardless of the number of particles in either half. We also assume that the size of the hole is such that only one particle can pass through it in one unit of time.

One way to implement this model is to choose a particle at random and move it to the other side. This procedure is cumbersome, because our only interest is the number of particles on each side. That is, we need to know only n, the number of particles on the left side; the number on the right side is $N - n$. Because each particle has the same chance to go through the hole in the partition, the probability per unit time that a particle moves from left to right equals the number of particles on the left side divided by the total number of particles; that is, the probability of a move from left to right is n/N. The algorithm for simulating the evolution of the model is given by the following steps:

1. Generate a random number r from a uniformly distributed set of random numbers in the unit interval $0 \le r < 1$.

2. If $r \le n/N$, move a particle from left to right, that is, let $n \to n - 1$; otherwise, move a particle from right to left, $n \to n + 1$.

3. Increase the "time" by 1.

Problem 1.2. Particles in a box

(a) The applet at `<stp.clarku.edu/simulations/approachtoequilibrium/box.html>` implements this algorithm and plots the evolution of n. Describe the behavior of $n(t)$ for various values of N. Does the system approach equilibrium? How would you characterize equilibrium? In what sense is equilibrium better defined as N becomes larger? Does your definition of equilibrium depend on how the particles were initially distributed between the two halves of the box?

(b) When the system is in equilibrium, does the number of particles on the left-hand side remain a constant? If not, how would you describe the nature of equilibrium?

(c) If $N \gtrsim 32$, does the system return to its initial state during the time you have patience to watch the system?

(d) How does $\bar{n}$, the mean number of particles on the left-hand side, depend on N after the system has reached equilibrium? For simplicity, the program computes various averages from time $t = 0$. Why would such a calculation not yield the correct equilibrium average values? What is the purpose of the `Zero averages` button?

(e) Define the quantity σ by the relation

$$\sigma^2 = \overline{(n - \overline{n})^2}. \tag{1.2}$$

What does σ measure? What would be its value if n were constant? How does σ depend on N? How does the ratio $\sigma/\overline{n}$ depend on N?

From Problems 1.1 and 1.2 we conclude that after some time the macroscopic quantities of interest become independent of time on the average, and we say that the system has reached equilibrium. In equilibrium the macroscopic quantities exhibit fluctuations about their average values. We also learned that the relative fluctuations about the average become smaller as the number of constituents is increased and the details of the dynamics are irrelevant as far as the general tendency of macroscopic systems to approach equilibrium. These properties of macroscopic systems are independent of the dynamics, the nature of the particls, and many other details.

How can we understand why the systems considered in Problems 1.1 and 1.2 exhibit a direction of time? There are two general approaches that we can take. One way would be to study the dynamics of the system.[5] A much simpler way is to change the question and take advantage of the fact that the equilibrium state of a macroscopic system is independent of time on the average and hence time is irrelevant in equilibrium. For the simple system considered in Problem 1.2 we will see that counting the number of ways that the particles can be distributed between the two halves of the box will give us much insight into the nature of equilibrium. This information tells us nothing about the approach of the system to equilibrium, but it will give us insight into why there is a direction of time.

Let us call each distinct arrangement of the particles between the two halves of the box a *configuration* or in general, a *microstate*. A given particle can be in either the left half or the right half of the box. Because the halves are equivalent, a given particle is equally likely to be in either half if the system is in equilibrium. For $N = 2$, the four possible configurations are shown in Table 1.1. Note that each configuration has a probability of $1/4$ if the system is in equilibrium.

configuration		n	$W(n)$
L	L	2	1
L	R		
R	L	1	2
R	R	0	1

Table 1.1: The four possible ways in which $N = 2$ particles can be distributed between the two halves of a box. The quantity $W(n)$ is the number of configurations corresponding to the macroscopic state characterized by n.

Now let us consider $N = 4$ for which there are $2 \times 2 \times 2 \times 2 = 2^4 = 16$ configurations (see Table 1.2). From a macroscopic point of view, we do not care which particle is in which half of the box, but only the number of particles on the left. Hence, the macroscopic state or *macrostate* is specified by n. Let us assume as before that all configurations are equally probable in equilibrium. We see from Table 1.2 that there is only one configuration with all particles on the left and the most probable macrostate is $n = 2$.

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[5]The dynamics of the particles in Problem 1.2 is discussed in Section 1.13.1.

For larger N, the probability of the most probable macrostate with $n = N/2$ is much greater than the macrostate with $n = N$, which has a probability of only $1/2^N$ corresponding to a single configuration. The latter configuration is "special" and is said to be nonrandom, while the configurations with $n \approx N/2$, for which the distribution of the particles is approximately uniform, are said to be "random." So we can see that the equilibrium macrostate corresponds to the most probable state.

configuration				n	$W(n)$	$P(n)$
L	L	L	L	4	1	1/16
R	L	L	L	3		
L	R	L	L	3	4	4/16
L	L	R	L	3		
L	L	L	R	3		
R	R	L	L	2		
R	L	R	L	2		
R	L	L	R	2	6	6/16
L	R	R	L	2		
L	R	L	R	2		
L	L	R	R	2		
R	R	R	L	1		
R	R	L	R	1	4	4/16
R	L	R	R	1		
L	R	R	R	1		
R	R	R	R	0	1	1/16

Table 1.2: The sixteen possible ways in which $N = 4$ particles can be distributed between the two halves of a box. The quantity $W(n)$ is the number of configurations corresponding to the macroscopic state characterized by n. The probability $P(n)$ of the macrostate n is calculated assuming that each configuration is equally likely.

Problem 1.3. Enumeration of possible configurations

(a) Calculate the number of possible configurations for each macrostate n for $N = 8$ particles. What is the probability that $n = 8$? What is the probability that $n = 4$? It is possible to count the number of configurations for each n by hand if you have enough patience, but because there are a total of $2^8 = 256$ configurations, this counting would be very tedious. An alternative is to derive an expression for the number of ways that n particles out of N can be in the left half of the box. One way to motivate such an expression is to enumerate the possible configurations for smaller values of N and see if you can observe a pattern.

(b) From part (a) we see that the macrostate with $n = N/2$ is much more probable than the macrostate with $n = N$. Why?

We observe from this example and our counting of the number of configurations that the macroscates that give us the least amount of information about the associated microstates are the

most probable. Suppose that we wish to know where particle 1 is, given that $N = 4$. If $n = 4$, we know with certainty that particle 1 is on the left. If $n = 3$, the probability that particle 1 is on the left is 3/4. And if $n = 2$, we only know that particle 1 is on the left with probability 1/2. In this sense the macrostate $n = 2$ is more random than macrostates $n = 4$ and $n = 3$.

We also observed that if an isolated macroscopic system changes in time due to the removal of an internal constraint, it tends to evolve from a less random to a more random state. And once the system reaches its most random state, fluctuations corresponding to an appreciably nonuniform state are very rare. These observations and our reasoning based on counting the number of configurations corresponding to a particular macrostate allows us to conclude that

> *A system in a nonuniform macrostate will change in time on the average so as to approach its most random macrostate where it is in equilibrium.*

This conclusion is independent of the nature of the dynamics.

Note that our simulations involved watching the system evolve, but our discussion of the number of configurations corresponding to each macrostate did not involve the dynamics in any way. Instead this approach involved the enumeration of the configurations and assigning them equal probabilities assuming that the system is isolated and in equilibrium. We will find that it is much easier to understand equilibrium systems by ignoring the time altogether.

In the simulation of Problem 1.1 the total energy was conserved, and hence the macroscopic quantity of interest that changed from the specially prepared initial state with $n_2 = N$ to the most random macrostate with $n_2 \approx N/3$ was not the total energy. So what macroscopic quantity changed besides n_1, n_2, and n_3 (the number of particles in each third of the box)? Based on our previous discussions, we can tentatively say that the quantity that changed is the entropy. This statement is no more meaningful than saying that balls fall near the earth's surface because of gravity. We conjecture that the entropy is associated with the number of configurations associated with a given macrostate. If we make this association, we see that the entropy is greater after the system has reached equilibrium than in the system's initial state. Moreover, if the system were initially prepared in a random state, the mean value of n_2 and hence the entropy would not change. Hence, we can conclude the following:

> *The entropy of an isolated system increases or remains the same when an internal constraint is removed.*

This statement is equivalent to the second law of thermodynamics. You might want to skip to Chapter 4, where this identification of the entropy is made explicit.

As a result of the two simulations that we have considered and our discussions, we can make some additional tentative observations about the behavior of macroscopic systems.

Fluctuations in equilibrium. Once a system reaches equilibrium, the macroscopic quantities of interest do not become independent of the time, but *exhibit fluctuations about their average values.* That is, in equilibrium only the *average* values of the macroscopic variables are independent of time. For example, for the particles in the box problem $n(t)$ changes with t, but its average value $\overline{n}$ does not. [6] If N is large, fluctuations corresponding to a very nonuniform distribution of the

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[6]We have not been very careful to define the meaning of the average value $\overline{n}$. One way to do so is to average $n(t)$ over some interval of time. Another way is to do an ensemble average. That is, run the same simulation many times with different sets of random number sequences and then average the results at a given time (see Section 1.9).

particles almost never occur, and the relative fluctuations, $\sigma/\overline{n}$ (see (1.2)), become smaller as N is increased.[7]

History independence. The properties of *equilibrium systems are independent of their history*. For example, $\overline{n}$ would be the same whether we had started with $n(t = 0) = 0$ or $n(t = 0) = N$. In contrast, as members of the human race, we are all products of our history. One consequence of history independence is that it is easier to understand the properties of equilibrium systems by ignoring the dynamics of the particles. (The global constraints on the dynamics are important. For example, it is important to know if the total energy is a constant or not.) We will find that equilibrium statistical mechanics is essentially equivalent to counting configurations. The problem will be that this counting is difficult to do in general.

Need for statistical approach. Systems can be described in detail by specifying their *microstate*. Such a description corresponds to giving all the information that is possible. For a system of classical particles, a microstate corresponds to specifying the position and velocity of each particle. In our analysis of Problem 1.2, we specified only in which half of the box a particle was located, so we used the term configuration rather than microstate. The terms are frequently used interchangeably.

From our simulations, we see that the microscopic state of the system changes in a complicated way that is difficult to describe. However, from a macroscopic point of view, the description is much simpler. Suppose that we simulated a system of many particles and saved the trajectories of the particles as a function of time. What could we do with this information? If the number of particles is 10^6 or more or if we ran long enough, we would have a problem storing the data. Do we want to have a detailed description of the motion of each particle? Would this data give us much insight into the macroscopic behavior of the system? As we have found, the trajectories of the particles are not of much interest, and it is more useful to develop a probabilistic approach. That is, the presence of a large number of particles motivates us to use statistical methods. In Section 1.8 we will discuss another reason why a probabilistic approach is necessary.

We will find that the laws of thermodynamics depend on the fact that the number of particles in macroscopic systems is enormous. A typical measure of this number is Avogadro's number which is approximately 6×10^{23}, the number of atoms in a mole. When there are so many particles, predictions of the average properties of the system become meaningful, and deviations from the average behavior become less and less important as the number of atoms is increased.

An analogous example that illustrates the need for a statistical apporach is the stock market. Assume that you wish to invest in stocks with the goal of making money in the short term. And suppose that you could obtain information about all the transactions that are taking place in the world at any one time. This information might be very helpful in planning your investments, but its much too much information to be useful. Averages such as the Dow Jones, Standard & Poor 500, and the Nasdaq, which represent averages over subsets of stocks, are much more useful.

Equal a priori probabilities. In our analysis of the probability of each macrostate in Prob-

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[7]In this introductory chapter some of our general statements need to be qualified. For example, just because a system has constant macroscopic properties does not mean that it is in equilibrium. This statement applies only to isolated systems, for example, systems with fixed energy, volume, and number of particles. If the system is driven by external forces or currents that are time-independent, the observable macroscopic properties of the system can also be time independent, and the system is said to be in a *steady state*. For example, consider a metal bar with one end in contact with a large system at temperature T_{hot} and the other end in contact with a large system at temperature T_{cold}. If $T_{\text{hot}} > T_{\text{cold}}$, energy will be continually transported from the "hot" end to the "cold" end.

lem 1.2, we assumed that each configuration was equally probable. That is, each configuration of an isolated system occurs with equal probability if the system is in equilibrium. We will make this assumption explicit for isolated systems in Chapter 4.

Existence of different phases. So far our simulations of interacting systems have been restricted to dilute gases. What do you think would happen if we made the density higher? Would a system of interacting particles form a liquid or a solid if the temperature or the density were chosen appropriately? The existence of different phases is investigated in Problem 1.4.

Problem 1.4. Different phases

(a) The applet/application at `<stp.clarku.edu/simulations/lj.html>` simulates an isolated system of N particles interacting via the Lennard-Jones potential. Choose $N = 64$ and $L = 18$ so that the density $\rho = N/L^2 \approx 0.2$. The initial positions are chosen at random except that no two particles are allowed to be closer than σ. Run the simulation and satisfy yourself that this choice of density and resultant total energy corresponds to a gas. What is your criterion?

(b) Slowly lower the total energy of the system. (The total energy is lowered by rescaling the velocities of the particles.) If you are patient, you might be able to observe "liquid-like" regions. How are they different than "gas-like" regions?

(c) If you decrease the total energy further, you will observe the system in a state roughly corresponding to a solid. What is your criteria for a solid? Explain why the solid that we obtain in this way will not be a perfect crystalline solid.

(d) Describe the motion of the individual particles in the gas, liquid, and solid phases.

(e) Conjecture why a system of particles interacting via the Lennard-Jones potential in (1.1) can exist in different phases. Is it necessary for the potential to have an attractive part for the system to have a liquid phase? Is the attractive part necessary for there to be a solid phase? Describe a simulation that would help you answer this question.

It is remarkable that a system with the same interparticle interaction can be in different phases. At the microscopic level, the dynamics of the particles is governed by the same equations of motion. What changes? How does such a phase change occur at the microscopic level? Why doesn't a liquid crystallize immediately when its temperature is lowered quickly? What happens when it does begin to crystallize? We will find in later chapters that phase changes are examples of *cooperative* effects. Familiar examples of phase transitions are the freezing and boiling of water. Another example with which you might be familiar is the loss of magnetism of nickel or iron above a certain temperature (358°C for nickel). Other phase transitions are the occurrence of gridlock on a highway when the density of vehicles exceeds a certain value, and the occurrence of an epidemic as a function of immune response and population density.

1.6   Measuring the Pressure and Temperature

The obvious macroscopic variables that we can measure in our simulations of the system of particles interacting via the Lennard-Jones potential include the average kinetic and potential energies, the

number of particles, and the volume. We also learned that the entropy is a relevant macroscopic variable, but we have not learned how to determine it from a simulation.[8] We know from our everyday experience that there are at least two other macroscopic variables that are relevant for describing a macrostate, namely, the pressure and the temperature.

The pressure is relatively easy to measure because we are familiar with force and pressure from courses in mechanics. To remind you of the relation of the pressure to the momentum flux, consider N particles in a container of volume V and linear dimension L. The center of mass momentum of the particles is zero. For simplicity, we will consider an *ideal gas*, which is a system of particles in which we can ignore the forces between the particles. In this case the pressure arises from the collisions of the particles with the walls of the container. The pressure P is the force per unit area acting normal to the surface:

$$P = \frac{F_x}{A}. \tag{1.3}$$

We have written P as a scalar because the pressure is the same in all directions on the average. From Newton's second law, we can rewrite (1.3) as

$$P = \frac{1}{A}\frac{d(mv_x)}{dt}. \tag{1.4}$$

From (1.4) we see that the pressure is related to the amount of momentum transferred to the wall, which we have assumed to be reflecting.[9]

Problem 1.5. Nature of temperature

(a) Summarize what you know about temperature. What reasons do you have for thinking that it has something to do with energy?

(b) Discuss what happens to the temperature of a hot cup of coffee. What happens, if anything, to the temperature of its surroundings?

The relation between temperature and energy is not simple. For example, one way to increase the energy of a glass of water would be to lift it. However, this action would not affect the temperature of the water. So the temperature has nothing to do with the motion of the center of mass of the system. As another example, if we placed a container of water on a moving conveyor belt, the temperature of the water would not change. We also know that temperature is a property associated with many particles. It would be absurd to refer to the temperature of a single molecule.

This discussion suggests that temperature has something to do with energy, but it has missed the most fundamental property of temperature, that is, *the temperature is the quantity that becomes equal when two systems are allowed to exchange energy with one another*. (Think about what happens to a cup of hot coffee.) In Problem 1.6 we identify the temperature from this point of view for a system of particles.

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[8]We will find that it is very difficult to determine the entropy directly by making either measurements in the laboratory or during a simulation. Entropy, unlike pressure and temperature, has no mechanical analog.

[9]Because most of our simulations are done using toroidal boundary conditions, we will use the relation of the pressure to the *virial*, a mechanical quantity that involves all the particles in the system, not just those colliding with a wall. See Gould, Tobochnik, and Christian, Chapter 8. The relation of the pressure to the virial is usually considered in graduate courses in mechanics.

Problem 1.6. Identification of the temperature

(a) Consider two systems of particles interacting via the Lennard-Jones potential given in (1.1). Select the applet/application at `<stp.clarku.edu/simulations/thermalcontact.html>`. For system A, we take $N_A = 81$, $\epsilon_{AA} = 1.0$, and $\sigma_{AA} = 1.0$; for system B, we have $N_B = 64$, $\epsilon_{AA} = 1.5$, and $\sigma_{AA} = 1.2$. Both systems are in a square box with linear dimension $L = 12$. In this case, toroidal boundary conditions are not used and the particles also interact with fixed particles (with infinite mass) that make up the walls and the partition between them. Initially, the two systems are isolated from each other and from their surroundings. Run the simulation until each system appears to be in equilibrium. Does the kinetic energy and potential energy of each system change as the system evolves? Why? What is the mean potential and kinetic energy of each system? Is the total energy of each system fixed (to within numerical error)?

(b) Remove the barrier and let the two systems interact with one another.[10] We choose $\epsilon_{AB} = 1.25$ and $\sigma_{AB} = 1.1$. What quantity is exchanged between the two systems? (The volume of each system is fixed.)

(c) Monitor the kinetic and potential energy of each system. After equilibrium has been established between the two systems, compare the average kinetic and potential energies to their values before the two systems came into contact.

(d) We are looking for a quantity that is the same in both systems after equilibrium has been established. Are the average kinetic and potential energies the same? If not, think about what would happen if you doubled the N and the area of each system? Would the temperature change? Does it make more sense to compare the average kinetic and potential energies or the average kinetic and potential energies per particle? What quantity does become the same once the two systems are in equilibrium? Do any other quantities become approximately equal? What do you conclude about the possible identification of the temperature?

From the simulations in Problem 1.6, you are likely to conclude that the temperature is proportional to the average kinetic energy per particle. We will learn in Chapter 4 that the proportionality of the temperature to the average kinetic energy per particle holds only for a system of particles whose kinetic energy is proportional to the square of the momentum (velocity).

Another way of thinking about temperature is that temperature is what you measure with a thermometer. If you want to measure the temperature of a cup of coffee, you put a thermometer into the coffee. Why does this procedure work?

Problem 1.7. Thermometers

(a) Describe some of the simple thermometers with which you are familiar.

(b) On what physical principles do these thermometers operate?

(c) What requirements must a thermometer have?

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[10]In order to ensure that we can continue to identify which particle belongs to system A and system B, we have added a spring to each particle so that it cannot wander too far from its original lattice site.

Now lets imagine a simulation of a simple thermometer. Imagine a special particle, a "demon," that is able to exchange energy with a system of particles. The only constraint is that the energy of the demon E_d must be non-negative. The behavior of the demon is given by the following algorithm:

1. Choose a particle in the system at random and make a trial change in one of its coordinates.

2. Compute ΔE, the change in the energy of the system due to the change.

3. If $\Delta E \leq 0$, the system gives the surplus energy $|\Delta E|$ to the demon, $E_d \to E_d + |\Delta E|$, and the trial configuration is accepted.

4. If $\Delta E > 0$ and the demon has sufficient energy for this change, then the demon gives the necessary energy to the system, $E_d \to E_d - \Delta E$, and the trial configuration is accepted. Otherwise, the trial configuration is rejected and the configuration is not changed.

Note that the total energy of the system and the demon is fixed.

We consider the consequences of these simple rules in Problem 1.8. The nature of the demon is discussed further in Section 4.9.

Problem 1.8. The demon and the ideal gas

(a) The applet/application at `<stp.clarku.edu/simulations/demon>` simulates a demon that exchanges energy with an ideal gas of N particles moving in d spatial dimensions. Because the particles do not interact, the only coordinate of interest is the velocity of the particles. In this case the demon chooses a particle at random and changes its velocity in one of its d directions by an amount chosen at random between $-\Delta$ and $+\Delta$. For simplicity, the initial velocity of each particle is set equal to $+v_0\hat{x}$, where $v_0 = (2E_0/m)^{1/2}/N$, E_0 is the desired total energy of the system, and m is the mass of the particles. For simplicity, we will choose units such that $m = 1$. Choose $d = 1$, $N = 40$, and $E_0 = 10$ and determine the mean energy of the demon $\overline{E}_d$ and the mean energy of the system $\overline{E}$. Why is $\overline{E} \neq E_0$?

(b) What is $\overline{e}$, the mean energy per particle of the system? How do $\overline{e}$ and $\overline{E}_d$ compare for various values of E_0? What is the relation, if any, between the mean energy of the demon and the mean energy of the system?

(c) Choose $N = 80$ and $E_0 = 20$ and compare $\overline{e}$ and $\overline{E}_d$. What conclusion, if any, can you make?[11]

(d) Run the simulation for several other values of the initial total energy E_0 and determine how $\overline{e}$ depends on $\overline{E}_d$ for fixed N.

(e) From your results in part (d), what can you conclude about the role of the demon as a thermometer? What properties, if any, does it have in common with real thermometers?

(f) Repeat the simulation for $d = 2$. What relation do you find between $\overline{e}$ and $\overline{E}_d$ for fixed N?

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[11]There are finite size effects that are order $1/N$.

(g) Suppose that the energy momentum relation of the particles is not $\epsilon = p^2/2m$, but is $\epsilon = cp$, where c is a constant (which we take to be unity). Determine how $\bar{e}$ depends on $\overline{E}_d$ for fixed N and $d = 1$. Is the dependence the same as in part (d)?

(h) Suppose that the energy momentum relation of the particles is $\epsilon = Ap^{3/2}$, where A is a constant (which we take to be unity). Determine how $\bar{e}$ depends on $\overline{E}_d$ for fixed N and $d = 1$. Is this dependence the same as in part (d) or part (g)?

(i) The simulation also computes the probability $P(E_d)\delta E$ that the demon has energy between E_d and $E_d + \delta E$. What is the nature of the dependence of $P(E_d)$ on E_d? Does this dependence depend on the nature of the system with which the demon interacts?

1.7   Work, Heating, and the First Law of Thermodynamics

If you watch the motion of the individual particles in a molecular dynamics simulation, you would probably describe the motion as "random" in the sense of how we use random in everyday speech. The motion of the individual molecules in a glass of water would exhibit similar motion. Suppose that we were to expose the water to a low flame. In a simulation this process would roughly correspond to increasing the speed of the particles when they hit the wall. We say that we have transferred energy to the system *incoherently* because each particle would continue to move more or less at random.

You learned in your classical mechanics courses that the change in energy of a particle equals the work done on it and the same is true for a collection of particles as long as we do not change the energy of the particles in some other way at the same time. Hence, if we squeeze a plastic container of water, we would do *work* on the system, and we would see the particles near the wall move *coherently*. So we can distinguish two different ways of transferring energy to the system. That is, *heating transfers energy incoherently and doing work transfers energy coherently.*

Lets consider a molecular dynamics simulation again and suppose that we have increased the energy of the system by either compressing the system and doing work on it or by randomly increasing the speed of the particles that reach the walls of the container. Roughly speaking, the first way would initially increase the potential energy of interaction and the second way would initially increase the kinetic energy of the particles. If we increase the total energy by the same amount, could we tell by looking at the particle trajectories after equilibrium has been reestablished how the energy had been increased? The answer is no, because for a given total energy, volume, and number of particles, the kinetic energy and the potential energy would have unique equilibrium values. (See Problem 1.6 for a demonstration of this property.) We conclude that the energy of the gas can be changed by doing work on it or by heating it or by both processes. This statement is equivalent to the *first law of thermodynamics* and from the microscopic point of view is simply a statement of conservation of energy.

Our discussion implies that the phrase "adding heat" to a system makes no sense, because we cannot distinguish "heat energy" from potential energy and kinetic energy. Nevertheless, we frequently use the word "heat" in everyday speech. For example, we might way "Please turn on the heat" and "I need to heat my coffee." We will avoid such uses, and whenever possible avoid the use of the noun "heat." Why do we care? Because there is no such thing as heat! Once upon

a time, scientists thought that there was a fluid in all substances called *caloric* or heat that could flow from one substance to another. This idea was abandoned many years ago, but is still used in common language. Go ahead and use heat outside the classroom, but we won't use it here.

1.8   *The Fundamental Need for a Statistical Approach

In Section 1.5 we discussed the need for a statistical approach when treating macroscopic systems from a microscopic point of view. Although we can compute the trajectory (the position and velocity) of each particle for as long as we have patience, our disinterest in the trajectory of any particular particle and the overwhelming amount of information that is generated in a simulation motivates us to develop a statistical approach.

We now discuss why there is a more fundamental reason why we must use probabilistic methods to describe systems with more than a few particles. The reason is that under a wide variety of conditions, even the most powerful supercomputer yields positions and velocities that are meaningless! In the following, we will find that the trajectories in a system of many particles depend sensitively on the initial conditions. Such a system is said to be *chaotic*. This behavior forces us to take a statistical approach even for systems with as few as three particles.

As an example, consider a system of $N = 11$ particles moving in a box of linear dimension L (see the applet/application at `<stp.clarku.edu/simulations/sensitive.html>`). The initial conditions are such that all particles have the same velocity $v_x(i) = 1$, $v_y(i) = 0$, and the particles are equally spaced vertically, with $x(i) = L/2$ for $i = 1, \ldots, 11$ (see Fig. 1.3(a)). Convince yourself that for these special initial conditions, the particles will continue moving indefinitely in the x-direction (using toroidal boundary conditions).

Now let us stop the simulation and change the velocity of particle 6, such that $v_x(6) = 1.000001$. What do you think happens now? In Fig. 1.3(b) we show the positions of the particles at time $t = 8.0$ after the change in velocity of particle 6. Note that the positions of the particles are no longer equally spaced and the velocities of the particles are very different. So in this case, a small change in the velocity of one particle leads to a big change in the trajectories of all the particles.

Problem 1.9. Irreversibility

The applet/application at `<stp.clarku.edu/simulations/sensitive.html>` simulates a system of $N = 11$ particles with the special initial condition described in the text. Confirm the results that we have discussed. Change the velocity of particle 6 and stop the simulation at time t and reverse all the velocities. Confirm that if t is sufficiently short, the particles will return approximately to their initial state. What is the maximum value of t that will allow the system to return to its initial positions if t is replaced by $-t$ (all velocities reversed)?

An important property of chaotic systems is their *extreme sensitivity to initial conditions*, that is, the trajectories of two identical systems starting with slightly different initial conditions will diverge exponentially in a short time. For such systems we cannot predict the positions and velocities of the particles very far into the future because even the slightest error in our measurement of the initial conditions would make our prediction entirely wrong if the elapsed time is sufficiently long. That is, we cannot answer the question, "Where is particle 2 at time t?" if t is sufficiently
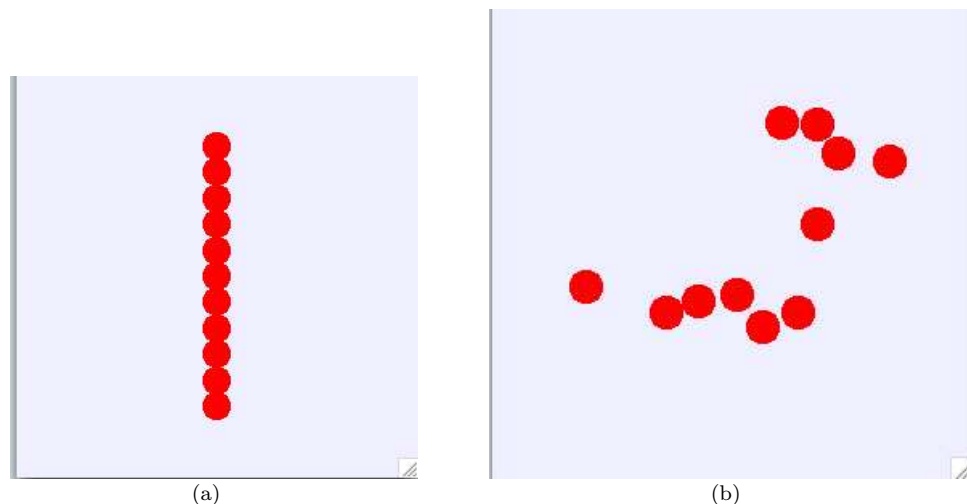
Figure 1.3: (a) A special initial condition for $N = 11$ particles such that their motion remains parallel indefinitely. (b) The positions of the particles at time $t = 8.0$ after the change in $v_x(6)$. The only change in the initial condition from part (a) is that $v_x(6)$ was changed from 1 to 1.000001.

long. It might be disturbing to realize that our answers are meaningless if we ask the wrong questions.

Although Newton's equations of motion are time reversible, this reversibility cannot be realized in practice for chaotic systems. Suppose that a chaotic system evolves for a time t and all the velocities are reversed. If the system is allowed to evolve for an additional time t, the system will not return to its original state unless the velocities are specified with infinite precision. This lack of practical reversibility is related to what we observe in macroscopic systems. If you pour milk into a cup of coffee, the milk becomes uniformly distributed throughout the cup. You will never see a cup of coffee spontaneously return to the state where all the milk is at the surface because to do so, the positions and velocities of the milk and coffee molecules must be chosen so that the molecules of milk return to this very special state. Even the slightest error in the choice of positions and velocities will ruin any chance of the milk returning to the surface. This sensitivity to initial conditions provides the foundation for the arrow of time.

1.9 *Time and Ensemble Averages

We have seen that although the computed trajectories are meaningless for chaotic systems, averages over the trajectories are meaningful. That is, although a computed trajectory might not be the one that we thought we were computing, the positions and velocities that we compute are consistent with the constraints we have imposed, in this case, the total energy E, the volume V, and the number of particles N. This reasoning suggests that macroscopic properties such as the temperature and pressure must be expressed as averages over the trajectories.

Solving Newton's equations numerically as we have done in our simulations yields a time average. If we do a laboratory experiment to measure the temperature and pressure, our measurements also would be equivalent to a time average. As we have mentioned, time is irrelevant in equilibrium. We will find that it is easier to do calculations in statistical mechanics by doing an *ensemble* average. We will discuss ensemble averages in Chapter 3. In brief an ensemble average is over many mental copies of the system that satisfy the same known conditions. A simple example might clarify the nature of these two types of averages. Suppose that we want to determine the probability that the toss of a coin results in "heads." We can do a time average by taking one coin, tossing it in the air many times, and counting the fraction of heads. In contrast, an ensemble average can be found by obtaining many similar coins and tossing them into the air at one time.

It is reasonable to assume that the two ways of averaging are equivalent. This equivalence is called the *quasi-ergodic hypothesis*. The use of the term "hypothesis" might suggest that the equivalence is not well accepted, but it reminds us that the equivalence has been shown to be rigorously true in only a few cases. The sensitivity of the trajectories of chaotic systems to initial conditions suggests that a classical system of particles moving according to Newton's equations of motion passes through many different microstates corresponding to different sets of positions and velocities. This property is called *mixing*, and it is essential for the validity of the quasi-ergodic hypothesis.

In summary, macroscopic properties are averages over the microscopic variables and give predictable values if the system is sufficiently large. One goal of statistical mechanics is to give a microscopic basis for the laws of thermodynamics. In this context it is remarkable that these laws depend on the fact that gases, liquids, and solids are chaotic systems. Another important goal of statistical mechanics is to calculate the macroscopic properties from a knowledge of the intermolecular interactions.

1.10 *Models of Matter

There are many models of interest in statistical mechanics, corresponding to the wide range of macroscopic systems found in nature and made in the laboratory. So far we have discussed a simple model of a classical gas and used the same model to simulate a classical liquid and a solid.

One key to understanding nature is to develop models that are simple enough to analyze, but that are rich enough to show the same features that are observed in nature. Some of the more common models that we will consider include the following.

1.10.1 The ideal gas

The simplest models of macroscopic systems are those for which there is no interaction between the individual particles. For example, if a system of particles is very dilute, collisions between the particles will be rare and can be neglected under most circumstances. In the limit that the interactions between the particles can be neglected completely, the model is known as the *ideal gas*. The classical ideal gas allows us to understand much about the behavior of dilute gases, such as those in the earth's atmosphere. The quantum version will be useful in understanding

blackbody radiation (Section 6.9), electrons in metals (Section 6.10), the low temperature behavior of crystalline solids (Section 6.11), and a simple model of superfluidity (Section 6.12).

The term "ideal gas" is a misnomer because it can be used to understand the properties of solids and other interacting particle systems under certain circumstances, and because in many ways the neglect of interactions is not ideal. The historical reason for the use of this term is that the neglect of interparticle interactions allows us to do some calculations analytically. However, the neglect of interparticle interactions raises other issues. For example, how does an ideal gas reach equilibrium if there are no collisions between the particles?

1.10.2   Interparticle potentials

As we have mentioned, the most popular form of the potential between two neutral atoms is the Lennard-Jones potential[12] given in (1.1). This potential has an weak attractive tail at large r and is strongly repulsive at shorter distances. The Lennard-Jones potential is appropriate for closed-shell systems, that is, rare gases such as Ar or Kr. The Lennard-Jones potential is a very important model system and is the standard potential for studies where the focus is on fundamental issues, rather than on the properties of a specific material.

An even simpler interaction is the hard core interaction given by

$$V(r) = \begin{cases} \infty & (r \leq \sigma) \\ 0. & (r > \sigma) \end{cases} \tag{1.5}$$

A system of particles interacting via (1.5) is called a system of hard spheres, hard disks, or hard rods depending on whether the spatial dimension is three, two, or one, respectively. Note that $V(r)$ in (1.5) is purely repulsive.

1.10.3   Lattice models

In another class of models, the positions of the particles are restricted to a lattice or grid and the momenta of the particles are irrelevant. In the most popular model of this type the "particles" correspond to magnetic moments. At high temperatures the magnetic moments are affected by external magnetic fields, but the interaction between moments can be neglected.

The simplest, nontrivial model that includes interactions is the *Ising model*, the most important model in statistical mechanics. The model consists of spins located on a lattice such that each spin can take on one of two values designated as up and down or ± 1. The interaction energy between two neighboring spins is $-J$ if the two spins are in the same state and $+J$ if they are in opposite states. One reason for the importance of this model is that it is one of the simplest to have a phase transition, in this case, a phase transition between a ferromagnetic state and a paramagnetic state.

If we consider spin up to correspond to a particle and spin down to correspond to an empty site, then the same model, now called a lattice gas, can be used to understand the transition from

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[12]This potential is named after John Lennard-Jones, 1894–1954, a theoretical chemist and physicist at Cambridge University.

gas to fluid. The Ising model and the corresponding lattice gas model are the simplest models to exhibit a phase transition.

We will focus on three classes of models – the ideal classical and quantum gas, classical systems of interacting particles, and the Ising model and its extensions. These models will be used in many contexts to illustrate the ideas and techniques of statistical mechanics.

1.11   Importance of Simulations

Only simple models such as the ideal gas or special cases such as the two-dimensional Ising model can be analyzed by analytical methods. Much of what is done in statistical mechanics is to establish the general behavior of a model and then relate it to the behavior of another model. This way of understanding is not as strange as it first might appear. How many different systems in classical mechanics can be solved exactly?

Statistical physics has grown in importance over the past several decades because powerful computers and new computer algorithms have allowed us to explore the consequences of more complex systems. Simulations play an important intermediate role between theory and experiment. As our models become more realistic, it is likely that they will require the computer for understanding many of their properties. In a simulation we start with a microscopic model for which the variables represent the microscopic constituents and determine the consequences of their interactions. Frequently the goal of our simulations is to explore these consequences so that we have a better idea of what type of theoretical analysis might be possible and what type of laboratory experiments should be done. Simulations allow us to compute many different kinds of quantities, some of which cannot be measured in a laboratory experiment.

Not only can we simulate reasonably realistic models, we also can study models that are impossible to realize in the laboratory, but are useful for providing a deeper theoretical understanding of real systems. For example, a comparison of the behavior of a model in three and four spatial dimensions can yield insight into why the three-dimensional system behaves the way it does.

Simulations cannot replace laboratory experiments and are limited by the finite size of the systems and by the short duration of our runs. For example, at present the longest simulations of simple liquids are for no more than 10^{-6} s.

Not only have simulations made possible new ways of doing research, they also make it possible to illustrate the important ideas of statistical mechanics. We hope that the simulations that we have already discussed have already convinced you of their utility. For this reason, we will consider many simulations throughout these notes.

1.12   Summary

This introductory chapter has been designed to whet your appetite, and at this point it is not likely that you will fully appreciate the significance of such concepts as entropy and the direction of time. We are reminded of the book, *All I Really Need to Know I Learned in Kindergarten*.[13]

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[13]Robert Fulghum, *All I Really Need to Know I Learned in Kindergarten*, Ballantine Books (2004).

In principle, we have discussed most of the important ideas in thermodynamics and statistical physics, but it will take you a while before you understand these ideas in any depth.

We also have not discussed the tools necessary to solve any problems. Your understanding of these concepts and the methods of statistical and thermal physics will increase as you work with these ideas in different contexts. You will find that the unifying aspects of thermodynamics and statistical mechanics are concepts such as the nature of equilibrium, the direction of time, and the existence of cooperative effects and different phases. However, there is no unifying equation such as Newton's second law of motion in mechanics, Maxwell's equations in electrodynamics, and Schrödinger's equation in nonrelativistic quantum mechanics.

There are many subtleties that we have glossed over so that we could get started. For example, how good is our assumption that the microstates of an isolated system are equally probable? This question is a deep one and has not been completely answered. The answer likely involves the nature of chaos. Chaos seems necessary to insure that the system will explore a large number of the available microstates, and hence make our assumption of equal probabilities valid. However, we do not know how to tell a priori whether a system will behave chaotically or not.

Most of our discussion concerns equilibrium behavior. The "dynamics" in thermodynamics refers to the fact that we can treat a variety of thermal processes in which a system moves from one equilibrium state to another. Even if the actual process involves non-equilibrium states, we can replace the non-equilibrium states by a series of equilibrium states which begin and end at the same equilibrium states. This type of reasoning is analogous to the use of energy arguments in mechanics. A ball can roll from the top of a hill to the bottom, rolling over many bumps and valleys, but as long as there is no dissipation due to friction, we can determine the ball's motion at the bottom without knowing anything about how the ball got there.

The techniques and ideas of statistical mechanics are now being used outside of traditional condensed matter physics. The field theories of high energy physics, especially lattice gauge theories, use the methods of statistical mechanics. New methods of doing quantum mechanics convert calculations to path integrals that are computed numerically using methods of statistical mechanics. Theories of the early universe use ideas from thermal physics. For example, we speak about the universe being quenched to a certain state in analogy to materials being quenched from high to low temperatures. We already have seen that chaos provides an underpinning for the need for probability in statistical mechanics. Conversely, many of the techniques used in describing the properties of dynamical systems have been borrowed from the theory of phase transitions, one of the important areas of statistical mechanics.

Thermodynamics and statistical mechanics have traditionally been applied to gases, liquids, and solids. This application has been very fruitful and is one reason why condensed matter physics, materials science, and chemical physics are rapidly evolving and growing areas. Examples of new materials include high temperature superconductors, low-dimensional magnetic and conducting materials, composite materials, and materials doped with various impurities. In addition, scientists are taking a new look at more traditional condensed systems such as water and other liquids, liquid crystals, polymers, crystals, alloys, granular matter, and porous media such as rocks. And in addition to our interest in macroscopic systems, there is growing interest is *mesoscopic* systems, systems that are neither microscopic nor macroscopic, but are in between, that is, between $\sim 10^2$ to $\sim 10^6$ particles.

Thermodynamics might not seem to be as interesting to you when you first encounter it.

However, an understanding of thermodynamics is important in many contexts including societal issues such as global warming, electrical energy production, fuel cells, and other alternative energy sources.

The science of information theory uses many ideas from statistical mechanics, and recently, new optimization methods such as simulated annealing have been borrowed from statistical mechanics.

In recent years statistical mechanics has evolved into the more general field of *statistical physics*. Examples of systems of interest in the latter area include earthquake faults, granular matter, neural networks, models of computing, genetic algorithms, and the analysis of the distribution of time to respond to email. Statistical physics is characterized more by its techniques than by the problems that are its interest. This universal applicability makes the techniques more difficult to understand, but also makes the journey more exciting.

1.13 Supplementary Notes

1.13.1 Approach to Equilibrium

In Problem 1.2 we learned that $n(t)$ decreases in time from its initial value to its equilibrium value in an almost deterministic manner if $N \gg 1$. It is instructive to derive the time dependence of $n(t)$ to show explicitly how chance can generate deterministic behavior.

We know that if we run the simulation once, $n(t)$ will exhibit fluctuations and not decay monotonically to equilibrium. Suppose that we do the simulation many times and average the results of each run at a given time t. As discussed in Section 1.9, this average is an ensemble average, which we will denote as $\overline{n}(t)$. If there are $\overline{n}(t)$ particles on the left side after t moves, the change in $\overline{n}$ in the time interval Δt is given by

$$\Delta\overline{n} = \Big[\frac{-\overline{n}(t)}{N} + \frac{N - \overline{n}(t)}{N}\Big]\Delta t. \tag{1.6}$$

(We defined the time so that the time interval $\Delta t = 1$ in our simulations.) Equation (1.6) is equivalent to assuming that the change in $\overline{n}$ in one time step is equal to the probability that a particle is removed from the left plus the probability that it is added to the right. If we treat $\overline{n}$ and t as continuous variables and take the limit $\Delta t \to 0$, we have

$$\frac{\Delta\overline{n}}{\Delta t} \to \frac{d\overline{n}}{dt} = 1 - \frac{2\overline{n}(t)}{N}. \tag{1.7}$$

The solution of the differential equation (1.7) is

$$\overline{n}(t) = \frac{N}{2}\Big[1 + e^{-2t/N}\Big], \tag{1.8}$$

where we have used the initial condition $\overline{n}(t = 0) = N$. Note that $\overline{n}(t)$ decays exponentially to its equilibrium value $N/2$. How does this form (1.8) compare to your simulation results for various values of N?

Note that we can define a *relaxation time* τ as the time it takes the difference $[\overline{n}(t) - N/2]$ to decrease to $1/e$ of its initial value. Because $\tau = N/2$, $\overline{n}(t)$ for large N varies slowly and we are justified in rewriting the difference equation (1.6) as a differential equation.

Problem 1.10. Independence of initial conditions

Show that if the number of particles on the left-hand side of the box at $t = 0$ is equal to $n(0)$ rather than $N/2$, the solution of (1.7) is

$$\bar{n}(t) = \frac{N}{2} - \frac{N}{2}\Big[1 - \frac{2n(0)}{N}\Big]e^{-2t/N}. \tag{1.9}$$

Note that $\bar{n}(t) \to N/2$ as $t \to \infty$ independent of the value of $n(0)$.

1.13.2 Mathematics refresher

As discussed in Section 1.12, there is no unifying equation in statistical mechanics such as Newton's second law of motion to be solved in a variety of contexts. For this reason we will not use only one mathematical tool, but instead will need many tools. Section 1.13.2 summarizes the mathematics of thermodynamics which makes much use of partial derivatives. Appendix A summarizes some of the mathematical formulas and relations that we will use. If you can do the following problems, you have a good background for most of the mathematics that we will use in the following chapters.

Problem 1.11. Derivatives

Calculate the derivative with respect to x of the following functions: e^x, e^{3x}, e^{ax}, $\ln x$, $\ln x^2$, $\ln 3x$, $\ln 1/x$, $\sin x$, $\cos x$, $\sin 3x$, and $\cos 2x$.

Problem 1.12. Integrals

Calculate the following integrals:

$$\int_1^2 \frac{dx}{2x^2} \tag{1.10a}$$

$$\int_1^2 \frac{dx}{4x} \tag{1.10b}$$

$$\int_1^2 e^{3x}\,dx \tag{1.10c}$$

Problem 1.13. Partial derivatives

Calculate the partial derivative of $x^2 + xy + 3y^2$ with respect to x and y.

Vocabulary

thermodynamics, statistical mechanics
macroscopic system
configuration, microstate, macrostate
specially prepared state, equilibrium, fluctuations
thermal contact, temperature
sensitivity to initial conditions
models, computer simulations

Additional Problems

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Table 1.3: Listing of inline problems.

Problem 1.14. The dye is cast

(a) What do you observe when a small amount of black dye is placed in a glass of water?

(b) Suppose that a video were taken of this process and the video was run backward without your knowledge. Would you be able to observe whether the video was being run forward or backward?

(c) Suppose that you could watch a video of the motion of an individual ink molecule. Would you be able to know that the video was being shown forward or backward?

Problem 1.15. Irreversibility in everyday experience

Describe several examples based on your everyday experience that illustrate the unidirectional temporal behavior of macroscopic systems. For example, what happens to ice placed in a glass of water at room temperature? What happens if you make a small hole in an inflated tire? What happens if you roll a ball on a hard surface?

Problem 1.16. Fluids as metaphor

(a) In what contexts can we treat water as a fluid? In what context can water not be treated as a fluid?

(b) Why is "heat" treated as a fluid in everyday speech? After all most people are not familiar with the caloric theory of heat!

(c) What evidence can you cite from your everyday experience that the molecules in a glass of water or in the surrounding air are in seemingly endless random motion?

Problem 1.17. Temperature

How do you know that two objects are at the same temperature? How do you know that two bodies are at different temperatures?

Problem 1.18. Time reversal invariance

Show that Newton's equations for a system of N particles are time reversal invariant.

Problem 1.19. Properties of macroscopic systems

Summarize your understanding of the properties of macroscopic systems.

Problem 1.20. What's in a name?

Ask some friends why a ball falls when released above the Earth's surface. Explain why the answer "gravity" is not really an explanation.

Problem 1.21. Randomness

What is your understanding of the concept of "randomness" at this time? Does "random motion" imply that the motion occurs according to unknown rules?

Problem 1.22. Meaning of abstract concepts

Write a paragraph on the meanings of the abstract concepts, "energy" and "justice." (See the Feynman Lectures, Vol. 1, Chapter 4, for a discussion of why it is difficult to define such abstract concepts.)

Problem 1.23. Bicycle pump

Suppose that the handle of a plastic bicycle pump is rapidly pushed inward. Predict what happens to the temperature of the air inside the pump and explain your reasoning. (This problem is given here to determine how you think about this type of problem at this time. Similar problems will appear in later chapters to see if and how your reasoning has changed.)

Problem 1.24. Granular matter

A box of glass beads is another example of a macroscopic system if the number of beads is sufficiently large. In what ways is such a system different than the macroscopic systems such as a glass of water that we have discussed in this chapter?

Suggestions for Further Reading

P. W. Atkins, *The Second Law*, Scientific American Books (1984). A qualitative introduction to the second law of thermodynamics and its implications.

J. G. Oliveira and A.-L. Barabási, "Darwin and Einstein correspondence patterns," Nature **437**, 1251 (2005). The authors found the probability that Darwin and Einstein would respond to a letter in τ days is well approximated by a power law, $P(\tau) \sim \tau^{-a}$ with $a \approx 3/2$. How long does it take you to respond to an email?

Manfred Eigen and Ruthild Winkler, *How the Principles of Nature Govern Chance*, Princeton University Press (1993).

Richard Feynman, R. B. Leighton, and M. Sands, *Feynman Lectures on Physics*, Addison-Wesley (1964). Volume 1 has a very good discussion of the nature of energy and work.

Harvey Gould, Jan Tobochnik, and Wolfgang Christian, *An Introduction to Computer Simulation Methods*, third edition, Addison-Wesley (2006), `<sip.clarku.edu/>`.

F. Reif, *Statistical Physics*, Volume 5 of the Berkeley Physics Series, McGraw-Hill (1967). This text was probably the first to make use of computer simulations to explain some of the basic properties of macroscopic systems.

Jeremy Rifkin, *Entropy: A New World View*, Bantom Books (1980). Although this book raises some important issues, it, like many other popular books and articles, it misuses the concept of entropy. For more discussion on the meaning of entropy and how it should be introduced, see `<www.entropysite.com/>` and `<www.entropysimple.com/>`.

A listing of many of the textbooks on statistical mechanics and thermodynamics can be found at `<stp.clarku.edu/books>`. Some of our favorites are listed in the following. It is a good idea to look at several books while you are learning a subject for the first time. Sometimes the same argument with slightly different wording can seem clearer.

Daniel J. Amit and Yosef Verbin, *Statistical Physics*, World Scientific (1999).

Ralph Baierlein, *Thermal Physics*, Cambridge University Press, New York (1999).

Craig F. Bohren and Bruce A. Albrecht, *Atmospheric Thermodynamics*, Oxford University Press (1998).

Stephen Blundell and Katherine Blundell, *Thermal Physics*, Oxford University Press (2006).

Debashish Chowdhury and Dietrich Stauffer, *Principles of Equilibrium Statistical Mechanics*, Wiley-VCH (2000). This text is more advanced than ours, but contains many accessible gems.

F. Mandl, *Statistical Physics*, second edition, John Wiley & Sons (1988).

F. Reif, *Fundamentals of Statistical and Thermal Physics*, McGraw-Hill (1965). Instructors will notice that our presentation owns a large debt to the two books by Reif on statistical physics.

Daniel V. Schroeder, *An Introduction to Thermal Physics*, Addison-Wesley (2000). Schroeder's text has many interesting applications.

Chapter 2

Thermodynamic Concepts and Processes

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14 January 2008

We introduce the concepts of temperature, energy, work, heating, entropy, engines, and the laws of thermodynamics and related macroscopic concepts.

2.1   Introduction

In this chapter we will discuss ways of thinking about macroscopic systems and introduce the basic concepts of thermodynamics. Because these ways of thinking are very different from the ways that we think about microscopic systems, most students of thermodynamics initially find it difficult to apply the abstract principles of thermodynamics to concrete problems. However, the study of thermodynamics has many rewards as was appreciated by Einstein:

> A theory is the more impressive the greater the simplicity of its premises, the more different kinds of things it relates, and the more extended its area of applicability. Therefore the deep impression that classical thermodynamics made to me. It is the only physical theory of universal content which I am convinced will never be overthrown, within the framework of applicability of its basic concepts.[1]

The essence of thermodynamics can be summarized by two laws: (1) Energy is conserved and (2) entropy increases. These statements of the laws are deceptively simple. What is energy? You are probably familiar with the concept of energy from other courses, but can you define it? Abstract concepts such as energy and entropy are not easily defined nor understood. However, as you apply these concepts in a variety of contexts, you will gradually come to understand them.[2]

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[1] A. Einstein, *Autobiographical Notes*, Open Court Publishing Company (1991).
[2] The nature of thermodynamics is nicely summarized in the song, First and Second Law, by Michael Flanders and Donald Swann, <www.nyanko.pwp.blueyonder.co.uk/fas/anotherhat_first.html>.
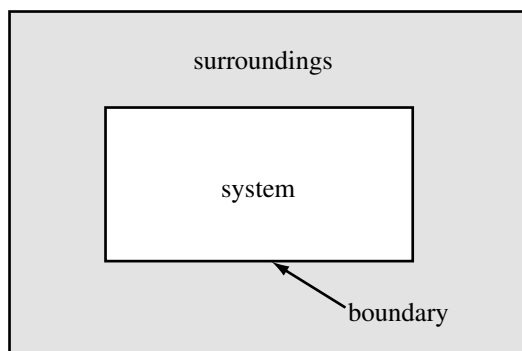
Figure 2.1: Schematic of a thermodynamic system.

Because thermodynamics describes the macroscopic properties of macroscopic systems without appeal to arguments based on the nature of their microcopic constituents, the concepts of energy and entropy in this context are very abstract. So why bother introducing thermodynamics as a subject in its own right, when we could more easily introduce energy and entropy from microscopic considerations? Besides the intellectual challenge, an important reason is that the way of thinking required by thermodynamics can be applied in other contexts where the microscopic properties of the system are poorly understood or very complex. However, there is no need to forget the general considerations that we discussed in Chapter 1. And you are also encouraged to read ahead, especially in Chapter 4 where the nature of entropy is introduced from first principles.

2.2 The System

The first step in applying thermodynamics is to select the appropriate part of the universe of interest. This part of the universe is called the *system*. In this context the term system is simply anything that we wish to consider. The system is defined by a closed surface called the *boundary* (see Figure 2.1)). The boundary may be real or imaginary and may or may not be fixed in shape or size. The system might be as obvious as a block of steel, water in a container, or the gas in a balloon. Or the system might be defined by an imaginary fixed boundary within a flowing liquid.

The remainder of the universe is called the *surroundings*. We usually take the surroundings to be that part of the universe that is affected by changes in the system. For example, if an ice cube is placed in a glass of water, we might take the ice to be the system and the water to be the surroundings. In this case the amount of water would need to be very large compared to the size of the ice cube. In this example we could ignore the interaction of the ice cube with the air in the room and the interaction of the glass with the table on which the glass is set. However, if the size of the ice cube and the amount of water were about the same, we would need to to consider the ice cube and water to be the system and the air in the room to be the surroundings. The choice depends on the questions of interest. The surroundings need not surround the system.

2.3 Thermodynamic Equilibrium

Macroscopic systems often exhibit some memory of their recent history. A stirred cup of tea continues to swirl. But if we wait for a while, we will no longer observe any large scale motion. A hot cup of coffee cools and takes on the temperature of its surroundings regardless of its initial temperature. The final states of such systems are called *equilibrium* states, which are characterized by their time independence, history independence, and relative simplicity.

Time independence means that the measurable macroscopic properties (such as the temperature, pressure, and density) of equilibrium systems do not change with time except for very small fluctuations that we can observe only under special conditions. In contrast, nonequilibrium states change with time. The time scale for changes may be seconds or years, and cannot be determined from thermodynamic arguments alone. We can say for sure that a system is not in equilibrium if its properties change with time, but time independence during our observation time is not sufficient to determine if a system is in equilibrium. It is possible that we just did not observe the system long enough.[3]

As in Chapter 1 the *macrostate* of a system refers to its bulk properties such as its temperature and pressure. Only a relatively few quantities are needed to specify the macrostate of a system in equilibrium. For example, if you drop an ice cube into a cup of coffee, the temperature immediately afterward will vary throughout the coffee until the coffee reaches equilibrium. Before equilibrium is reached, we must specify the temperature everywhere in the coffee. Once equilibrium is reached, the temperature will be uniform throughout and only one number is needed to specify the temperature.

History independence implies that a system can come to the same final equilibrium macrostate[4] through an infinity of possible ways. The final macrostate has lost all memory of how it was produced. For example, if we put several cups of coffee in the same room, they will all reach the same final temperature, regardless of their different initial temperatures or how much milk was added. However, there are many examples where the history of the system is important. For example, a metal cooled quickly may contain defects that depend on the detailed history of how the metal was cooled. Such a system is not in equilibrium.

It is difficult to know for certain whether a system is in equilibrium because the time it takes a system to reach equilibrium may be very long and our measurements might not indicate whether a system's macroscopic properties are changing. In practice, the criterion for equilibrium is circular. Operationally, a system is in equilibrium if its properties can be consistently described by the laws of thermodynamics.

The circular nature of thermodynamics is not fundamentally different than that of other fields of physics. For example, the law of conservation of energy can never be disproved, because we can always make up new forms of energy to make it true. If we find that we are continually making up new forms of energy for every new system we find, then we would discard the law of conservation of energy as not being useful. As an example, if we were to observe a neutron at rest decay into an electron and proton (beta decay) and measure the energy and momentum of the decay products, we would find an apparent violation of energy conservation in the vast majority of

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[3]A spin glass is an example of a system that can take days or even longer to each equilibrium. A theoretical model of a spin glass is the Ising model with the exchange constant $J = \pm 1$ at random. See for example, <en.wikipedia.org/wiki/Spin_glass>.

[4]Because thermodynamics deals only with macrostates (and not microstates), we will frequently use the term state instead of macrostate.

decays. Historically, Pauli did not reject energy conservation, but instead suggested that a third particle (the neutrino) is also emitted. Pauli's suggestion was made in 1930, but the (anti)neutrino was not detected until 1956. In this example our strong belief in conservation of energy led to a new prediction and discovery.

The same is true for thermodynamics. We find that if we use the laws of thermodynamics for systems that experimentally appear to be in equilibrium, then everything works out fine. In some systems such as glasses that we suspect are not in thermal equilibrium, we must be very careful in interpreting our measurements according to the laws of thermodynamics.

2.4   Temperature

The concept of temperature plays a central role in thermodynamics and is related to the physiological sensation of hot and cold. Because such a sensation is an unreliable measure of temperature, we will develop the concept of temperature by considering what happens when two bodies are placed in thermal contact. The most important property of the temperature is its tendency to become equal. For example, if we put a hot and a cold body into *thermal contact*, the temperature of the hot body decreases and the temperature of the cold body increases until both bodies are at the same temperature and the two bodies are in *thermal equilibrium*.

Problem 2.1. Physiological sensation of temperature

(a) Suppose you are blindfolded and place one hand in a pan of warm water and the other hand in a pan of cold water. Then your hands are placed in another pan of water at room temperature. What temperature would each hand perceive?

(b) What are some other examples of the subjectivity of our perception of temperature?

To define temperature more carefully, consider two systems separated by an *insulating* wall.[5] A wall is said to be *insulating* if the thermodynamic variables of one system can be changed without influencing the thermodynamic variables of the other system. For example, if we place one system under a flame, the temperature, pressure, and the volume of the second system would remain unchanged. If the wall between the two systems were *conducting*, then the other system would be affected. Insulating and conducting walls are idealizations. A good approximation to the former is the wall of a thermos bottle; a thin sheet of copper is a good approximation to the latter.

Consider two systems surrounded by insulating walls, except for a common conducting wall. For example, suppose that one system is a cup of coffee in a vacuum flask and the other system is mercury or alcohol enclosed in a glass tube. (The glass tube is in thermal contact with the coffee.) We know that the height of the mercury column will reach a time-independent value, and hence the coffee and the mercury are in equilibrium. Next suppose that we dip the mercury thermometer into a cup of tea in another vacuum flask. If the height of the mercury column is the same as it was when placed into the coffee, we say that the coffee and tea are at the same temperature. This conclusion can be generalized as

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[5]An insulating wall is sometimes called an *adiabatic wall*.

> If two bodies are in thermal equilibrium with a third body, they are in thermal equilibrium with each other (zeroth law of thermodynamics).

This conclusion is sometimes called the *zeroth law of thermodynamics*. The zeroth law implies the existence of some universal property of systems in thermal equilibrium and allows us to obtain the temperature of a system without a direct comparison to some standard. Note that this conclusion is not a logical necessity, but an empirical fact. If person A is a friend of B and B is a friend of C, it does not follow that A is a friend of C.

Problem 2.2. Describe some other measurements that also satisfy a law similar to the zeroth law.

Any body whose macroscopic properties change in a well-defined manner can be used to measure temperature. A *thermometer* is a system with some convenient macroscopic property that changes with the temperature in a known way. Examples of convenient macroscopic properties include the length of an iron rod, and the magnitude of the electrical resistance of gold. In all these cases we need to measure only a single quantity to indicate the temperature.

Problem 2.3. Why are thermometers relatively small devices in comparison to the system of interest?

To use different thermometers, we need to make them consistent with one another. To do so, we choose a standard thermometer that works over a wide range of temperatures and define reference temperatures which correspond to physical processes that always occur at the same temperature. The familiar gas thermometer is based on the fact that the temperature T of a dilute gas is proportional to its pressure P at constant volume. The temperature scale that is based on the gas thermometer is called the *ideal gas temperature scale*. The unit of temperature is called the *kelvin* (K). We need two points to define a linear function. We write

$$T(P) = aP + b, \tag{2.1}$$

where a and b are constants. We may choose the magnitude of the unit of temperature in any convenient way. The gas temperature scale has a natural zero — the temperature at which the pressure of an ideal gas vanishes — and hence we take $b = 0$. The second point is established by the *triple point* of water, the unique temperature and pressure at which ice, water, and water vapor coexist. The temperature of the triple point is *defined* to be 273.16 K exactly. Hence, the temperature of a fixed volume gas thermometer is given by

$$T = 273.16 \frac{P}{P_{\text{tp}}}, \qquad \text{(ideal gas temperature scale)} \tag{2.2}$$

where P is the pressure of the ideal gas thermometer, and P_{tp} is its pressure at the triple point. Equation (2.2) holds for a fixed amount of matter in the limit $P \to 0$. From (2.2) we see that the kelvin is defined as the fraction $1/273.16$ of the temperature of the triple point of water.

Note that the gas scale of temperature is based on experiment, and there is no a priori reason to prefer this scale to any other. However, we will show in Section 2.16 that the ideal gas temperature defined by (2.2) is consistent with the thermodynamic temperature scale. Also note that we have defined the temperature in terms of a quantity that is easy to measure.

triple point	273.16 K	definition
steam point	373.12 K	experiment
ice point	273.15 K	experiment

Table 2.1: Fixed points of the ideal gas temperature scale.

At low pressures all gas thermometers read the same temperature regardless of the gas that is used. The relation (2.2) holds only if the gas is sufficiently dilute that the interactions between the molecules can be ignored. Helium is the most useful gas because it liquefies at a temperature lower than any other gas.

The historical reason for the choice of 273.16 K for the triple point of water is that it gave, to the accuracy of the best measurements then available, 100 K for the difference between the ice point (the freezing temperature at standard pressure[6]) and the steam point (the boiling temperature at standard pressure of water). However, more accurate measurements now give the difference as 99.97 K (see Table 2.1).

It is convenient to define the *Celsius* scale:

$$T_{\text{celius}} = T - 273.15, \tag{2.3}$$

where T is the ideal gas temperature. Note that the Celsius and ideal gas temperatures differ only by the shift of the zero. By convention the degree sign is included with the C for Celsius temperature (°C), but no degree sign is used with K for kelvin.

Problem 2.4. Temperature scales

(a) The Fahrenheit scale is defined such that the ice point is at 32°F and the steam point is 212°F. Derive the relation between the Fahrenheit and Celsius temperature scales.

(b) What is body temperature (98.6°F) on the Celsius and Kelvin scales?

(c) A meteorologist in Canada reports a temperature of 30°C. How does this temperature compare to 70°F?

(d) The *centigrade* temperature scale is defined as

$$T_{\text{centigrade}} = (T - T_{\text{ice}}) \frac{100}{T_{\text{steam}} - T_{\text{ice}}}, \tag{2.4}$$

where T_{ice} and T_{steam} are the ice and steam points of water (see Table 2.1). By definition, there is 100 centigrade units between the ice and steam points. How does the centigrade unit defined in (2.4) compare to the kelvin or Celsius unit?

(e) What were the contributions of Anders Celsius (1701–1744) and Gabriel Fahrenheit (1686–1736)?

Problem 2.5. What is the range of temperatures that is familiar to you from your everyday experience and from your prior studies?

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[6]Standard atmospheric pressure is the pressure of the earth's atmosphere under normal conditions at sea level and is defined to be 1.013×10^5 N/m^2. The SI unit of pressure is N/m^2; this unit has been given the name *pascal* (Pa). Note that the names of SI units are not capitalized.

2.5 Pressure Equation of State

As we have discussed, the equilibrium macrostates of a thermodynamic system are much simpler to describe than nonequilibrium states. For example, the pressure P of a simple fluid (gas or liquid) consisting of a single species is uniquely determined its (number) density $\rho = N/V$, and temperature T, where N is the number of particles and V is the volume of the system. That is, the quantities P, T, and ρ are not independent, but are connected by a relation of the general form

$$P = f(T, \rho). \tag{2.5}$$

This relation is called the *pressure equation of state*. Each of these three quantities can be regarded as a function of the other two, and the macrostate of the system is determined by any two of the three. Note that we have implicitly assumed that the thermodynamic properties of a fluid are independent of its shape.

In general, the pressure equation of state is very complicated and must be determined either empirically or from a simulation or from an approximate theoretical calculation (an application of statistical mechanics). One of the few exceptions is the *ideal gas* for which the equation of state is very simple. As discussed in Section 1.10, the ideal gas represents a mathematical idealization in which the potential energy of interaction between the molecules is very small in comparison to their kinetic energy and the system can be treated classically. For an ideal gas, we have for fixed temperature the empirical relation $P \propto 1/V$ at fixed temperature or

$$PV = \text{constant.} \qquad \text{(fixed temperature)} \tag{2.6}$$

The relation (2.6) is sometimes called Boyle's law and was published by Robert Boyle in 1660.[7] Note that the relation (2.6) is not a law of physics, but an empirical relation. An equation such as (2.6), which relates different states of a system all at the same temperature, is called an *isotherm*.

We also have the empirical relation

$$V \propto T. \qquad \text{(fixed pressure)} \tag{2.7}$$

Some textbooks refer to (2.7) as Charles's law, but it should be called the *law of Gay-Lussac*.

We can express the empirical relations (2.6) and (2.7) as $P \propto T/V$. In addition, if we hold T and P constant and introduce more gas into the system, we find that the pressure increases in proportion to the amount of gas. If N is the number of gas molecules, we can write

$$PV = NkT, \qquad \text{(ideal gas pressure equation of state)} \tag{2.8}$$

where the constant of proportionality k in (2.8) is found experimentally to have the same value for all gases in the limit $P \to 0$. The value of k is

$$k = 1.38 \times 10^{-23} \, \text{J/K}, \qquad \text{(Boltzmann's constant)} \tag{2.9}$$

and is called *Boltzmann's constant*. The equation of state (2.8) will be derived using statistical mechanics in Section 4.5.

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[7]You can learn about the first modern chemist at `<en.wikipedia.org/wiki/Robert_Boyle>`.

Because the number of particles in a typical gas is very large, it sometimes is convenient to measure this number relative to the number of particles in one (gram) mole of gas.[8] A mole of any substance consists of Avogadro's number $N_A = 6.022 \times 10^{23}$ of that substance. If there are ν moles, then $N = \nu N_A$, and the ideal gas equation of state can be written as

$$PV = \nu N_A kT = \nu RT, \tag{2.10}$$

where

$$R = N_A k = 8.314 \, \text{J/K mole} \tag{2.11}$$

is the gas constant.

Real gases do not satisfy the ideal gas equation of state except in the limit of low density. For now we will be satisfied with considering a simple phenomenological[9] equation of state of a real gas with an interparticle interaction similar to the Lennard-Jones potential (see Figure 1.1). The simplest phenomenological pressure equation of state that describes the behavior of real gases at moderate densities is due to van der Waals and has the form

$$(P + \frac{N^2}{V^2}a)(V - Nb) = NkT, \qquad \text{(van der Waals equation of state)} \tag{2.12}$$

where a and b are empirical constants characteristic of a particular gas. The parameter b takes into account the finite size of the molecules by decreasing the effective available volume to any given molecule. The parameter a is associated with the attractive interactions between the molecules. We will derive this approximate equation of state in Section 8.2.

2.6 Some Thermodynamic Processes

A change from one equilibrium macrostate of the system to another is called a *thermodynamic process*. Thermodynamics does not determine how much time such a process will take, and the final macrostate is independent of the amount of time it took to reach this final equilibrium state. To describe a process in terms of thermodynamic variables, the system must be in thermodynamic equilibrium. However, for the process to occur, the system cannot be exactly in thermodynamic equilibrium because at least one thermodynamic variable is changing. If the change is sufficiently slow, the process is *quasistatic*, and the system can be considered to be in a succession of equilibrium states. A *quasistatic process* is an idealized concept. Although no physical process is quasistatic, we can imagine real processes that approach the limit of quasistatic processes. We will consider thermodynamic processes where a system is taken from an initial to a final macrostate by a continuous succession of intermediate equilibrium states. The name thermodynamics is a misnomer because thermodynamics treats only equilibrium states and not dynamics.

Some thermodynamic processes can go only in one direction and others can go in either direction. For example, a scrambled egg cannot be converted to a whole egg. Processes that can go only in one direction are called *irreversible*. A process is *reversible* if it is possible to restore the

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[8]A mole is defined as the quantity of matter that contains as many objects (for example, atoms or molecules) as number of atoms in exactly $12 \, \text{g}$ of $^1 2\text{C}$.

[9]Phenomenological is a word that we will use often. It means a description of the phenomena that is not derived from fundamental considerations.

system and its surroundings to their original condition. (The surroundings include any body that was affected by the change.) That is, if the change is reversible, the status quo can be restored everywhere.

Processes such as stirring the cream in a cup of coffee or passing an electric current through a resistor are irreversible because once the process is done, there is no way of reversing the process. But suppose we make a small and very slow frictionless change of a constraint such as an increase in the volume, which we then reverse. Because there is no "friction," we do no net work in this process. At the end of the process, the constraints and the energy of the system return to their original values and the macrostate of the system is unchanged. In this case we can say that this process is reversible. No real process is truly reversible because it would require an infinite time to occur. The relevant question is whether the process approaches reversibility.

Consider a gas in a closed, insulated container that is divided into two chambers by an impermeable partition. The gas is initially confined to one chamber and then allowed to expand freely into the second chamber to fill the entire container. What is the nature of this process? It is certainly not quasistatic. But we can imagine this process to be performed quasistatically. We could divide the second chamber into many small chambers separated by partitions and puncture each partition in turn, allowing the expanded gas to come into equilibrium. So in the limit of an infinite number of partitions, such a process would be quasistatic. However this process would not be reversible, because the gas would never return to its original volume.

Problem 2.6. Are the following processes reversible or irreversible?

(a) Air is pumped into a tire.

(b) Air leaks out of a tire.

(c) The breaking of a vehicle coming to a complete stop.

2.7 Work

During a process the surroundings can do work on the system of interest or the system can do work on its surroundings. We now obtain an expression for the mechanical work done on a system in a quasistatic process. For simplicity, we assume the system to be a fluid. Because the fluid is in equilibrium, we can characterize it by a uniform pressure P. For simplicity, we assume that the fluid is contained in a cylinder of cross-sectional area A fitted with a movable piston (see Figure 2.2). The piston allows no gas or liquid to escape. We can add weights to the piston causing it to compress the fluid. Because the pressure is defined as the force per unit area, the magnitude of the force exerted by the fluid on the piston is given by PA, which also is the force exerted by the piston on the fluid. If the piston is displaced quasistatically by an amount dx, then the work done *on* the fluid by the piston is given by[10]

$$dW = -(PA)\,dx = -P\,(A dx) = -PdV. \tag{2.14}$$

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[10]Equation (2.14) can be written as

$$\frac{dW}{dt} = -P\frac{dV}{dt}, \tag{2.13}$$

if you wish to avoid the use of differentials (see Section 2.26.1).
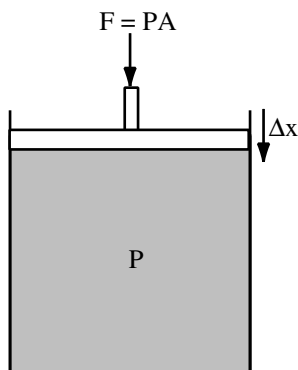
Figure 2.2: Example of work done on a fluid enclosed within a cylinder fitted with a piston when the latter moves a distance Δx.

The negative sign in (2.14) is present because if the volume of the fluid is decreased, the work done by the piston is positive.

If the volume of the fluid changes quasistatically from an initial volume V_1 to a final volume V_2, the system remains very nearly in equilibrium, and hence its pressure at any stage is a function of its volume and temperature. Hence, the total work is given by the integral

$$W_{1\to2} = -\int_{V_1}^{V_2} P(T,V)\,dV. \qquad \text{(quasistatic process)} \tag{2.15}$$

Note that the work done on the fluid is positive if $V_2 < V_1$ and is negative if $V_2 > V_1$.

For the special case of an ideal gas, the work done on a gas that is compressed at constant temperature (an *isothermal process*) is given by

$$W_{1\to2} = -NkT\int_{V_1}^{V_2} \frac{dV}{V} \tag{2.16}$$

$$= -NkT\ln\frac{V_2}{V_1}. \qquad \text{(ideal gas at constant temperature)} \tag{2.17}$$

We have noted that the pressure P must be uniform throughout the fluid. But compression cannot occur if pressure gradients are not present. To move the piston from its equilibrium position, we must add (remove) a weight from it. Then for a moment, the total weight on the piston will be greater (less) than PA. This difference is necessary if the piston is to move down and do work on the gas. If the movement is sufficiently slow, the pressure departs only slightly from its equilibrium value. What does "sufficiently slow" mean? To answer this question, we have to go beyond the macroscopic reasoning of thermodynamics and consider the molecules that comprise the fluid. If the piston is moved down a distance Δx, then the density of the molecules near the piston becomes greater than the bulk of the fluid. Consequently, there is a net movement of molecules away from the piston until the density again becomes uniform. The time τ for the fluid to return to equilibrium is given by $\tau \approx \Delta x/v_s$, where v_s is the mean speed of the molecules (see Section 6.4). For comparison, the characteristic time τ_p for the process is $\tau_p \approx \Delta x/v_p$, where
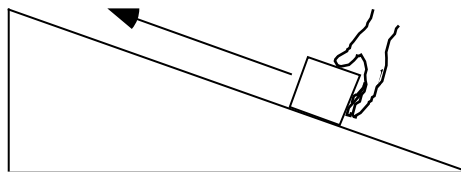
Figure 2.3: A block on an frictionless incline. The figure is taken from Loverude et al.

v_p is the speed of the piston. If the process is to be quasistatic, it is necessary that $\tau \ll \tau_p$ or $v_p \ll v_s$. That is, the speed of the piston must be much less than the mean speed of the molecules, a condition that is easy to satisfy in practice.

Problem 2.7. Work

To refresh your understanding of work in the context of mechanics, look at Figure 2.3 and explain whether the following quantities are positive, negative, or zero:

(a) The work done on the block by the hand.

(b) The work done on the block by the earth.

(c) The work done on the hand by the block (if there is no such work, state so explicitly).

Work depends on the path. The solution of the following example illustrates that the work done on a system depends not only on the initial and final states, but also on the intermediate states, that is, on the path.

Example 2.1. Cyclic processes

Figure 2.4 shows a cyclic path ABCDA in the PV diagram of an ideal gas. How much work is done on the gas during this cyclic process? (Look at the figure before you attempt to answer the question.)

Solution. During the isobaric expansion $A \to B$, the work done on the gas is

$$W_{AB} = -P_2(V_2 - V_1). \tag{2.18}$$

No work is done from $B \to C$ and from $D \to A$. The work done on the gas from $C \to D$ is

$$W_{CD} = -P_1(V_1 - V_2). \tag{2.19}$$

The net work done on the gas is then

$$W_{\text{net}} = W_{AB} + W_{CD} = -P_2(V_2 - V_1) - P_1(V_1 - V_2) \tag{2.20}$$

$$= -(P_2 - P_1)(V_2 - V_1) < 0. \tag{2.21}$$

The result is that the net work done on the gas is the negative of the area enclosed by the path. If the cyclic process were carried out in the reverse order, the net work done on the gas would be positive.

Because the system was returned to its original pressure and volume, why is the net amount of work done not zero? What would be the work done if the gas were taken from V_2 to V_1 along the diagonal path connecting C and A?
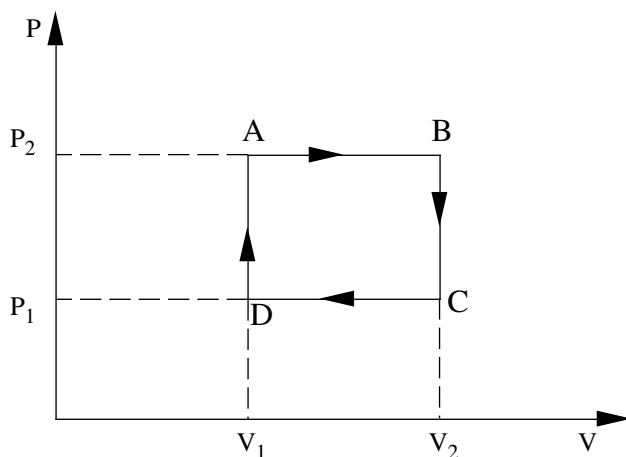
Figure 2.4: A simple cyclic process. What is the net work done on the gas?

2.8 The First Law of Thermodynamics

If we think of a macroscopic system as consisting of many interacting particles, we know that it has a well defined total energy which satisfies a conservation principle. This simple justification of the existence of a thermodynamic energy function is very different from the historical development because thermodynamics was developed before the atomic theory of matter was well accepted. Historically, the existence of a macroscopic conservation of energy principle was demonstrated by purely macroscopic observations as outlined in the following.[11]

Consider a system enclosed by insulating walls. Such a system is *thermally isolated*. An *adiabatic process* is one in which the macrostate of the system is changed only by work done on the system. We know from overwhelming empirical evidence that the amount of work needed to change the macrostate of a thermally isolated system depends only on the initial and final states and not on the intermediate states through which the system passes. This independence of the path under these conditions implies that we can define a function E such that for a change from macrostate 1 to macrostate 2, the work done on a thermally isolated system equals the change in E:

$$W = E_2 - E_1 = \Delta E. \qquad \text{(adiabatic process)} \qquad (2.22)$$

The quantity E is called the (internal) energy of the system.[12] The internal energy in (2.22) is measured with respect to the center of mass.[13] The energy E is an example of a *state* function, that is, it characterizes the state of a macroscopic system and is independent of the path.

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[11]These experiments were done by Joseph Black (1728–1799), Benjamin Thompson (Count Rumford) (1753–1814), Robert Mayer (1814–1878), and James Joule (1818–1889). Mayer and Joule are now recognized as the co-discovers of the first law of thermodynamics, but Mayer received little recognition at the time of his work.

[12]Another common notation for the internal energy is U.

[13]Microscopically, the internal energy of a system of particles is the sum of the kinetic energy in a reference frame in which the center of mass velocity is zero and the potential energy arising from the forces of the particles on each other.

Problem 2.8. What is the difference between the total energy and the internal energy?

If we choose a convenient reference macrostate as the zero of energy, then E has an unique value for each macrostate of the system because W is independent of the path for an adiabatic process. (Remember that in general W depends on the path.)

If we relax the condition that the change be adiabatic and allow the system to interact with its surroundings, we would find in general that $\Delta E \neq W$. (The difference between ΔE and W is zero for an adiabatic process.) We know that we can increase the energy of a system by doing work on it or by heating it as a consequence of a temperature difference between it and its surroundings. In general, the change in the internal energy of a closed system (fixed number of particles) is given by

$$\Delta E = W + Q. \qquad \text{(first law of thermodynamics)} \tag{2.23}$$

The quantity Q is the change in the system's energy due to heating ($Q > 0$) or cooling ($Q < 0$) and W is the work done *on* the system. Equation (2.23) expresses the law of conservation of energy and is known as the *first law of thermodynamics*. This equation is equivalent to saying that there are two macroscopic ways of changing the internal energy of a system: doing work and heating.

One consequence of the first law of thermodynamics is that ΔE is independent of the path, even though the amount of work W does depend on the path. And because W depends on the path and ΔE does not, the amount of heating also depends on the path. From one point of view, the first law of thermodynamics expresses what seems obvious to us today, namely, conservation of energy. However, from another point of view, the first law implies that although the work done and the amount of heating depend on the path, their sum is independent of the path.

Problem 2.9. A cylindrical pump contains one mole of a gas. The piston fits tightly so that no air escapes and friction is negligible between the piston and the cylinder walls. The pump is thermally insulated from its surroundings. The piston is quickly pressed inward. What will happen to the temperature of the gas? Explain your reasoning.

So far we have considered two classes of thermodynamic quantities. One class consists of *state functions* because they have a specific value for each macroscopic state of the system. An example of such a function is the internal energy E. As we have discussed, there are other quantities, such as work and energy transfer due to heating, that do not depend on the macrostate of the system. These latter quantities depend on the thermodynamic process by which the system changed from one state to another.

The energy of a system is a state function. The mathematical definition of a state function goes as follows. Suppose that $f(x)$ is a state function that depends on the parameter x. If x changes from x_1 to x_2, then the change in f is

$$\Delta f = \int_{x_1}^{x_2} df = f(x_2) - f(x_1). \tag{2.24}$$

That is, the change in f depends only on the end points x_1 and x_2. We say that df is an exact differential. State functions have exact differentials. Examples of inexact and exact differentials are given in Section 2.26.1.

Originally, many scientists thought that there was a fluid called *heat* in all substances which could flow from one substance to another. This idea was abandoned many years ago, but is still

used in everyday language. Thus, people talk about adding heat to a system. We will avoid this use and whenever possible we will avoid the use of the noun "heat" altogether. Instead, we will refer to a process as heating or cooling if it changes the internal energy of a system without changing any external parameters such as the external pressure. Heating occurs whenever two solids at different temperatures are brought into thermal contact. In everyday language we would say that heat flows from the hot to the cold body. However, we prefer to say that energy is transferred from the hotter to the colder body. There is no need to invoke the noun "heat," and it is misleading to say that heat "flows" from one body to another.

To understand better that there is no such thing as the amount of heat in a body, consider the following simple analogy adapted from Callen.[14] A farmer owns a pond, fed by one stream and drained by another. The pond also receives water from rainfall and loses water by evaporation. The pond is the system of interest, the water within it is analogous to the internal energy, the process of transferring water by the streams is analogous to doing work, the process of adding water by rainfall is analogous to heating, and the process of evaporation is analogous to cooling. The only quantity of interest is the water, just as the only quantity of interest is energy in the thermal case. An examination of the change in the amount of water in the pond cannot tell us how the water got there. The terms rain and evaporation refer only to methods of water transfer, just as the terms heating and cooling refer only to methods of energy transfer.

Another example is due to Bohren and Albrecht.[15] Take a small plastic container and add just enough water to it so that its temperature can be conveniently measured. Let the water and the bottle come into equilibrium with their surroundings. Measure the temperature of the water, cap the bottle, and shake the bottle until you are too tired to continue further. Then uncap the bottle and measure the water temperature again. If there were a "whole lot of shaking going on," you would find the temperature had increased a little.

In this example, the temperature of the water increased without heating. We did work on the water, which resulted in an increase in its internal energy as manifested by a rise in the temperature. The same increase in temperature could have been obtained by bringing the water into contact with a body at a higher temperature. But it would be impossible to determine by making measurements on the water whether shaking or heating had been responsible for taking the system from its initial to its final state. (To silence someone who objects that you heated the water with "body heat," wrap the bottle with an insulating material.)

Problem 2.10. How could the owner of the pond distinguish between the different types of water transfer assuming that the owner has flow meters, a tarpaulin, and a vertical pole?

Problem 2.11. Convert the following statement to the language used by physicists, "I am cold, please turn on the heat."

Before the equivalence of heating and energy transfer was well established, a change in energy by heating was measured in calories. One calorie is the amount of energy needed to raise the temperature of one gram of water from $14.5°C$ to $15.5°C$. We now know that one calorie is equivalent to $4.186 \, J$, but the use of the calorie for energy transfer by heating and the joule for work still persists. Just to cause confusion, the calorie we use to describe the energy content of foods is actually a kilocalorie.

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[14]See page 20.
[15]See page 25.

2.9 Energy Equation of State

In (2.8) we gave the pressure equation of state for an ideal gas. Now that we know that the internal energy is a state function, we need to know how E depends on two of the three variables, T, ρ, and N (for a simple fluid). The form of the *energy equation of state* for an ideal gas must also be determined empirically or calculated from first principles using statistical mechanics (see Section 4.5). From these considerations the energy equation of state for a monatomic gas is given by

$$E = \frac{3}{2}NkT. \qquad \text{(ideal gas energy equation of state)} \qquad (2.25)$$

Note that the energy of an ideal gas is independent of its density (for a fixed number of particles).

The approximate thermal equation of state of a real gas corresponding to the pressure equation of state (2.12) is given by

$$E = \frac{3}{2}NkT - N\frac{N}{V}a. \qquad \text{(van der Waals energy equation of state)} \qquad (2.26)$$

Note that the energy depends on the density if the interactions between particles is included.

Example 2.2. Work is done on an ideal gas at constant temperature. What is the change in the energy[16] of the gas?

Solution. Because the energy of an ideal gas depends only on the temperature (see (2.25)), there is no change in its internal energy for an isothermal process. Hence, $\Delta E = 0 = Q + W$, and

$$Q = -W = NkT \ln\frac{V_2}{V_1}. \qquad \text{(isothermal process for an ideal gas)} \qquad (2.27)$$

We see that if work is done on the gas ($V_2 < V_1$), then the gas must give energy to its surroundings so that its temperature does not change.

Extensive and intensive variables. The thermodynamic variables that we have introduced so far may be divided into two classes. Quantities such as the density ρ, the pressure P, and the temperature T are *intensive* variables and are *independent* of the size of the system. Quantities such as the volume V and the internal energy E are *extensive* variables and are *proportional* to the number of particles in the system (at fixed density). As we will see in Section 2.10, it often is convenient to convert extensive quantities to a corresponding intensive quantity by defining the ratio of two extensive quantities. For example, the energy per particle and the energy per per unit mass are intensive quantities.

2.10 Heat Capacities and Enthalpy

We know that the temperature of a macroscopic system usually increases when we transfer energy to it by heating.[17] The magnitude of the increase in temperature depends on the nature of the

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[16]We actually mean the internal energy, but the meaning should be clear from the context.

[17] What is a common counterexample?

body and how much of it there is. The amount of energy transfer due to heating required to produce a unit temperature rise in a given substance is called the *heat capacity* of the substance. Here again we see the archaic use of the word "heat." But because the term "heat capacity" is common, we are forced to use it. If a body undergoes an increase of temperature from T_1 to T_2 accompanied by an energy transfer Q, then the average heat capacity is given by the ratio

$$\text{average heat capacity} = \frac{Q}{T_2 - T_1}. \tag{2.28}$$

The value of the heat capacity depends on what constraints are imposed. We introduce the heat capacity at constant volume by the relation

$$C_V = \left(\frac{\partial E}{\partial T}\right)_V. \tag{2.29}$$

Note that if the volume V is held constant, the change in energy of the system is due only to the energy transferred by heating. We have adopted the common notation in thermodynamics of enclosing partial derivatives in parentheses and using subscripts to denote the variables that are held constant. In this context, it is clear that the differentiation in (2.29) is at constant volume, and we will write $C_V = \partial E/\partial T$ if there is no ambiguity.[18] (See Section 2.26.1 for a discussion of the mathematics of thermodynamics.)

Equation (2.29) together with (2.25) can be used to obtain the heat capacity at constant volume of a monatomic ideal gas:

$$C_V = \frac{3}{2}Nk. \qquad \text{(monatomic ideal gas)} \tag{2.30}$$

Note that the heat capacity at constant volume of an ideal gas is independent of the temperature.

The heat capacity is an extensive quantity, and it is convenient to introduce the *specific heat* which depends only on the nature of the material, not on the amount of the material. The conversion to an intensive quantity can be achieved by dividing the heat capacity by the amount of the material expressed in terms of the number of moles, the mass, or the number of particles. We will use lower case c for specific heat; the distinction between the various kinds of specific heats will be clear from the context and the units of c.

The enthalpy. The combination of thermodynamic variables $E + PV$ occurs sufficiently often to acquire its own name. The *enthalpy H* is defined as

$$H = E + PV. \qquad \text{(enthalpy)} \tag{2.31}$$

We can use (2.31) to find a simple expression for C_P, the heat capacity at constant pressure. From (2.14) and (2.23), we have $dE = dQ - PdV$ or $dQ = dE + PdV$ (at constant pressure). From the identity, $d(PV) = PdV + VdP$, we can write $dQ = dE + d(PV) - VdP$. At constant pressure $dQ = dE + d(PV) = d(E + PV) = dH$. Hence, we can define the heat capacity at constant pressure as

$$C_P = \frac{\partial H}{\partial T}, \tag{2.32}$$

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[18]Although the number of particles also is held constant, we will omit the subscript N in (2.29) and in other partial derivatives to reduce the number of subscripts.

where we have suppressed noting that the pressure P is held constant during differentiation. We will learn that the enthalpy is another state function that often makes the analysis of a system simpler. At this point, we can only see that C_P can be expressed more simply in terms of the enthalpy.

We can find the C_P for an ideal gas by writing $H = E + PV = \frac{3}{2}NKT + NkT$ and using the relation (2.32) to find that $C_P = \frac{5}{2}Nk$. Note also that we used the two equations of state for an ideal gas, (2.8) and (2.25), to obtain C_P, and we did not have to make an independent measurement or calculation.

Why is C_P bigger than C_V? Unless we prevent it from doing so, a system normally expands as its temperature increases. The system has to do work on its surroundings as it expands. Hence, when a system is heated at constant pressure, energy is needed both to increase the temperature of the system and to do work on its surroundings. In contrast, if the volume is kept constant, no work is done on the surroundings and the heating only has to supply the energy required to raise the temperature of the system. In Chapter 7 we will derive the general relation $C_P > C_V$ for any thermodynamic system.

Problem 2.12. The heat capacity

(a) Give some examples of materials that have a relatively small and a relatively large heat capacity.

(b) Why do we have to distinguish between the heat capacity at constant volume and the heat capacity at constant pressure?

Example 2.3. A water heater holds $150\,\text{kg}$ of water. How much energy is required to raise the water temperature from $18°\text{C}$ to $50°\text{C}$?

Solution. The (mass) specific heat of water is $c = 4184\,\text{J/kg K}$. (The difference between the specific heats of water at constant volume and constant pressure is negligible at room temperatures.) The energy required to raise the temperature by $32°\text{C}$ is

$$Q = mc(T_2 - T_1) = 150\,\text{kg} \times (4184\,\text{J/kg K}) \times (50°\text{C} - 18°\text{C}) = 2 \times 10^7\,\text{J}. \qquad (2.33)$$

We have assumed that the specific heat is constant in this temperature range.

Note that because the kelvin is exactly the same magnitude as a degree Celsius, it often is more convenient to express temperature *differences* in degrees Celsius.

Example 2.4. A $1.5\,\text{kg}$ glass brick is heated to $180°\text{C}$ and then plunged into a cold bath containing $10\,\text{kg}$ of water at $20°\text{C}$. Assume that none of the water boils and that there is no heating of the surroundings. What is the final temperature of the water and the glass? The specific heat of glass is approximately $750\,\text{J/kg K}$.

Solution. Conservation of energy implies that

$$\Delta E_{\text{glass}} + \Delta E_{\text{water}} = 0, \qquad (2.34a)$$

or

$$m_{\text{glass}} c_{\text{glass}} (T - T_{\text{glass}}) + m_{\text{water}} c_{\text{water}} (T - T_{\text{water}}) = 0. \qquad (2.34b)$$

The final equilibrium temperature T is the same for both. We solve for T and obtain

$$T = \frac{m_{\text{glass}}c_{\text{glass}}T_{\text{glass}} + m_{\text{water}}c_{\text{water}}T_{\text{water}}}{m_{\text{glass}}c_{\text{glass}} + m_{\text{water}}c_{\text{water}}} \tag{2.35a}$$

$$= \frac{(1.5\,\text{kg})(750\,\text{J/kg K})(180°\text{C}) + (10\,\text{kg})(4184\,\text{J/kg K})(20°\text{C})}{(1.5\,\text{kg})(750\,\text{J/kg K}) + (10\,\text{kg})(4184\,\text{J/kg K})} \tag{2.35b}$$

$$= 24.2°\text{C}. \tag{2.35c}$$

Example 2.5. The temperature of two moles of helium gas is increased from $20°\text{C}$ to $40°\text{C}$ at constant volume. How much energy is needed to accomplish this temperature change?

Solution. Because the amount of He gas is given in moles, we need to know the molar specific heat. From (2.30) and (2.11), we have that $c_V = 3R/2 = 1.5 \times 8.314 = 12.5\,\text{J/mole K}$. Because c_V is constant (an excellent approximation), we have

$$\Delta E = Q = \int C_V\,dT = \nu c_V \int dT = 2\,\text{mole} \times 12.5\,\frac{\text{J}}{\text{mole K}} \times 20\,\text{K} = 500\,\text{J}. \tag{2.36}$$

Example 2.6. At very low temperatures the heat capacity of an insulating solid is proportional to T^3. If we take $C = AT^3$ for a particular solid, what is the energy needed to raise the temperature from T_1 to T_2? The difference between C_V and C_P can be ignored at low temperatures. (In Section 6.11, we will use the Debye theory to express the constant A in terms of the speed of sound and other parameters and find the range of temperatures for which the T^3 behavior is a reasonable approximation.)

Solution. Because C is temperature dependent, we have to express the energy added as an integral:

$$Q = \int_{T_1}^{T_2} C(T)\,dT. \tag{2.37}$$

In this case we have

$$Q = A\int_{T_1}^{T_2} T^3\,dT = \frac{A}{4}(T_2^4 - T_1^4). \tag{2.38}$$

General relation between C_P and C_V. The first law can be used to find the general relation (2.42) between C_P and C_V. The derivation involves straightforward, but tedious manipulations of thermodynamic derivatives. We give it here to give a preview of the general nature of thermodynamic arguments.

From (2.31) and (2.32), we have

$$C_P = \left(\frac{\partial H}{\partial T}\right)_P = \left(\frac{\partial E}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P. \tag{2.39}$$

If we consider E to be a function of T and V, we can write

$$dE = \left(\frac{\partial E}{\partial T}\right)_V dT + \left(\frac{\partial E}{\partial V}\right)_T dV. \tag{2.40}$$

We divide both sides of (2.40) by ΔT, take the limit $\Delta T \to 0$ at constant P, and obtain

$$\left(\frac{\partial E}{\partial T}\right)_P = C_V + \left(\frac{\partial E}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P. \tag{2.41}$$

If we eliminate $(\partial E/\partial T)_P$ in (2.39) by using (2.41), we obtain our desired result:

$$C_P = C_V + \left(\frac{\partial E}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P. \qquad \text{(general result)} \tag{2.42}$$

Equation (2.42) is a general relation that depends only on the first law. A more useful general relation between C_P and C_V that depends on the second law of thermodynamics will be derived in Section 2.24.2.

For the special case of an ideal gas, $\partial E/\partial V = 0$ and $\partial V/\partial T = Nk/P$, and hence

$$C_P = C_V + Nk \qquad \text{(ideal gas)} \tag{2.43}$$

2.11 Adiabatic Processes

So far we have considered processes at constant temperature, constant volume, and constant pressure.[19] We have also considered *adiabatic processes* which occur when the system does not exchange energy with its surroundings due to a temperature difference. Note that an adiabatic process need not be isothermal. For example, a chemical reaction that occurs within a container that is well insulated is not isothermal.

Problem 2.13. Give an example of an isothermal process that is not adiabatic.

We now show that the pressure of an ideal gas changes more rapidly for a given change of volume in a quasistatic adiabatic process than it does in an isothermal process. For an adiabatic process the first law reduces to

$$dE = dW. \qquad \text{(adiabatic process)} \tag{2.44}$$

For an ideal gas we have $\partial E/\partial V = 0$, and hence (2.40) reduces to

$$dE = C_V dT = -PdV, \qquad \text{(ideal gas only)} \tag{2.45}$$

where we have used (2.44). The easiest way to proceed is to eliminate P in (2.45) using the ideal gas law $PV = NkT$:

$$C_V dT = -NkT\frac{dV}{V} \tag{2.46}$$

We next eliminate Nk in (2.46) in terms of $C_P - C_V$ and express (2.46) as

$$\frac{C_V}{C_P - C_V}\frac{dT}{T} = \frac{1}{\gamma - 1}\frac{dT}{T} = -\frac{dV}{V}. \tag{2.47}$$

---

[19]These processes are called *isothermal*, *isochoric*, and *isobaric*, respectively.

The symbol γ is the ratio of the heat capacities:

$$\gamma = \frac{C_P}{C_V}. \tag{2.48}$$

For an ideal gas C_V and C_P and hence γ are independent of temperature, and we can integrate (2.47) to obtain

$$TV^{\gamma-1} = \text{constant.} \qquad \text{(quasistatic adiabatic process)} \tag{2.49}$$

For an ideal monatomic gas, we have from (2.30) and (2.43) that $C_V = 3Nk/2$ and $C_P = 5Nk/2$, and hence

$$\gamma = 5/3. \qquad \text{(ideal monatomic gas)} \tag{2.50}$$

Problem 2.14. Use (2.49) and the ideal gas pressure equation of state in (2.8) to show that in a quasistatic adiabatic processes P and V are related as

$$PV^{\gamma} = \text{constant.} \tag{2.51}$$

Also show that T and P are related as

$$TP^{(1-\gamma)/\gamma} = \text{constant.} \tag{2.52}$$

The relations (2.49)–(2.52) hold for a quasistatic adiabatic process of an ideal gas; the relation (2.51) is the easiest relation to derive.[20] Because $\gamma > 1$, the relation (2.51) implies that for a given volume change, the pressure changes more for an adiabatic process than it does for a comparable isothermal process for which $PV = \text{constant}$. We can understand the reason for this difference as follows. For an isothermal compression the pressure increases and the internal energy of an ideal gas does not change. For an adiabatic compression the energy increases because we have done work on the gas and no energy can be transferred to the surroundings. The increase in the energy causes the temperature to increase. Hence in an adiabatic compression, both the decrease in the volume and the increase in the temperature cause the pressure to increase faster.

In Figure 2.5 we show the P-V diagram for both isothermal and adiabatic processes. The adiabatic curve has a steeper slope than the isothermal curves at any point. From (2.51) we see that the slope of an adiabatic curve for an ideal gas is

$$\left(\frac{\partial P}{\partial V}\right)_{\text{adiabatic}} = -\gamma \frac{P}{V}, \tag{2.53}$$

in contrast to the slope of an isothermal curve for an ideal gas:

$$\left(\frac{\partial P}{\partial V}\right)_T = -\frac{P}{V}. \tag{2.54}$$

How can the ideal gas relations $PV^{\gamma} = \text{constant}$ and $PV = NkT$ both be correct? The answer is that $PV = \text{constant}$ only for an isothermal process. A quasistatic ideal gas process cannot be both adiabatic and isothermal. During an adiabatic process, the temperature of an ideal gas must change.

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[20] An easier derivation is suggested in Problem 2.20.
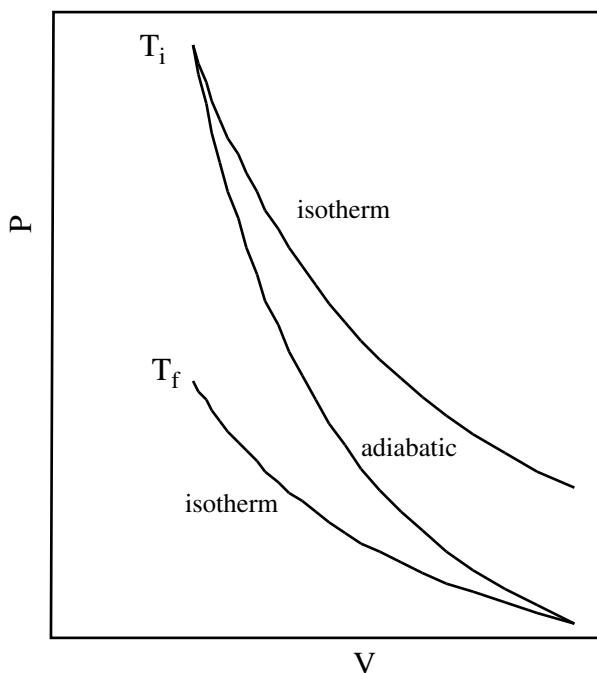
Figure 2.5: A *P-V* diagram for adiabatic and isothermal processes. The two processes begin at the same initial temperature, but the adiabatic process has a steeper slope and ends at a higher temperature.

Problem 2.15. Although we do work on an ideal gas when we compress it isothermally, why does the energy of the gas not increase?

Example 2.7. Adiabatic and isothermal expansion

Two identical systems each contain $\nu = 0.06$ mole of an ideal gas at $T = 300\,\text{K}$ and $P = 2.0 \times 10^5\,\text{Pa}$. The pressure in the two systems is reduced by a factor of two allowing the systems to expand, one adiabatically and one isothermally. What are the final temperatures and volumes of each system? Assume that $\gamma = 5/3$.

Solution. The initial volume V_1 is given by

$$V_1 = \frac{\nu R T_1}{P_1} = \frac{0.060\,\text{mole} \times 8.3\,\text{J/(K mole)} \times 300\,\text{K}}{2.0 \times 10^5\,\text{Pa}} = 7.5 \times 10^{-4}\,\text{m}^3. \tag{2.55}$$

For the isothermal system, PV remains constant, so the volume doubles as the pressure decreases by a factor of two and hence $V_2 = 1.5 \times 10^{-3}\,\text{m}^3$. Because the process is isothermal, the temperature remains at $300\,\text{K}$.

For adiabatic compression we have

$$V_2^\gamma = \frac{P_1 V_1^\gamma}{P_2}, \tag{2.56}$$

or

$$V_2 = \left(\frac{P_1}{P_2}\right)^{1/\gamma} V_1 = 2^{3/5} \times 7.5 \times 10^{-4}\,\text{m}^3 = 1.14 \times 10^{-3}\,\text{m}^3. \tag{2.57}$$

In this case we see that for a given pressure change, the volume change for the adiabatic process is greater. We leave it as an exercise to show that $T_2 = 250\,\text{K}$.

Problem 2.16. Air initially at $20°\text{C}$ is compressed by a factor of 15.

(a) What is the final temperature assuming that the compression is adiabatic and $\gamma = 1.4$, the value of γ for air at the relevant range of temperatures? By what factor does the pressure increase?

(b) What is the final pressure assuming the compression is isothermal?

(c) In which case does the pressure change more?

How much work is done in a quasistatic adiabatic process? Because $Q = 0$, $\Delta E = W$. For an ideal gas, $\Delta E = C_V \Delta T$ for any process. Hence for a quasistatic adiabatic process

$$W = C_V(T_2 - T_1). \qquad \text{(quasistatic adiabatic process for an ideal gas)} \tag{2.58}$$

We leave it to Problem 2.17 to show that (2.58) can be expressed in terms of the pressure and volume as

$$W = \frac{P_2 V_2 - P_1 V_1}{\gamma - 1}. \tag{2.59}$$

Problem 2.17. Another way to derive (2.59), the work done in a quasistatic adiabatic process, is to use the relation (2.51). Work out the steps.

Example 2.8. Compression in a Diesel engine occurs quickly enough so that very little heating of the environment occurs and thus the process may be considered adiabatic. If a temperature of $500°\text{C}$ is required for ignition, what is the compression ratio? Assume that the air can be treated as an ideal gas with $\gamma = 1.4$[21] and the temperature is $20°\text{C}$ before compression.

Solution. Equation (2.49) gives the relation between T and V for a quasistatic adiabatic process. We write T_1 and V_1 and T_2 and V_2 for the temperature and volume at the beginning and the end of the piston stroke. Then (2.51) becomes

$$T_1 V_1^{\gamma - 1} = T_2 V_2^{\gamma - 1}. \tag{2.60}$$

Hence the compression ratio V_1/V_2 is

$$\frac{V_1}{V_2} = \left(\frac{T_2}{T_1}\right)^{1/(\gamma - 1)} = \left(\frac{773\,\text{K}}{293\,\text{K}}\right)^{1/0.4} = 11. \tag{2.61}$$

It is only an approximation to assume that the compression is quasistatic.

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[21]The ratio γ equals 5/3 only for an ideal gas of particles with no spatial extent. We will learn in Section 6.3 how to calculate γ for molecules with rotational and vibrational contributions to the energy.

2.12 The Second Law of Thermodynamics

The consequences of the first law of thermodynamics can be summarized by the statements that (a) energy is conserved in thermal processes and (b) heating is a form of energy transfer. We also noted that the internal energy of a system can be identified with the sum of the potential and kinetic energies of the particles (in a reference frame in which the center of mass velocity is zero.)

As discussed in Chapter 1, there are many processes that do not occur in nature, but whose occurrence would be consistent with the first law. For example, the first law does not prohibit energy from being transferred spontaneously from a cold body to a hot body, yet it has never been observed. There is another property of systems that must be taken into account, and this property is called the *entropy*.[22]

Entropy is another example of a state function. One of the remarkable achievements of the nineteenth century was the reasoning that such a state function must exist without any idea of how to measure its value directly. In Chapter 4 we will learn about the relation between the entropy and the number of possible microscopic states, but for now we will follow a logic that does not depend on any knowledge of the microscopic behavior.

It is not uncommon to use heating as a means of doing work. For example, power plants burn oil or coal to turn water into steam which in turn turns a turbine in a magnetic field creating electricity which then can do useful work in your home. Can we completely convert all the energy created by chemical reactions into work? Or more simply can we cool a system and use *all* the energy lost by the system to do work? Our everyday experience tells us that we cannot. If it were possible, we could power a boat to cross the Atlantic by cooling the sea and transferring energy from the sea to drive the propellers. We would need no fuel and travel would be much cheaper. Or instead of heating a fluid by doing electrical work on a resistor, we could consider a process in which a resistor cools the fluid and produces electrical energy at its terminals. The fact that these processes do not occur is summarized in one of the statements of the second law of thermodynamics:

> It is impossible to construct an engine which, operating in a cycle, will produce no other effect than the extraction of heat from a reservoir and the performance of an equivalent amount of work.[23]

The second law implies that a *perpetual motion machine of the second kind* does not exist. Such a machine would convert heat completely into work (see Figure 2.6).

What about the isothermal expansion of an ideal gas? Does this process violate the second law? When the gas expands, it does work on the piston which causes the gas to lose energy. Because the process is isothermal, the gas must absorb energy so that its internal energy remains constant. (The internal energy of an ideal gas depends only on the temperature.) We have

$$\Delta E = Q + W = 0. \tag{2.62}$$

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[22]This thermodynamic variable was named by Rudolf Clausius in 1850 who formed the word *entropy* (from the Greek word for transformation) so as to be as similar as possible to the word energy.

[23]The original statement by Kelvin is "It is impossible by means of inanimate material agency to derive mechanical effect from any portion of matter by cooling it below the temperature of the coldest of the surrounding objects." Planck wrote that "It is impossible to construct an engine, which working in a complete cycle, will produce no effect other than the raising of a weight and the cooling of a heat reservoir." See Zemansky and Dittman, p. 147.

energy absorbed
from atmosphere

Q

magic box

light
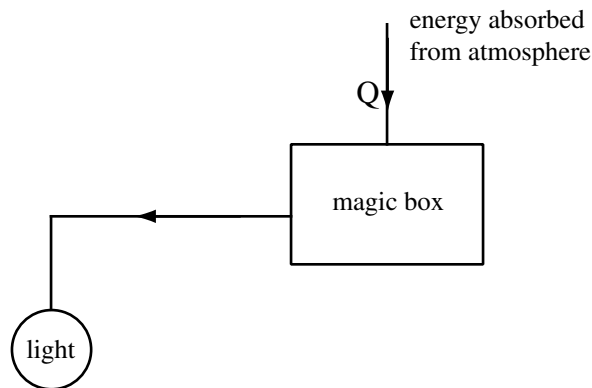
Figure 2.6: A machine that converts energy transferred by heating into work with 100% efficiency violates the Kelvin statement of the second law of thermodynamics.

We see that $W = -Q$, that is, the work done on the gas is $-W$ and the work done by the gas is Q. We conclude that we have completely converted the absorbed energy into work. However, this conversion does not violate the Kelvin-Planck statement because the macrostate of the gas is different at the end than at the beginning, that is, the isothermal expansion of an ideal gas is not a cyclic process. We cannot use the gas to make an engine.

Another statement of the second law based on the empirical observation that energy does not spontaneously go from a colder to a hotter body can be stated as

> No process is possible whose sole result is cooling a colder body and heating a hotter body (Clausius statement).

The Kelvin and the Clausius statements of the second law look different, but each statement implies the other so their consequences are identical.

A more abstract version of the second law that is not based directly on experimental observations, but that is more convenient in many contexts, can be expressed as

> There exists an additive function of state known as the entropy S that can never decrease in an isolated system.

Because the entropy cannot decrease in an isolated system, we conclude that the entropy is a *maximum* for an isolated system in equilibrium.[24] The term *additive* means that if the entropy of two systems is S_A and S_B, respectively, the total entropy of the combined system is $S_{\text{total}} = S_A + S_B$. In the following we adopt this version of the second law and show that the Kelvin and Clausius statements follow from it.

The statement of the second law in terms of the entropy is applicable only to isolated systems (a system enclosed by insulating, rigid, and impermeable walls). The systems of usual interest can exchange energy with its surroundings. In many cases the surroundings may be idealized as

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[24]Maximum and minimum principles are ubiquitous in physics. Leonhard Euler wrote that "Nothing whatsoever takes place in the universe in which some relation of maximum and minimum does not appear."

a large body that does not interact with the rest of the universe. For example, we can take the surroundings of a cup of hot water to be the atmosphere in the room. In this case we can treat the *composite* system, system plus surroundings, as isolated. For the composite system, we have for any process

$$\Delta S_{\text{composite}} \geq 0, \tag{2.63}$$

where $S_{\text{composite}}$ is the entropy of the system plus its surroundings.

If a change is reversible, we cannot have $\Delta S_{\text{composite}} > 0$, because if we reverse the change we would have $\Delta S_{\text{composite}} < 0$, a violation of the Clausius statement. Hence, the only possibility is that

$$\Delta S_{\text{composite}} = 0. \qquad \text{(reversible process)} \tag{2.64}$$

To avoid confusion, we will use the term reversible to be equivalent to a constant entropy process. The condition for a process to be reversible requires only that the total entropy of a closed system is constant; the entropies of its parts may either increase or decrease.

2.13 The Thermodynamic Temperature

The Clausius and Kelvin statements of the second law arose from the importance of heat engines to the development of thermodynamics. A seemingly different purpose of thermodynamics is to determine the conditions of equilibrium. These two purposes are linked by the fact that whenever there is a difference of temperature, work can be extracted.

In the following, we derive the properties of the thermodynamic temperature from the second law. In Section 2.16 we will show that this temperature is the same as the ideal gas scale temperature.

Consider an isolated composite system that is partitioned into two *subsystems A* and *B* by a fixed, impermeable, insulating wall. For the composite system we have

$$E = E_A + E_B = \text{constant}, \tag{2.65}$$

$V = V_A + V_B = \text{constant}$, and $N = N_A + N_B = \text{constant}$. Because the entropy is additive, we can write the total entropy as

$$S(E_A, V_A, N_A, E_B, V_B, N_B) = S_A(E_A, V_A, N_A) + S_B(E_B, V_B, N_B). \tag{2.66}$$

Most divisions of the energy E_A and E_B between subsystems A and B do not correspond to thermal equilibrium.

For thermal equilibrium to be established, we replace the fixed, impermeable, *insulating* wall by a fixed, impermeable, *conducting* wall so that the two subsystems are in thermal contact and energy transfer by heating or cooling can occur. We say that we have removed an *internal constraint*. According to our statement of the second law, the values of E_A and E_B will be such that the entropy of the system becomes a maximum. To find the value of E_A that maximizes S as given by (2.66), we calculate

$$dS = \left(\frac{\partial S_A}{\partial E_A}\right)_{V_A, N_A} dE_A + \left(\frac{\partial S_B}{\partial E_B}\right)_{V_B, N_B} dE_B. \tag{2.67}$$

Because the total energy of the system is conserved, we have $dE_B = -dE_A$, and hence

$$dS = \Big[\Big(\frac{\partial S_A}{\partial E_A}\Big)_{V_A,N_A} - \Big(\frac{\partial S_B}{\partial E_B}\Big)_{V_B,N_B}\Big] dE_A. \tag{2.68}$$

The condition for equilibrium is that $dS = 0$ for arbitrary values of dE_A, and hence

$$\Big(\frac{\partial S_A}{\partial E_A}\Big)_{V_A,N_A} = \Big(\frac{\partial S_B}{\partial E_B}\Big)_{V_B,N_B}. \tag{2.69}$$

Because the temperatures of the two systems are equal in thermal equilibrium, we conclude that the derivative $\partial S/\partial E$ must be associated with the temperature. We will find that it is convenient to define the thermodynamic temperature T as

$$\frac{1}{T} = \Big(\frac{\partial S}{\partial E}\Big)_{V,N}, \qquad \text{(thermodynamic definition of temperature)} \tag{2.70}$$

which implies that the condition for thermal equilibrium is

$$\frac{1}{T_A} = \frac{1}{T_B}. \tag{2.71}$$

Of course we can rewrite (2.71) as $T_A = T_B$.

We have found that if two systems are separated by a conducting wall, energy will be transferred until each of the systems reaches the same temperature. We now suppose that the two subsystems are initially separated by an insulating wall and that the temperatures of the two subsystems are almost equal with $T_A > T_B$. If this constraint is removed, we know that energy will be transferred across the conducting wall and the entropy of the composite system will increase. From (2.68) we can write the change in entropy as

$$\Delta S \approx \Big[\frac{1}{T_A} - \frac{1}{T_B}\Big]\Delta E_A > 0, \tag{2.72}$$

where T_A and T_B are the initial values of the temperatures. The condition that $T_A > T_B$, requires that $\Delta E_A < 0$ in order for $\Delta S > 0$ in (2.72) to be satisfied. Hence, we conclude that the definition (2.70) of the thermodynamic temperature implies that energy is transferred from a system with a higher value of T to a system with a lower value of T. We can express (2.72) as: *No process exists in which a cold body becomes cooler while a hotter body becomes still hotter and the constraints on the bodies and the state of its surroundings are unchanged.* We recognize this statement as the Clausius statement of the second law.

The definition (2.70) of T is not unique, and we could have replaced $1/T$ by other functions of temperature such as $1/T^2$ or $1/\sqrt{T}$. However, we will find in Section 2.16 that the definition (2.70) implies that the thermodynamic temperature is identical to the ideal gas scale temperature.

Note that the inverse temperature can be interpreted as the response of the entropy to a change in the energy of the system. In Section 2.17, we will derive the condition for *mechanical equilibrium*, and in Section 4.5 we will derive the condition for *chemical equilibrium*. These two conditions complement the condition for thermal equilibrium. All three conditions must be satisfied for *thermodynamic equilibrium* to be established.

2.14   The Second Law and Heat Engines

A body that can change the temperature of another body without changing its own temperature and without doing work is known as a *heat bath*. The term is archaic, but we will adopt it because of its common usage.[25] A heat bath can be either a heat source or a heat sink. Examples of a heat source and a heat sink depending on the circumstances are the earth's ocean and atmosphere. If we want to measure the electrical conductivity of a small block of copper at a certain temperature, we can place it into a large body of water that is at the desired temperature. The temperature of the copper will become equal to the temperature of the large body of water, whose temperature will be unaffected by the copper.

For pure heating or cooling the increase in the entropy is given by

$$dS = \left(\frac{\partial S}{\partial E}\right)_{V,N} dE. \tag{2.73}$$

In this case $dE = dQ$ because no work is done. If we express the partial derivative in (2.73) in terms of T, we can rewrite (2.73) as

$$dS = \frac{dQ}{T}. \qquad \text{(pure heating)} \tag{2.74}$$

We emphasize that the relation (2.74) holds only for quasistatic changes. Note that (2.74) implies that *the entropy does not change in a quasistatic, adiabatic process.*

We now use (2.74) to discuss the problem that stimulated the development of thermodynamics – the efficiency of heat engines. We know that an engine converts energy from a heat source to work and returns to its initial state. According to (2.74), the transfer of energy from a heat source lowers the entropy of the source. If the energy transferred is used to do work, the work done must be done on some other system. Because the process of doing work may be quasistatic (for example, compressing a gas), the work need not involve a change of entropy. But if all of the energy transferred is converted into work, the total entropy would decrease, and we would violate the entropy statement of the second law. Hence, we arrive at the conclusion summarized in Kelvin's statement of the second law: no process is possible whose sole result is the complete conversion of energy into work.

The simplest possible engine works in conjunction with a heat source at temperature T_{high} and a heat sink at temperature T_{low}. In a cycle the heat source transfers energy Q_{high} to the engine, and the engine does work W and transfers energy Q_{low} to the heat sink (see Figure 2.7). At the end of one cycle, the energy and entropy of the engine are unchanged because they return to their original values. An engine of this type is known as a *Carnot engine*.

By energy conservation, we have $Q_{\text{high}} = W + Q_{\text{low}}$, or $W = Q_{\text{high}} - Q_{\text{low}}$, where in this context Q_{high} and Q_{low} are positive quantities. From the second law we have that

$$\Delta S_{\text{total}} = \Delta S_{\text{high}} + \Delta S_{\text{low}} = -\frac{Q_{\text{high}}}{T_{\text{high}}} + \frac{Q_{\text{low}}}{T_{\text{low}}} \geq 0. \tag{2.75}$$

We rewrite (2.75) as

$$\frac{Q_{\text{low}}}{Q_{\text{high}}} \geq \frac{T_{\text{low}}}{T_{\text{high}}}. \tag{2.76}$$
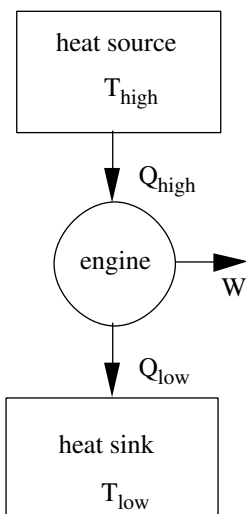
Figure 2.7: Schematic energy transfer diagram for an ideal heat engine. By convention, the quantities Q_{high}, Q_{low}, and W are taken to be positive.

The *thermal efficiency* η of the engine is defined as

$$\eta = \frac{\text{what you obtain}}{\text{what you pay for}} \tag{2.77}$$

$$= \frac{W}{Q_{\text{high}}} = \frac{Q_{\text{high}} - Q_{\text{low}}}{Q_{\text{high}}} = 1 - \frac{Q_{\text{low}}}{Q_{\text{high}}}. \tag{2.78}$$

From (2.78) we see that the engine is most efficient when the ratio $Q_{\text{low}}/Q_{\text{high}}$ is as small as possible. Equation (2.76) shows that $Q_{\text{low}}/Q_{\text{high}}$ is a minimum when the cycle is reversible so that

$$\Delta S_{\text{total}} = 0, \tag{2.79}$$

and

$$\frac{Q_{\text{low}}}{Q_{\text{high}}} = \frac{T_{\text{low}}}{T_{\text{high}}}. \tag{2.80}$$

For these conditions we find that the maximum thermal efficiency is

$$\eta = 1 - \frac{T_{\text{low}}}{T_{\text{high}}}. \qquad \text{(maximum thermal efficiency)} \tag{2.81}$$

Note that the temperature in (2.81) is the thermodynamic temperature.

The result (2.81) illustrates the remarkable power of thermodynamics. We have concluded that all reversible engines operating between a heat source and a heat sink with the same pair of temperatures have the same efficiency and that no irreversible engine working between the same pair of temperatures can have a greater efficiency. This statement is known as *Carnot's principle*.

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[25]The term thermal bath is also sometimes used.

Based on general principles, we have been able to determine the maximum efficiency of a reversible engine without knowing anything about the details of the engine.

Real engines never reach the maximum thermodynamic efficiency because of the presence of mechanical friction and because the processes cannot really be quasistatic. For these reasons, real engines seldom attain more than 30–40% of the maximum thermodynamic efficiency. Nevertheless, the basic principles of thermodynamics are an important factor in their design. We will discuss other factors that are important in the design of heat engines in Chapter 7.

Example 2.9. A Carnot engine

A Carnot engine extracts 240 J from a heat source and rejects 100 J to a heat sink at 15°C in one cycle. How much work does the engine do in one cycle? What is its efficiency? What is the temperature of the heat source?

Solution. From the first law we have

$$W = 240 \,\text{J} - 100 \,\text{J} = 140 \,\text{J}.$$

The efficiency is given by

$$\eta = \frac{W}{Q_{\text{high}}} = \frac{140}{240} = 0.583 = 58.3\%. \tag{2.82}$$

We can use this result for η and the general relation (2.81) to solve for T_{high}:

$$T_{\text{high}} = \frac{T_{\text{low}}}{1 - \eta} = \frac{288 \,\text{K}}{1 - 0.583} = 691 \,\text{K}.$$

Note that to calculate the efficiency, we must use the thermodynamic temperature.

Example 2.10. The cycle of a hypothetical engine is illustrated in Figure 2.8. Let $P_1 = 1 \times 10^6$ Pa, $P_2 = 2 \times 10^6$ Pa, $V_1 = 5 \times 10^{-3} \,\text{m}^3$, and $V_2 = 25 \times 10^{-3} \,\text{m}^3$. If the energy absorbed by heating the engine is 5×10^4 J, what is the efficiency of the engine?

Solution. The work done by the engine equals the area enclosed:

$$W = \frac{1}{2}(P_2 - P_1)(V_2 - V_1). \tag{2.83}$$

Confirm that $W = 1 \times 10^4$ J. The efficiency is given by

$$\eta = \frac{W}{Q_{\text{absorbed}}} = \frac{1 \times 10^4}{5 \times 10^4} = 0.20. \tag{2.84}$$

The maximum efficiency of a heat engine depends on the temperatures T_{high} and T_{low} in a simple way and not on the details of the cycle or working substance. The *Carnot cycle* is a particular sequence of idealized processes of an ideal gas that yields the maximum thermodynamic efficiency given in (2.81). The four steps of the Carnot cycle (two adiabatic and two isothermal steps) are illustrated in Figure 2.9. The initial state is at the point A. The gas is in contact with a hot heat bath at temperature T_{high} so that the temperature of the gas also is T_{high}. The piston is pushed in as far as possible so the volume is reduced. As a result of the relatively high temperature and small volume, the pressure of the gas is high.
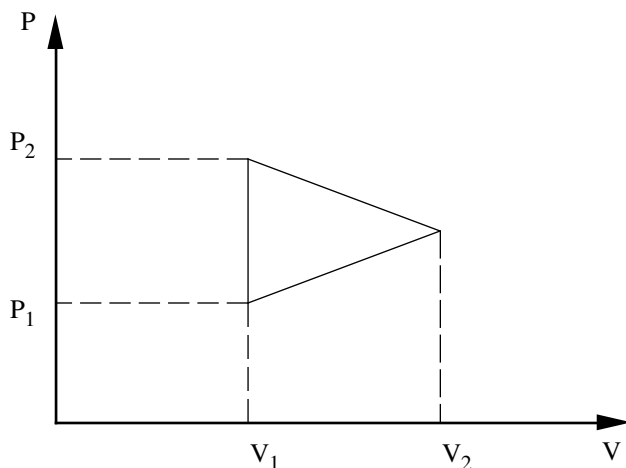
Figure 2.8: The cycle of the hypothetical engine considered in Example 2.10.

1. $A \rightarrow B$, *isothermal expansion.* The gas expands while it is in contact with the heat source. During the expansion the high pressure gas pushes on the piston and the piston turns a crank. This step is a power stroke of the engine and the engine does work. To keep the gas at the same temperature, the engine must absorb energy by being heated by the heat source.

    We could compress the gas isothermally and return the gas to its initial state. Although this step would complete the cycle, exactly the same amount of work would be needed to push the piston back to its original position and hence no net work would be done. To make the cycle useful, we have to choose a cycle so that not all the work of the power stroke is lost in restoring the gas to its initial pressure, temperature, and volume. The idea is to reduce the pressure of the gas so that during the compression step less work has to be done. One way of reducing the pressure is to lower the temperature of the gas by doing an adiabatic expansion.

2. $B \rightarrow C$, *adiabatic expansion.* We remove the thermal contact of the gas with the hot bath and allow the volume to continue to increase so that the gas expands adiabatically. Both the pressure and the temperature of the gas decrease. The step from $B \rightarrow C$ is still a power stroke, but now we are cashing in on the energy stored in the gas, because it can no longer take energy from the heat source.

3. $C \rightarrow D$, *isothermal compression.* We now begin to restore the gas to its initial condition. At C the gas is placed in contact with the heat sink at temperature T_{low}, to ensure that the pressure remains low. We now do work on the gas by pushing on the piston and compressing the gas. As the gas is compressed, the temperature of the gas tends to rise, but the thermal contact with the cold bath ensures that the temperature remains at the same temperature T_{low}. The extra energy is dumped to the heat sink.

4. $D \rightarrow A$, *adiabatic compression.* At D the volume is almost what it was initially, but the
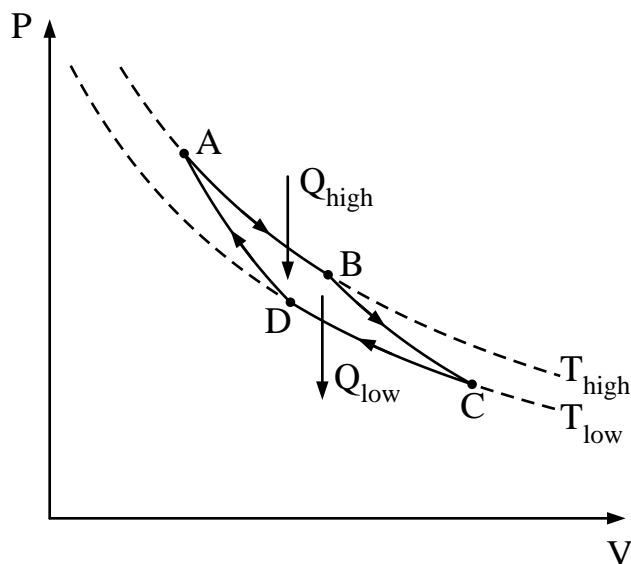
Figure 2.9: The four steps of the Carnot cycle.

temperature of the gas is too low. Before the piston returns to its initial state, we remove the contact with the heat sink and allow the work of adiabatic compression to raise the temperature of the gas to T_{high}.

These four steps represent a complete cycle and the idealized engine is ready to go through another cycle. Note that a net amount of work has been done, because more work was done *by* the gas during its power strokes than was done *on* the gas while it was compressed. The reason is that the work done during the compression steps was against a lower pressure. The result is that we have extracted useful work. But some of the energy of the gas was discarded into the heat sink while the gas was being compressed. Hence, the price we have had to pay to do work by having the gas heated by the heat source is to throw away some of the energy to the heat sink.

Example 2.11. The Carnot cycle for an ideal gas

Determine the changes in the various thermodynamic quantities of interest during each step of the Carnot cycle and show that the efficiency of a Carnot cycle whose working substance is an ideal gas is given by $\eta = 1 - T_{\text{high}}/T_{\text{low}}$.

Solution. We will use the *PV* diagram for the engine shown in Figure 2.9. During the isothermal expansion from A to B, energy Q_{high} is absorbed by the gas by heating at temperature T_{high}. The expanding gas does a positive amount of work against its environment. Because $\Delta E = 0$ for an ideal gas along an isotherm,

$$Q_{\text{high}} = -W_{\text{A}\to\text{B}} = NkT_{\text{high}} \ln \frac{V_B}{V_A}, \tag{2.85}$$

where W_{AB} is the (negative) work done on the gas.

During the adiabatic expansion from $B \rightarrow C$, $Q_{B \rightarrow C} = 0$ and $W_{B \rightarrow C} = C_V(T_C - T_B)$. Similarly, $W_{C \rightarrow D} = -NkT_{\text{low}} \ln V_D/V_C$, and

$$Q_{\text{low}} = -NkT_{\text{low}} \ln \frac{V_D}{V_C} = NkT_{\text{low}} \ln \frac{V_C}{V_D}. \tag{2.86}$$

(By convention Q_{high} and Q_{low} are both positive.) Finally, during the adiabatic compression from $D \rightarrow A$, $Q_{D \rightarrow A} = 0$ and $W_{D \rightarrow A} = C_V(T_D - T_A)$. We also have $W_{\text{net}} = Q_{\text{high}} - Q_{\text{low}}$.

Because the product $TV^{\gamma-1}$ is a constant in a quasistatic adiabatic process, we have

$$T_{\text{high}} V_B^{\gamma-1} = T_{\text{low}} V_C^{\gamma-1} \tag{2.87a}$$

$$T_{\text{low}} V_D^{\gamma-1} = T_{\text{high}} V_A^{\gamma-1}, \tag{2.87b}$$

which implies that

$$\frac{V_B}{V_A} = \frac{V_C}{V_D}. \tag{2.88}$$

The net work is given by

$$W_{\text{net}} = Q_{\text{high}} - Q_{\text{low}} = Nk(T_{\text{high}} - T_{\text{low}}) \ln \frac{V_C}{V_D}. \tag{2.89}$$

The efficiency is given by

$$\eta = \frac{W_{\text{net}}}{Q_{\text{high}}} = \frac{T_{\text{high}} - T_{\text{low}}}{T_{\text{high}}} = 1 - \frac{T_{\text{low}}}{T_{\text{high}}}, \tag{2.90}$$

as was found earlier by general arguments.

2.15 Entropy Changes

As we have mentioned, the impetus for developing thermodynamics was the industrial revolution and the efficiency of engines. However, similar reasoning can be applied to other macroscopic systems to calculate the change in entropy.

Example 2.12. Change in entropy of a solid

A solid with constant heat capacity C is taken from an initial temperature T_1 to a final temperature T_2. What is its change in entropy? (Ignore the small difference in the heat capacities at constant volume and constant pressure.)

Solution. We assume that the temperature of the solid is increased by putting the solid in contact with a succession of heat baths at temperatures separated by a small amount ΔT. Then the entropy change is given by

$$S_2 - S_1 = \int_{T_1}^{T_2} \frac{dQ}{T} = \int_{T_1}^{T_2} C(T) \frac{dT}{T}. \tag{2.91}$$

Because the heat capacity C is a constant, we find

$$\Delta S = S_2 - S_1 = C \int_{T_1}^{T_2} \frac{dT}{T} = C \ln \frac{T_2}{T_1}. \tag{2.92}$$

Note that if $T_2 > T_1$, the entropy has increased.

How can we determine the entropy of a solid? We know how to measure the temperature and the energy, but we have no entropy meter. Instead we have to determine the entropy *indirectly*. If the volume is held constant, we can determine the temperature dependence of the entropy by doing many successive measurements of the heat capacity and by doing the integral in (2.91). Note that such a determination gives only the entropy difference. We will discuss how to determine the absolute value of the entropy in Section 2.20.

Entropy changes due to thermal contact. A solid with heat capacity C_A at temperature T_A is placed in contact with another solid with heat capacity C_B at a lower temperature T_B. What is the change in entropy of the system after the two bodies have reached thermal equilibrium? Assume that the heat capacities are independent of temperature and the two solids are isolated from their surroundings.

From Example 2.4 we know that the final equilibrium temperature is given by

$$T = \frac{C_A T_A + C_B T_B}{C_A + C_B}. \tag{2.93}$$

Although the process is irreversible, we can calculate the entropy change by considering any process that takes a body from one temperature to another. For example, we can imagine that a body is brought from its initial temperature T_B to the temperature T in many successive infinitesimal steps by placing it in successive contact with a series of reservoirs at infinitesimally greater temperatures. At each contact the body is arbitrarily close to equilibrium and has a well defined temperature. For this reason, we can apply the result (2.92) which yields $\Delta S_A = C_A \ln T/T_A$. The total change in the entropy of the system is given by

$$\Delta S = \Delta S_A + \Delta S_B = C_A \ln \frac{T}{T_A} + C_B \ln \frac{T}{T_B}, \tag{2.94}$$

where T is given by (2.93). Substitute real numbers for T_A, T_B, C_A, and C_B and convince yourself that $\Delta S \geq 0$. Does the sign of ΔS depend on whether $T_A > T_B$ or $T_A < T_B$?

Example 2.13. Entropy change of water in contact with a heat bath

One kilogram of water at $0°C$ is brought into contact with a heat bath at $50°C$. What is the change of entropy of the water, the bath, and the combined system consisting of both the water and the heat bath?

Solution. The change in entropy of the water is given by

$$\Delta S_{\text{H}_2\text{0}} = C \ln \frac{T_2}{T_1} = 4184 \ln \frac{273 + 50}{273 + 0} = 703.67 \, \text{J/K}. \tag{2.95}$$

Why does the factor of 273 enter in (2.95)? The amount of energy transferred to the water from the heat bath is

$$Q = C(T_2 - T_1) = 4184 \times 50 = 209,200 \text{ J}. \tag{2.96}$$

The change in entropy of the heat bath is

$$\Delta S_B = \frac{-Q}{T_2} = -\frac{209200}{323} = -647.68 \text{ J/K}. \tag{2.97}$$

Hence the total change in the entropy is

$$\Delta S = \Delta S_{\text{H}_2\text{0}} + \Delta S_B = 703.67 - 647.68 = 56 \text{ J/K}. \tag{2.98}$$

Problem 2.18. Water in contact with two heat baths

The temperature of one kilogram of water at $0°$C is increased to $50°$C by first bringing it into contact with a heat bath at $25°$C and then with a heat bath at $50°$C. What is the change in entropy of the entire system? How does this change in entropy compare with the change that was found in Example 2.13?

Example 2.14. More on the nature of a heat bath

A heat bath is a much larger system whose temperature remains unchanged when energy is added or subtracted from it. As an example consider two systems with constant volume heat capacities C_A and C_B that are initially at different temperatures T_A and T_B. What happens when the two systems are placed in thermal contact (and are isolated from their surroundings)? The volume of the two systems is fixed and the heat capacities are independent of temperature.

From the first law of thermodynamics we have

$$C_A T_A + C_B T_B = (C_A + C_B)T, \tag{2.99}$$

and

$$T = \frac{C_A}{C_A + C_B}T_A + \frac{C_B}{C_A + C_B}T_B. \tag{2.100}$$

The total change in the entropy is given by

$$\Delta S = \Delta S_A + \Delta S_B = C_A \ln \frac{T}{T_A} + C_B \ln \frac{T}{T_B}. \tag{2.101}$$

We write

$$\lambda = \frac{C_A}{C_B}, \tag{2.102}$$

express ΔS in terms of λ, and then take the limit $\lambda \to 0$. We have

$$\frac{T}{T_A} = \frac{C_A}{C_B(1 + C_A/C_B)} + \frac{1}{(1 + C_A/C_B)}\frac{T_B}{T_A} \tag{2.103a}$$

$$= \frac{1}{1 + \lambda}\left(1 + \frac{T_B}{T_A}\right). \tag{2.103b}$$

In the limit $\lambda \to 0$ (an infinite heat bath) we see from (2.103b) that $T = T_B$.

We next calculate the change in the entropy in the limit of an infinite heat bath. The first term in (2.101) gives

$$\Delta S_A = C_A \ln \frac{T}{T_A} \to C_A \ln \frac{T_B}{T_A}. \tag{2.104}$$

To evaluate the second term in (2.101) we write

$$\frac{T}{T_B} = \frac{1}{1+\lambda} \left(1 + \lambda \frac{T_A}{T_B}\right) \approx (1-\lambda)\left(1 + \lambda \frac{T_A}{T_B}\right) \tag{2.105a}$$

$$= 1 + \lambda \left(\frac{T_A}{T_B} - 1\right), \tag{2.105b}$$

where we have used the approximation $(1+x)^{-1} \approx 1 - x$. We have

$$\Delta S_B = C_B \ln \frac{T}{T_B} \to C_A \frac{1}{\lambda} \ln \left[1 + \lambda\left(\frac{T_A}{T_B} - 1\right)\right] \to C_A\left(\frac{T_A}{T_B} - 1\right). \tag{2.106}$$

where we have used the approximation $\ln(1 + x) \approx x$. Hence, the total change in the entropy of the system is given by

$$\Delta S = C_A\left[\ln \frac{T_B}{T_A} + \frac{T_A}{T_B} - 1\right]. \tag{2.107}$$

In Problem 2.55 you will be asked to show that ΔS in (2.107) is always greater than zero for $T_A \neq T_B$.

Example 2.15. Melting of ice

A beaker contains a mixture of 0.1 kg of ice and 0.1 kg of water. Suppose that we place the beaker over a low flame and melt 0.02 kg of the ice. What is the change of entropy of the ice-water mixture? (It takes 334 kJ to melt 1 kg of ice.)

Solution. If we add energy to ice at its melting temperature $T = 273.15$ K at atmospheric pressure, the effect is to melt the ice rather than to raise its temperature.

The addition of energy to the ice-water mixture is generally not a reversible process, but we can find the entropy change by considering a reversible process between the initial and final states. We melt 0.02 kg of ice in a reversible process by supplying $0.02 \text{ kg} \times 334 \text{ kJ/kg} = 6680$ J from a heat bath at 273.15 K, assuming that the ice-water mixture is in equilibrium with the heat bath. (We also implicitly assume that the mixture and the heat bath form an isolated composite system.) Hence, the entropy increase is given by $\Delta S = 6680/273.15 = 24.46$ J/K.

Entropy change in a free expansion. Consider an ideal gas of N particles in a closed, insulated container that is divided into two chambers by an impermeable partition (see Figure 2.10). The gas is initially confined to one chamber of volume V_A at a temperature T. The gas is then allowed to expand freely into a vacuum to fill the entire container of volume V_B. What is the change in entropy for this process?

Because the expansion is into a vacuum, no work is done by the gas. The expansion also is adiabatic because the container is thermally insulated. Hence, there is no change in the internal energy of the gas. It might be argued that $\Delta S = Q/T = 0$ because $Q = 0$. However, this conclusion would be incorrect because the relation $dS = dQ/T$ holds only for a quasistatic process.

partition
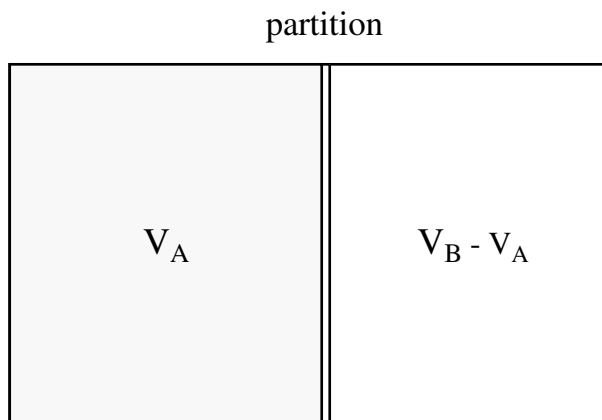
Figure 2.10: The free expansion of an isolated ideal gas. The second chamber is initially a vacuum and the total volume of the two chambers is V_B.

The expansion from V_A to V_B is an irreversible process. Left to itself, the system will not return spontaneously to its original state with all the particles in the left container. To calculate the change in the entropy, we may consider a quasistatic process that takes the system to the same final state. Because the gas is ideal, the internal energy depends only on the temperature, and hence the temperature of the ideal gas is unchanged. So we will calculate the energy added during an isothermal process to take the gas from volume V_A to V_B,

$$Q = NkT \ln \frac{V_B}{V_A}, \qquad (2.108)$$

where we have used (2.27). Hence, from (2.91), the entropy change is given by

$$\Delta S = \frac{Q}{T} = Nk \ln \frac{V_B}{V_A}. \qquad (2.109)$$

Note that $V_B > V_A$ and the entropy change is positive as expected.

Alternatively, we can argue that the work needed to restore the gas to its original macrostate is given by

$$W = -\int_{V_B}^{V_A} P \, dV = NkT \ln \frac{V_B}{V_A}, \qquad (2.110)$$

where we have used the fact that the process is isothermal. Hence, in this case $W = T\Delta S$, and the entropy increase of the universe requires work on the gas to restore it to its original state.

The discussion of the free expansion of an ideal gas illustrates two initially confusing aspects of thermodynamics. As mentioned, the name thermodynamics is a misnomer because thermodynamics treats only equilibrium states and not dynamics. Nevertheless, thermodynamics discusses processes that must happen over some interval of time. Also confusing is that we can consider processes that did not actually happen. In this case no energy by heating was transferred to the gas and the process was adiabatic. The value of Q calculated in (2.108) is the energy transferred

in an isothermal process. No energy is transferred by heating in an adiabatic process, but the entropy change is the same. For this reason we calculated the entropy change as if an isothermal process had occurred.

Quasistatic adiabatic processes. We have already discussed that quasistatic adiabatic processes have the special property that the entropy does not change, but we repeat this statement here to emphasize its importance. Because the process is adiabatic, $Q = 0$, and because the process is quasistatic, $\Delta S = Q/T = 0$, and there is no change in the entropy.

Maximum work. When two bodies are placed in thermal contact, no work is done, that is, $\Delta W = 0$ and $\Delta E = Q_A + Q_B = 0$. What can we do to extract the maximum work possible from the two bodies? From our discussion of heat engines, we know that we should not place them in thermal contact. Instead we run a Carnot (reversible) engine between the two bodies. However, unlike the reservoirs considered in the Carnot engine, the heat capacities of the two bodies are finite, and hence the temperature of each body changes as energy is transferred from one body to the other.

To extract the maximum work, we assume that the process is reversible, and we have

$$\Delta S = \Delta S_A + \Delta S_B = 0, \tag{2.111}$$

from which it follows using (2.91) that

$$C_A \ln \frac{T}{T_A} + C_B \ln \frac{T}{T_B} = 0. \tag{2.112}$$

If we solve (2.112) for T, we find that

$$T = T_A^{C_A/(C_A+C_B)} T_B^{C_B/(C_A+C_B)}. \tag{2.113}$$

We see that the final temperature for a reversible process is the geometrical average of T_A and T_B weighted by their respective heat capacities.

Problem 2.19.

(a) Suppose $T_A = 256\,\text{K}$ and $T_B = 144\,\text{K}$. What are the relative values of the final temperatures in (2.93) and (2.113) assuming that the heat capacities of the two bodies are equal?

(b) Show that the work performed by the heat engine in the reversible case is given by

$$W = \Delta E = C_A(T - T_A) + C_B(T - T_B). \tag{2.114}$$

Are all forms of energy equivalent? If you were offered $100\,\text{J}$ of energy, would you choose to have it delivered as compressed gas at room temperature or as a hot brick at $400\,\text{K}$? The answer might depend on what you want to do with the energy. If you want to lift a block of ice, the best choice would be to take the energy in the compressed gas. If you want to keep warm, the $400\,\text{K}$ object would be acceptable.

If you are not sure what you want to do with the energy, it is clear from the second law of thermodynamics that we should take the form of the energy that can be most directly converted into work, because there is no restriction on using stored energy for heating. What is different is

the *quality* of the energy, which we take to be a measure of its ability to do a variety of tasks. We can readily convert energy from higher to lower quality, but the second law of thermodynamics prevents us from going in the opposite direction with 100% efficiency.

We found in our discussion of the adiabatic free expansion of a gas that the entropy increases. Because the system has lost ability to do work, we can say that there has been a loss of the quality of energy. Suppose that we had let the gas undergo a quasistatic isothermal expansion instead of an adiabatic free expansion. Then the work done by the gas would have been (see (2.27)):

$$W = NkT \ln \frac{V_B}{V_A}. \tag{2.115}$$

After the adiabatic free expansion, the gas can no longer do this work, even though its energy is unchanged. If we compare (2.115) with (2.109), we see that the energy that becomes unavailable to do work in an adiabatic free expansion is

$$E_{\text{unavailable}} = T\Delta S. \tag{2.116}$$

Equation (2.116) indicates that entropy is a measure of the quality of energy. Given two systems with the same energy, the one with the lower entropy has the higher quality energy. An increase in entropy implies that some energy has become unavailable to do work.

2.16 Equivalence of Thermodynamic and Ideal Gas Scale Temperatures

So far we have assumed that the ideal gas scale temperature which we introduced in Section 2.4 is the same as the thermodynamic temperature defined by (2.70). We now show that the two temperatures are proportional and can be made equal if we choose the units of S appropriately.

The ideal gas temperature scale, which we denote as θ in this section to distinguish it from the thermodynamic temperature T, is defined by the relation

$$\theta = PV/Nk. \tag{2.117}$$

That is, θ is proportional to the pressure of a gas at a fixed low density and is equal to $273.16\,\text{K}$ at the triple point of water. The fact that $\theta \propto P$ is a matter of definition. Another important property of ideal gases is that the internal energy depends only on θ and is independent of the volume.

One way to show that T is proportional to θ is to consider a Carnot cycle (see Figure 2.9) with an ideal gas as the working substance. At every stage of the cycle we have

$$\frac{dQ}{\theta} = \frac{dE - dW}{\theta} = \frac{dE + PdV}{\theta}, \tag{2.118}$$

or

$$\frac{dQ}{\theta} = \frac{dE}{\theta} + Nk\frac{dV}{V}. \tag{2.119}$$

The first term on the right-hand side of (2.119) depends only on θ and the second term depends only on the volume. If we integrate (2.119) around one cycle, both θ and V return to their starting values, and hence the loop integral of the right-hand side of (2.119) is zero. We conclude that

$$\oint \frac{dQ}{\theta} = \frac{Q_{\text{cold}}}{\theta_{\text{cold}}} - \frac{Q_{\text{hot}}}{\theta_{\text{hot}}} = 0. \tag{2.120}$$

In Section 2.14 we showed that $Q_{\text{cold}}/Q_{\text{hot}} = T_{\text{cold}}/T_{\text{hot}}$ for a Carnot engine (see (2.80)). If we combine this result with (2.120), we find that

$$\frac{T_{\text{cold}}}{T_{\text{hot}}} = \frac{\theta_{\text{cold}}}{\theta_{\text{hot}}}. \tag{2.121}$$

It follows that the thermodynamic temperature T is proportional to the ideal gas scale temperature θ. From now on we shall assume that we have chosen suitable units for S so that $T = \theta$.

2.17   The Thermodynamic Pressure

In Section 2.13 we showed that the thermodynamic definition of temperature follows by considering the condition for the thermal equilibrium of two subsystems. In the following, we show that the pressure can be defined in an analogous way and that the pressure can be interpreted as a response of the entropy to a change in the volume.

As before, consider an isolated composite system that is partitioned into two subsystems. The subsystems are separated by a movable, insulating wall so that the energies and volumes of the subsystems can adjust themselves, but N_A and N_B are fixed. For simplicity, we assume that E_A and E_B have already changed so that thermal equilibrium has been established. For fixed total volume V, we have one independent variable which we take to be V_A; V_B is given by $V_B = V - V_A$. The value of V_A that maximizes S_{total} is given by

$$dS_{\text{total}} = \frac{\partial S_A}{\partial V_A} \, dV_A + \frac{\partial S_B}{\partial V_B} \, dV_B = 0. \tag{2.122}$$

Because $dV_A = -dV_B$, we can use (2.122) to write the condition for *mechanical equilibrium* as

$$\frac{\partial S_A}{\partial V_A} = \frac{\partial S_B}{\partial V_B}. \tag{2.123}$$

We define the thermodynamic pressure P as

$$\frac{P}{T} = \left(\frac{\partial S}{\partial V} \right)_{E,N}. \qquad \text{(thermodynamic definition of the pressure)} \tag{2.124}$$

For completeness, we define the *chemical potential* as the response of the entropy to a change in the number of particles:

$$\frac{\mu}{T} = -\left(\frac{\partial S}{\partial N} \right)_{E,V}. \qquad \text{(thermodynamic definition of the chemical potential)} \tag{2.125}$$

We will discuss the interpretation of μ in Section 4.12. You probably won't be surprised to learn that if two systems can exchange particles, then $\mu_1 = \mu_2$ is the condition for chemical equilibrium.

We will sometimes distinguish between thermal equilibrium, mechanical equilibrium, and chemical equilibrium for which the temperatures, pressures, and chemical potentials are equal, respectively.

2.18   The Fundamental Thermodynamic Relation

The first law of thermodynamics implies that the internal energy E is a function of state. For *any* change of state, the change in E is given by (2.187):

$$\Delta E = Q + W. \qquad \text{(any process)} \tag{2.126}$$

To separate the contributions to E due to heating and work, the constraints on the system have to be known. If the change is quasistatic, then the infinitesimal work done is

$$dW = -PdV, \qquad \text{(quasistatic process)} \tag{2.127}$$

and

$$dQ = TdS. \qquad \text{(quasistatic process)} \tag{2.128}$$

Thus, for an infinitesimal change in energy, we obtain

$$dE = TdS - PdV. \tag{2.129}$$

There are two ways of thinking about (2.129). As our derivation suggests this equation tells us the relation between changes in energy, entropy, and volume in a quasistatic process. However, because S, V, and E are functions of state, we can view (2.129) as the differential form (for fixed N) of the fundamental equation $E = E(S, V, N)$ that describes the relation between E, S, V, and N for all equilibrium states. We can also understand (2.129) by considering S as a function of E, V, and N and writing dS as

$$dS = \frac{\partial S}{\partial E} dE + \frac{\partial S}{\partial V} dV + \frac{\partial S}{\partial N} dN. \tag{2.130}$$

If we use the definitions (2.70), (2.124), and (2.125) of the various partial derivatives of $S(E, V, N)$, we can write

$$dS = \frac{1}{T} dE + \frac{P}{T} dV - \frac{\mu}{T} dN, \tag{2.131}$$

which is equivalent to (2.129) for a fixed number of particles.

If we know the entropy S as a function of E, V, and N, we can determine the corresponding responses T, P, and μ. For this reason we shall refer to E, V, and N as the natural variables in which S should be expressed. In this context S can be interpreted as a *thermodynamic potential* because its various partial derivatives yield the equations of state of the system. In Section 2.21 we shall discuss thermodynamic potentials that have different sets of natural variables.

We can alternatively consider E as a function of S, V, and N and rewrite (2.131) as

$$\boxed{dE = TdS - PdV + \mu dN}. \qquad \text{(fundamental thermodynamic relation)} \tag{2.132}$$

Equation (2.132) is a mathematical statement of the combined first and second laws of thermodynamics. Although there are very few equations in thermodynamics that are necessary to memorize, (2.132) is one of the few equations that you should know without thinking.

Many useful thermodynamic relations can be derived using (2.132). For example, if we regard E as a function of S, V, and N, we can write

$$dE = \frac{\partial E}{\partial S}\,dS + \frac{\partial E}{\partial V}\,dV + \frac{\partial E}{\partial N}\,dN. \tag{2.133}$$

If we compare (2.132) and (2.133), we see that

$$T = \left(\frac{\partial E}{\partial S}\right)_{V,N} \qquad P = -\left(\frac{\partial E}{\partial V}\right)_{S,N} \qquad \mu = \left(\frac{\partial E}{\partial N}\right)_{S,V}. \tag{2.134}$$

Note that $E(S, V, N)$ also can be interpreted as a thermodynamic potential. Or we can start with (2.132) and obtain (2.131) and the thermodynamic definitions of T, P, and μ.

2.19 The Entropy of an Ideal Gas

Because we know two equations of state of an ideal gas, (2.8) and (2.25), we can find the entropy of an ideal gas as a function of various combinations of E, T, P, and V (for fixed N). If we substitute $1/T = 3Nk/(2E)$ and $P/T = Nk/V$ into (2.131), we obtain

$$dS = \frac{3}{2}Nk\frac{dE}{E} + Nk\frac{dV}{V}. \tag{2.135}$$

We can integrate (2.135) to obtain the change in the entropy from state E_1, V_1 to state E_2, V_2:

$$\Delta S = \frac{3}{2}Nk\ln\frac{E_2}{E_1} + Nk\ln\frac{V_2}{V_1}. \tag{2.136}$$

We see that S is an additive quantity as we assumed; that is, S is proportional to N,

Frequently it is more convenient to express S in terms of T and V or T and P. To obtain $S(T, V)$ we substitute $E = 3NkT/2$ into (2.136) and obtain

$$\Delta S = \frac{3}{2}Nk\ln\frac{T_2}{T_1} + Nk\ln\frac{V_2}{V_1}. \tag{2.137}$$

Problem 2.20. Relation of T and P for a quasistatic adiabatic process

(a) Find $\Delta S(T, P)$ for an ideal gas.

(b) Use (2.137) to derive the relation (2.51) for a quasistatic adiabatic process.

2.20 The Third Law of Thermodynamics

We can calculate only differences in the entropy using purely thermodynamic relations as we did in Section 2.19. We can determine the absolute value of the entropy by using the third law of thermodynamics which states that

$$\lim_{T \to 0} S = 0. \qquad \text{(third law of thermodynamics)} \qquad (2.138)$$

A statement equivalent to (2.138) was first proposed by Nernst in 1906 on the basis of empirical observations.[26] The statistical basis of this law is discussed in Section 4.6. In the context of thermodynamics, the third law can be understood only as a consequence of empirical observations.

The most important consequence of the third law is that all heat capacities must go to zero as the temperature approaches zero. For changes at constant volume, we know that

$$S(T_2, V) - S(T_1, V) = \int_{T_1}^{T_2} \frac{C_V(T)}{T} \, dT. \qquad (2.139)$$

The condition (2.138) implies that in the limit $T_1 \to 0$, the integral in (2.139) must go to a finite limit, and hence we require that $C_V(T) \to 0$ as $T \to 0$. Similarly, we can argue that $C_P \to 0$ as $T \to 0$. Note that these conclusions about the low temperature behavior of C_V and C_P are independent of the nature of the system. Such is the power of thermodynamics. This low temperature behavior of the heat capacity was first established experimentally in 1910–1912.

As we will find in Section 4.6, the third law is a consequence of the fact that the most fundamental description of nature at the microscopic level is quantum mechanical. We have already seen that the heat capacity is a constant for an ideal classical gas. Hence, the thermal equation of state, $E = 3NkT/2$, as well as the pressure equation of state, $PV = NkT$, must cease to be applicable at sufficiently low temperatures.

Example 2.16. At very low temperature T, the heat capacity C of an insulating solid is proportional to T^3. If we take $C = AT^3$ for a particular solid, what is the entropy of the solid at temperature T?

Solution. As before, the entropy is given by (see (2.91)):

$$S(T) = \int_0^T \frac{C_V(T)}{T} dT, \qquad (2.140)$$

where we have used the fact that $S(T = 0) = 0$. We can integrate the right-hand side of (2.140) from $T = 0$ to the desired value of T to find the absolute value of S. The result in this case is $S = AT^3/3$.

2.21 Free Energies

We know that the entropy of an isolated system can never decrease. However, an isolated system is of little experimental interest, and we wish to consider the more typical case where the system

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[26]Walther Nernst (1864–1943) was awarded the 1920 Nobel prize in chemistry for his discovery of the third law and related work.

of interest is connected to a much larger system whose properties do not change significantly. As we have discussed, this larger system is called a heat bath. In the following we will consider a generalization of a heat bath; that is, a large system whose temperature and pressure are unchanged by interactions. For simplicity, we will still refer to such a system as a heat bath.

If a system is connected to a heat bath, then the entropy of the system may increase or decrease. The only thing we can say for sure is that the entropy of the system plus the heat bath must increase or remain unchanged. Because the entropy is additive, we have[27]

$$S_{\text{composite}} = S + S_{\text{bath}}, \tag{2.141}$$

and

$$\Delta S_{\text{composite}} = \Delta S + \Delta S_{\text{bath}} \geq 0, \tag{2.142}$$

where the properties of the system of interest are denoted by the absence of a subscript. Our goal is to determine if there is a property of the system alone (not the composite system) that is a maximum or a minimum. We begin by writing the change ΔS_{bath} in terms of the properties of the system. Because energy can be transferred between the system and heat bath, we have

$$\Delta S_{\text{bath}} = \frac{-Q}{T_{\text{bath}}}, \tag{2.143}$$

where Q is the amount of energy transferred by heating the system, and $-Q$ is the amount of energy transferred to the heat bath. If we use (2.143) and the fundamental thermodynamic relation, (2.132), we can rewrite (2.142) as

$$\Delta S_{\text{composite}} = \Delta S - \frac{Q}{T_{\text{bath}}}. \tag{2.144}$$

The application of the first law to the system gives

$$\Delta E = Q + W, \tag{2.145}$$

where ΔE is the change in the energy of the system and W is the work done on it. If the work done on the system is due to the heat bath, then $W = -P_{\text{bath}}\Delta V$, where ΔV is the change in volume of the system. Then we can write

$$\Delta S_{\text{composite}} = \Delta S - \frac{\Delta E - W}{T_{\text{bath}}} = \Delta S - \frac{\Delta E + P_{\text{bath}}\Delta V}{T_{\text{bath}}} \geq 0. \tag{2.146}$$

A little algebra leads to

$$\Delta E + P_{\text{bath}}\Delta V - T_{\text{bath}}\Delta S \leq 0. \tag{2.147}$$

This result suggests that we define the *availability* by

$$A = E + P_{\text{bath}}V - T_{\text{bath}}S, \tag{2.148}$$

so that (2.147) becomes

$$\Delta A = \Delta E + P_{\text{bath}}\Delta V - T_{\text{bath}}\Delta S \leq 0. \tag{2.149}$$

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[27]The following discussion is adapted from Mandl, pp. 89–92.

The availability includes properties of both the system and the heat bath. The significance of the availability will be discussed in the following.

We now look at some typical experimental situations and introduce a quantity that depends only on the properties of the system. As before, we assume that its volume and number of particles is fixed, and that its temperature equals the temperature of the heat bath, that is, we set $T_{\text{bath}} = T$ and $\Delta V = 0$. In this case we have

$$\Delta A = \Delta E - T\Delta S \equiv \Delta F \leq 0. \tag{2.150}$$

We have defined the *Helmholtz free energy* as

$$F = E - TS. \tag{2.151}$$

The inequality in (2.150) implies that if a constraint within the system is removed, then the system's Helmholtz free energy will *decrease*. At equilibrium the left-hand side of (2.150) will vanish, and F will be a minimum. Thus, F plays the analogous role for systems at constant T and V that was played by the entropy for an isolated system (constant E and V). We see that the Helmholtz free energy is a minimum for a given T, V, and N.

The entropy of an isolated system is a function of E, V, and N. What are the natural variables for F? From our discussion it should be clear that these variables are T, V, and N. The answer can be found by taking the differential of (2.151) and using (2.132). The result is

$$dF = dE - SdT - TdS \tag{2.152a}$$
$$= (TdS - PdV + \mu dN) - SdT - TdS \tag{2.152b}$$
$$= -SdT - PdV + \mu dN. \tag{2.152c}$$

We substituted $dE = TdS - PdV + \mu dN$ to go from (2.152a) to (2.152c).

From (2.152) we see that $F = F(T, V, N)$ and that S, P, and μ can be obtained by taking appropriate partial derivatives of F. For example,

$$S = -\left(\frac{\partial F}{\partial T}\right)_{V,N}, \tag{2.153}$$

$$P = -\left(\frac{\partial F}{\partial V}\right)_{T,N} \tag{2.154}$$

and

$$\mu = \left(\frac{\partial F}{\partial N}\right)_{T,V}. \tag{2.155}$$

The Helmholtz free energy is an example of a free energy or *thermodynamic potential*.[28] We can relax the condition of a fixed volume by requiring that the pressure be specified. In this case mechanical equilibrium requires that the pressure of the system equal the pressure of the bath. This case is common in experiments with fluids where the pressure is fixed at atmospheric pressure. We write $P_{\text{bath}} = P$ and express (2.147) as

$$\Delta A = \Delta E + P\Delta V - T\Delta S \equiv \Delta G \leq 0, \tag{2.156}$$

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[28]A more formal way of obtaining the various thermodynamic potentials is given in Section 2.26.2.

where we have defined the Gibbs free energy as

$$G = E - TS + PV = F + PV. \tag{2.157}$$

The natural variables of G can be found in the same way as we did for F. We find that $G = G(T, P, N)$ and

$$dG = dE - S dT - T dS + P dV + V dP \tag{2.158a}$$

$$= (T dS - P dV + \mu dN) - S dT - T dS + P dV + V dP \tag{2.158b}$$

$$= -S dT + V dP + \mu dN. \tag{2.158c}$$

We can use similar reasoning to conclude that G is a minimum at fixed temperature, pressure, and number of particles.

We can also relate G to the chemical potential using the following argument. Note that G and N are extensive variables, but T and P are not. Thus, G must be proportional to N:

$$G = N g(T, P), \tag{2.159}$$

where $g(T, P)$ is the Gibb's free energy per particle. This function must be the chemical potential because $\partial G / \partial N = g(T, P)$ from (2.159) and $\partial G / \partial N = \mu$ from (2.158). Thus, the chemical potential is the Gibbs free energy per particle:

$$\mu(T, P) = \frac{G}{N} = g(T, p). \tag{2.160}$$

Because g depends only on T and P, we have

$$dg = d\mu = \left(\frac{\partial g}{\partial P}\right)_T dP + \left(\frac{\partial g}{\partial T}\right)_P dT \tag{2.161}$$

$$= v dP - s dT, \tag{2.162}$$

where $v = V/N$ and $s = S/N$. Equation (2.162) is called the Gibbs-Duhem relation. The properties of G and the relation (2.162) will be important when we discuss processes involving a change of phase (see Section 7.2).

Another common thermodynamic potential is the *enthalpy H* which we defined in (2.31). This potential is similar to $E(S, V, N)$ except for the requirement of fixed P rather than fixed V.

Problem 2.21. Derivatives of the enthalpy

Show that

$$dH = T dS + V dP + \mu dN, \tag{2.163}$$

and

$$T = \left(\frac{\partial H}{\partial S}\right)_{P,N} \tag{2.164}$$

$$V = \left(\frac{\partial H}{\partial P}\right)_{S,N} \tag{2.165}$$

$$\mu = \left(\frac{\partial H}{\partial N}\right)_{S,P}. \tag{2.166}$$

potential	natural variables	partial derivatives
E	S, V, N	T, $-P$, μ
S	E, V, N	$1/T$, P/T, $-\mu/T$
$F = E - TS$	T, V, N	$-S$, $-P$, μ
$G = F + PV$	T, P, N	$-S$, V, μ
$\Omega = F - \mu N$	T, V, μ	$-S$, $-P$, $-N$

Table 2.2: The natural variables for the common thermodynamic potentials and their partial derivatives.

Problem 2.22. Show that H is a minimum for an equilibrium system at fixed entropy.

Landau potential. We have seen that we can define many thermodynamic potentials depending on which variables we constrain. A very useful thermodynamic potential is the thermodynamic potential for which the variables T, V, and μ are specified. This potential has no generally recognized name or symbol, but is sometimes called the *Landau potential* and is usually, but not always, denoted by Ω. Another common name is simply the *grand potential*. We will adopt the notation Ω and refer to Ω as the Landau potential in honor of Lev Landau. The Landau potential is the thermodynamic potential for which the variables T, V, and μ are specified and is given by

$$\Omega(T, V, \mu) = F - \mu N. \tag{2.167}$$

If we take the derivative of Ω and use the fact that $dF = -SdT - PdV + \mu dN$ (see (2.152)), we find that

$$d\Omega = dF - \mu dN - Nd\mu \tag{2.168a}$$
$$= -SdT - PdV - Nd\mu. \tag{2.168b}$$

From (2.168b) we have

$$S = -\left(\frac{\partial \Omega}{\partial T}\right)_{V,\mu}. \tag{2.169}$$

$$P = -\left(\frac{\partial \Omega}{\partial V}\right)_{T,\mu}. \tag{2.170}$$

$$N = -\left(\frac{\partial \Omega}{\partial \mu}\right)_{T,V}. \tag{2.171}$$

Because $G = N\mu$, we can write $\Omega = F - G$. Hence, if we use the definition $G = F + PV$, we obtain

$$\Omega(T, V, \mu) = F - \mu N = F - G = -PV. \tag{2.172}$$

The relation (2.172) will be very useful for obtaining the equation of state of various systems (see Section 6.10).

Table 2.2 summarizes the important thermodynamic potentials and their natural variables.

*Useful work and availability. The free energies that we have introduced are useful for understanding the maximum amount of useful work, W_{useful}, that can be done *by* a system when it is

connected to a heat bath. The system is not necessarily in thermal or mechanical equilibrium with its surroundings. In addition to the system of interest and its surroundings (the bath), we include a third body, namely, the body on which the system does useful work. The third body is thermally insulated. The total work W_{by} done *by* the system is the work done against its surroundings, $P_{\text{bath}}\Delta V$ plus the work done on the body, W_{useful}:

$$W_{\text{by}} = P_{\text{bath}}\Delta V + W_{\text{useful}}. \tag{2.173}$$

Because W_{by} is the work done by the system when its volume changes by ΔV, the first term in (2.173) does not contain a negative sign. This term is the work that is necessarily and uselessly performed by the system in changing its volume and thus also the volume of its surroundings. The second term is the useful work done by the system. In (2.147) we replace the work done on the heat bath, $P_{\text{bath}}\Delta V$, by the total work done by the system $P_{\text{bath}}\Delta V + W_{\text{useful}}$ to obtain

$$\Delta E + P_{\text{bath}}\Delta V + W_{\text{useful}} - T_{\text{bath}}\Delta S \leq 0, \tag{2.174}$$

or the useful work done is

$$W_{\text{useful}} \leq -(\Delta E + P_{\text{bath}}\Delta V - T_{\text{bath}}\Delta S) = -\Delta A, \tag{2.175}$$

Note that the maximum amount of useful work that can be done by the system is equal to $-\Delta A$. This relation explains the meaning of the terminology *availability* because only $-\Delta A$ is available for useful work. The rest of the work is wasted on the surroundings.

Problem 2.23. Maximum useful work

(a) Show that if the change in volume of the system is zero, $\Delta V = 0$, and the initial and final temperature are that of the heat bath, then the maximum useful work is $-\Delta F$.

(b) Show that if the initial and final temperature and pressure are that of the bath, then the maximum useful work is $-\Delta G$.

2.22 Thermodynamic Measurements

All thermodynamic measurements can be expressed in terms of partial derivatives. For example, the pressure P can be expressed as $P = -\partial F/\partial V$. Let us suppose that we make several thermodynamic measurements, for example, C_V, C_P, and K_T, the isothermal compressibility. The latter is defined as

$$K_T = -\frac{1}{V}\Big(\frac{\partial V}{\partial P}\Big)_T. \qquad \text{(isothermal compressibility)} \tag{2.176}$$

Suppose that we wish to know the (isobaric) thermal expansion coefficient α, which is defined as

$$\alpha = \frac{1}{V}\Big(\frac{\partial V}{\partial T}\Big)_P. \qquad \text{(thermal expansion coefficient)} \tag{2.177}$$

(The number of particles N is assumed to be held constant in the above derivatives.) Do we need to make an independent measurement of α or can we determine α by knowing the values of $C_V, C_P,$

and K_T? To answer this question and related ones, we first need to know how to manipulate partial derivatives. This aspect of thermodynamics can be confusing when first encountered.

Thermodynamic systems normally have two or more independent variables. For example, we can choose the combination E, V, N or T, P, N. Because there are many choices of combinations of independent variables, it is important to be explicit about which variables are independent and which variables are being held constant in any partial derivative. We suggest that you read Section 2.26.1 to review of some of the properties of partial derivatives. The following example illustrates the power of purely thermodynamic arguments based on the manipulation of thermodynamic derivatives.

Example 2.17. Thermodynamics of blackbody radiation

In Section 6.9 we show from first principles some of the basic results of blackbody radiation. In particular, we show that u, the energy per unit volume, is proportional to T^4 (see (6.137a)). In the following we obtain this result using thermodynamic arguments and two reasonable assumptions. The derivation is a bit abstract if you do not have a good background in blackbody radiation. The point of the example here is that the formalism of thermodynamics plus a few assumptions can lead to new results.

Solution. The two assumptions are that u depends only on T and the radiation exerts a pressure on the walls of the cavity given by

$$P = \frac{1}{3}u(T). \tag{2.178}$$

Equation (2.178) follows directly from Maxwell's electromagnetic theory and is obtained in Section 6.9 from first principles (see Problem 6.28).

We start from the fundamental thermodynamic relation $dE = TdS - PdV$, and write it as

$$dS = \frac{dE}{T} + \frac{P}{T}dV. \tag{2.179}$$

We let $E = Vu$, substitute $dE = V\,du + u\,dV$ and the relation (2.178) into (2.179), and write

$$dS = \frac{V}{T}du + \frac{u}{T}dV + \frac{1}{3}\frac{u}{T}dV = \frac{V}{T}\frac{du}{dT}dT + \frac{4}{3}\frac{u}{T}dV. \tag{2.180}$$

From (2.180) we have

$$\left(\frac{\partial S}{\partial V}\right)_T = \frac{4}{3}\frac{u}{T} \tag{2.181a}$$

$$\left(\frac{\partial S}{\partial T}\right)_V = \frac{V}{T}\frac{du}{dT}. \tag{2.181b}$$

Because the order of the derivatives is irrelevant, $\partial^2 S/\partial V\,\partial T$ and $\partial^2 S/\partial T\,\partial V$ are equal. Hence, we obtain:

$$\frac{4}{3}\frac{\partial}{\partial T}\left(\frac{u}{T}\right) = \frac{\partial}{\partial V}\left(\frac{V}{T}\right)\frac{du}{dT}. \tag{2.182}$$

Next we assume that u depends only on T and perform the derivatives in (2.182) to find

$$\frac{4}{3}\left[\frac{1}{T}\frac{du}{dT} - \frac{u}{T^2}\right] = \frac{1}{T}\frac{du}{dT}, \tag{2.183}$$

which reduces to

$$\frac{du}{dT} = 4\frac{u}{T}. \tag{2.184}$$

If we assume the form $u(T) = aT^n$ and substitute it in (2.184), we find that this form is a solution for $n = 4$:

$$u(T) = aT^4. \tag{2.185}$$

The constant a in (2.185) cannot be determined by thermodynamic arguments.

We can obtain the entropy by using the first partial derivative in (2.181). The result is

$$S = \frac{4}{3T}Vu(T) + \text{constant}. \tag{2.186}$$

The constant of integration in (2.186) must be set equal to zero to make S proportional to V. Hence, we conclude that $S = 4aVT^3/3$. This thermodynamic argument was first given by Boltzmann in 1884.

2.23 Maxwell Relations

Example 2.17 illustrates the power of thermodynamic arguments and indicates that it would be useful to relate various thermodynamic derivatives to one another. The *Maxwell relations*, which we derive in the following, relate the various thermodynamic derivatives of E, F, G, and H to one another and are useful for eliminating quantities that are difficult to measure in terms of quantities that can be measured directly. We will see that the Maxwell relations can be used to show that the internal energy and enthalpy of an ideal gas depend only on the temperature. More importantly, we also will answer the question posed in Section 2.22 and relate the coefficient of thermal expansion to other thermodynamic derivatives.

We start with the thermodynamic potential $E(S, V, N)$ and write

$$dE = TdS - PdV + \mu dN. \tag{2.187}$$

In the following we will assume that N is a constant. From (2.187) we have that

$$T = \left(\frac{\partial E}{\partial S}\right)_V. \tag{2.188}$$

and

$$P = -\left(\frac{\partial E}{\partial V}\right)_S. \tag{2.189}$$

Because the order of differentiation should be irrelevant, we obtain from (2.188) and (2.189)

$$\frac{\partial^2 E}{\partial V \partial S} = \frac{\partial^2 E}{\partial S \partial V}, \tag{2.190}$$

or

$$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V. \tag{2.191}$$

Equation (2.191) is of the Maxwell relations. The remaining Maxwell relations are obtained in Problem 2.24.

Problem 2.24. Maxwell relations

From the differentials of the thermodynamic potentials:

$$dF = -SdT - PdV \tag{2.192}$$

$$dG = -SdT + VdP \tag{2.193}$$

$$dH = TdS + VdP, \tag{2.194}$$

derive the Maxwell relations:

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \tag{2.195}$$

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P \tag{2.196}$$

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P. \tag{2.197}$$

Also consider a variable number of particles to derive the Maxwell relations

$$\left(\frac{\partial V}{\partial N}\right)_P = \left(\frac{\partial \mu}{\partial P}\right)_N, \tag{2.198}$$

and

$$\left(\frac{\partial \mu}{\partial V}\right)_N = -\left(\frac{\partial P}{\partial N}\right)_V. \tag{2.199}$$

2.24 Applications of the Maxwell Relations

The Maxwell relations depend on our identification of $(\partial E/\partial S)_V$ with the temperature, a relation that follows from the second law of thermodynamics. The Maxwell relations are not purely mathematical in content, but are different expressions of the second law. In the following, we use these relations to derive some useful relations between various thermodynamic quantities.

2.24.1 Internal energy of an ideal gas

We first show that the internal energy E of an ideal gas is a function only of T given the pressure equation of state, $PV = NkT$. That is, if we consider E as a function of T and V, we want to show that $(\partial E/\partial V)_T = 0$. From the fundamental thermodynamic relation, $dE = TdS - PdV$, we see that $(\partial E/\partial V)_T$ can be expressed as

$$\left(\frac{\partial E}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - P. \tag{2.200}$$

To show that E is a function of T only, we need to show that the right-hand side of (2.200) is zero. The term involving the entropy in (2.200) can be rewritten using the Maxwell relation (2.195):

$$\left(\frac{\partial E}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P. \tag{2.201}$$

Because $(\partial P/\partial T)_V = P/T$ for an ideal gas, we see that the right-hand side of (2.201) is zero.

Problem 2.25. Show that the enthalpy of an ideal gas is a function of T only.

2.24.2 Relation between heat capacities

As we have seen, it is much easier to calculate the heat capacity at constant volume than at constant pressure. However, it is usually easier to measure the heat capacity at constant pressure. For example, most solids expand when heated, and hence it is easier to make measurements at constant pressure. In the following, we derive a thermodynamic relation that relates C_V and C_P. Recall that

$$C_V = \Big(\frac{\partial E}{\partial T}\Big)_V = T\Big(\frac{\partial S}{\partial T}\Big)_V, \tag{2.202a}$$

and

$$C_P = \Big(\frac{\partial H}{\partial T}\Big)_P = T\Big(\frac{\partial S}{\partial T}\Big)_P. \tag{2.202b}$$

We consider S as a function of T and P and write

$$dS = \frac{\partial S}{\partial T}dT + \frac{\partial S}{\partial P}dP, \tag{2.203}$$

and take the partial derivative with respect to temperature at constant volume of both sides of (2.203):

$$\Big(\frac{\partial S}{\partial T}\Big)_V = \Big(\frac{\partial S}{\partial T}\Big)_P + \Big(\frac{\partial S}{\partial P}\Big)_T \Big(\frac{\partial P}{\partial T}\Big)_V. \tag{2.204}$$

We then use (2.202) to rewrite (2.204) as

$$\frac{C_V}{T} = \Big(\frac{\partial S}{\partial P}\Big)_T \Big(\frac{\partial P}{\partial T}\Big)_V + \frac{C_P}{T}. \tag{2.205}$$

Because we would like to express $C_P - C_V$ in terms of measurable quantities, we use the Maxwell relation (2.196) to eliminate $(\partial S/\partial P)$ and rewrite (2.205) as:

$$C_P - C_V = T\Big(\frac{\partial V}{\partial T}\Big)_P \Big(\frac{\partial P}{\partial T}\Big)_V. \tag{2.206}$$

We next use the identity (see (2.241)),

$$\Big(\frac{\partial V}{\partial T}\Big)_P \Big(\frac{\partial T}{\partial P}\Big)_V \Big(\frac{\partial P}{\partial V}\Big)_T = -1, \tag{2.207}$$

to eliminate $(\partial P/\partial T)_V$ and write:

$$C_P - C_V = -T\Big(\frac{\partial P}{\partial V}\Big)_T \Big(\frac{\partial V}{\partial T}\Big)_P^2. \tag{2.208}$$

If we substitute the definitions (2.176) of the isothermal compressibility K_T and (2.177) for the thermal expansion coefficient α, we obtain the desired general relation:

$$C_P - C_V = V\frac{T}{K_T}\alpha^2. \tag{2.209}$$

Note that (2.209) is more general that the relation (2.42) which depends on only the first law.
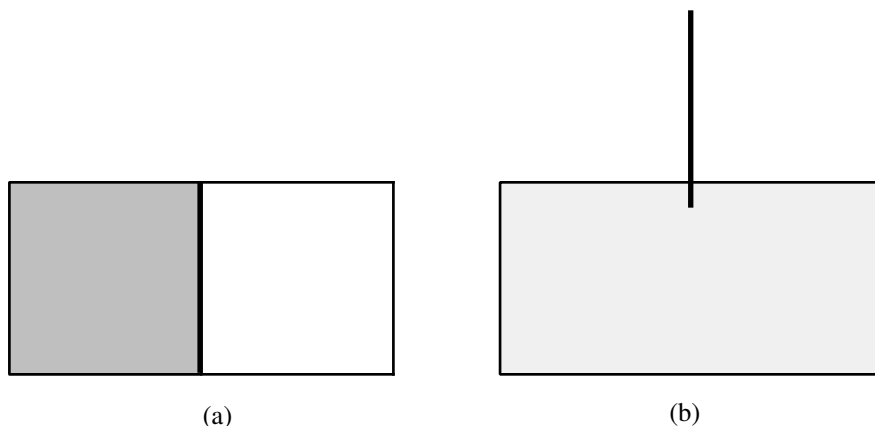
Figure 2.11: (a) A gas is kept in the left half of a box by a partition. The right half is evacuated. (b) The partition is removed and the gas expands irreversibly to fill the entire box.

For an ideal gas we have $K_T = 1/P$ and $\alpha = 1/T$ and (2.209) reduces to the familiar result (see (2.43))

$$C_P - C_V = Nk. \tag{2.210}$$

Although we will not derive these conditions here, it is plausible that the heat capacity and compressibility of equilibrium thermodynamic systems must be positive. Given these assumptions, we see from (2.209) that $C_P > C_V$ in general.

2.25   Applications to Irreversible Processes

Although the thermodynamic quantities of a system can be defined only when the system is in equilibrium, we have found that it is possible to obtain useful results for systems that pass through nonequilibrium states if the initial and final states are in equilibrium. In the following, we will consider some well known thermodynamic processes.

2.25.1   The Joule or free expansion process

In a Joule or free expansion the system expands into a vacuum while the entire system is thermally isolated (see Figure 2.11). The quantity of interest is the temperature change that is produced. Although this process is irreversible, we have learned that it can be treated by thermodynamics. Because $dQ = 0$ and $dW = 0$, the energy is a constant so that $dE(T, V) = 0$. This condition can be written as

$$dE = \left(\frac{\partial E}{\partial T}\right)_V dT + \left(\frac{\partial E}{\partial V}\right)_T dV = 0. \tag{2.211}$$

Hence, we obtain

$$\left(\frac{\partial T}{\partial V}\right)_E = -\frac{(\partial E/\partial V)_T}{(\partial E/\partial T)_V}, \tag{2.212}$$

$$= -\frac{1}{C_V}\left[T\left(\frac{\partial P}{\partial T}\right)_V - P\right]. \tag{2.213}$$

Equation (2.213) follows from the definition of C_V and from (2.201). The partial derivative $(\partial T/\partial V)_E$ is known as the Joule coefficient. For a finite change in volume, the total temperature change is found by integrating (2.213):

$$\Delta T = -\int_{V_1}^{V_2} \frac{1}{C_V}\left[T\left(\frac{\partial P}{\partial T}\right)_V - P\right]dV. \tag{2.214}$$

Because $(\partial P/\partial T)_V = P/T$ for an ideal gas, we conclude that the temperature of an ideal gas is unchanged in a free expansion. If the gas is not dilute, we expect that the intermolecular interactions are important and that the temperature will change in a free expansion. In Chapter 8 we will discuss several ways of including the effects of the intermolecular interactions. For now we will be satisfied with a simple modification of the ideal gas equation of state due to van der Waals (see (2.12)).

Problem 2.26. Free expansion

Calculate $(\partial T/\partial V)_E$ for the van der Waals equation of state (2.12) and show that a free expansion results in cooling.

The reason for the cooling of a real gas during a free expansion can be understood as follows. The derivative $(\partial E/\partial V)_T$ depends only on the potential energy of the particles because the temperature is held constant. As shown in Figure 1.1, the intermolecular potential is repulsive for small separations r and is attractive for large r. For a dilute gas the mean separation between the particles is greater than $r_0 = 2^{1/6}\sigma$, the distance at which the potential is a minimum. As the volume increases, the mean separation between the molecules increases and hence the energy of interaction becomes less negative, that is, increases. Hence we conclude that $(\partial E/\partial V)_T$ is positive. Because the heat capacity is always positive, we find that $(\partial T/\partial V)_E$ is negative and that real gases always cool in a free expansion.

2.25.2 Joule-Thomson process

The Joule-Thomson (or Joule-Kelvin[29] or porous plug) process is a steady state flow process in which a gas is forced through a porous plug or expansion valve from a region of high pressure P_1 to a region of lower pressure P_2 (see Figure 2.12). The gas is thermally isolated from its surroundings. The process is irreversible because the gas is not in equilibrium. We will see that a real gas is either cooled or heated in passing through the plug.

Consider a given amount (for example, one mole) of a gas that occupies a volume V_1 at pressure P_1 on the left-hand side of the valve and a volume V_2 at pressure P_2 on the right-hand side. The

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[29]William Thomson was later awarded a peerage and became Lord Kelvin.
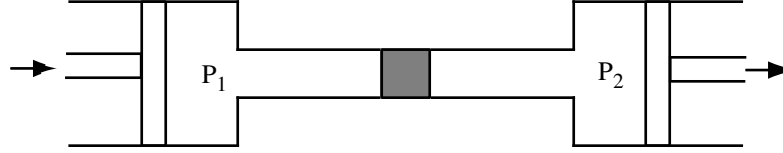
Figure 2.12: Schematic representation of the Joule-Thomson process. The two pistons ensure constant pressures on each side of the porous plug. The porous plug can be made by packing glass wool into a pipe. The process can be made continuous by using a pump to return the gas from the region of low pressure to the region of high pressure.

work done on the gas is given by

$$W = -\int_{V_1}^{0} P\,dV - \int_{0}^{V_2} P\,dV. \tag{2.215}$$

The pressure on each side of the porous plug is constant, and hence we obtain

$$W = P_1 V_1 - P_2 V_2. \tag{2.216}$$

Because the process takes place in an isolated cylinder, there is no energy transfer due to heating, and the change in the internal energy is given by

$$\Delta E = E_2 - E_1 = W = P_1 V_1 - P_2 V_2. \tag{2.217}$$

Hence, we obtain

$$E_2 + P_2 V_2 = E_1 + P_1 V_1, \tag{2.218}$$

which can be written as

$$H_2 = H_1. \tag{2.219}$$

That is, the Joule-Thomson process occurs at constant enthalpy. All we can say is that the final enthalpy equals the initial enthalpy; the intermediate states of the gas are nonequilibrium states for which the enthalpy is not defined.

The calculation of the temperature change in the Joule-Thomson effect is similar to our treatment of the Joule effect. Because the process occurs at constant enthalpy, it is useful to write

$$dH(T,P) = \left(\frac{\partial H}{\partial T}\right)_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP = 0. \tag{2.220}$$

As before, we assume that the number of particles is a constant. From (2.220) we have

$$dT = -\frac{(\partial H/\partial P)_T}{(\partial H/\partial T)_P}. \tag{2.221}$$

From the relation, $dH = T\,dS + V\,dP$, we have $(\partial H/\partial P)_T = T(\partial S/\partial P)_T + V$. If we substitute this relation in (2.221), use the Maxwell relation (2.196), and the definition $C_P = (\partial H/\partial T)_P$, we obtain

$$\left(\frac{\partial T}{\partial P}\right)_H = \frac{V}{C_P}(T\alpha - 1), \tag{2.222}$$

where the thermal expansion coefficient α is defined by (2.177). Note that the change in pressure dP is negative, that is, the gas goes from a region of high pressure to a region of low pressure. To find the temperature change produced in a finite pressure drop, we integrate (2.222) and find

$$\Delta T = T_2 - T_1 = \int_{P_1}^{P_2} \frac{V}{C_P} (T\alpha - 1) \, dP. \tag{2.223}$$

For an ideal gas, $\alpha = 1/T$ and $\Delta T = 0$ as expected.

To understand the nature of the temperature change in a real gas, we calculate α for the van der Waals equation of state (2.12). We write the latter in the form

$$P + a\rho^2 = \frac{\rho k T}{1 - b\rho}, \tag{2.224}$$

and take the derivative with respect to T at constant P:

$$2a\rho\Big(\frac{\partial \rho}{\partial T}\Big)_P = \frac{\rho k}{1 - b\rho} + \Big(\frac{\partial \rho}{\partial T}\Big)_P \frac{kT}{(1 - b\rho)^2}. \tag{2.225}$$

If we express α as

$$\alpha = -\frac{1}{\rho}\Big(\frac{\partial \rho}{\partial T}\Big)_P, \tag{2.226}$$

we can write (2.225) in the form:

$$\Big[\frac{kT}{(1 - b\rho)^2} - 2a\rho\Big]\alpha = \frac{k}{(1 - b\rho)}. \tag{2.227}$$

For simplicity, we consider only low densities in the following. In this limit we can write α as

$$\alpha = \frac{k(1 - b\rho)}{kT - 2a\rho(1 - b\rho)^2}, \tag{2.228a}$$

$$\approx \frac{1}{T}(1 - b\rho)\big[1 + 2a\beta\rho(1 - b\rho)^2\big], \tag{2.228b}$$

$$\approx \frac{1}{T}[1 - \rho(b - 2a\beta)]. \tag{2.228c}$$

From (2.228c) we obtain $(T\alpha - 1) = \rho(2a\beta - b)$ at low densities.

We can define an inversion temperature T_i at which the derivative $(\partial T/\partial P)_H$ changes sign. From (2.228) and (2.222), we see that $kT_i = 2a/b$ for a low density gas. For $T > T_i$, the gas warms as the pressure falls in the Joule-Thomson expansion. However, for $T < T_i$, the gas cools as the pressure falls.

For most gases T_i is well above room temperatures. Although the cooling effect is small, the effect can be made cumulative by using the cooled expanded gas in a heat exchanger to precool the incoming gas.

2.26 Supplementary Notes

2.26.1 The mathematics of thermodynamics

Because the notation of thermodynamics can be cumbersome, we have tried to simplify it whenever possible. However, one common simplification can lead to initial confusion.

Consider the functional relations:

$$y = f(x) = x^2, \tag{2.229}$$

and

$$x = g(z) = z^{1/2}. \tag{2.230}$$

If we write x in terms of z, we can write y as

$$y = h(z) = f(g(z)) = z. \tag{2.231}$$

We have given the composite function a different symbol h because this function is different from both f and g. But we would soon exhaust the letters of the alphabet, and we frequently write $y = f(z) = z$. Note that $f(z)$ is a different function than $f(x)$.

The notation is even more confusing in thermodynamics. Consider for example, the entropy S as a function of E, V, and N, which we write as $S(E, V, N)$. However, we frequently consider E as a function of T from which we would obtain another functional relation: $S(E(T, V, N), V, N)$. A mathematician would write the latter function with a different symbol, but we don't. In so doing we confuse the name of a function with that of a variable and use the same name (symbol) for the same physical quantity. This sloppiness can cause problems when we take partial derivatives. If we write $\partial S/\partial V$, is E or T to be held fixed? One way to avoid confusion is to write $(\partial S/\partial V)_E$ or $(\partial S/\partial V)_T$, but this notation can become cumbersome.

Another confusing aspect of the mathematics of thermodynamics is the use of differentials. Many authors, including Bohren and Albrecht,[30] have criticized their use. These authors and others argue for example that the first law should be written as

$$\frac{dE}{dt} = \frac{dQ}{dt} + \frac{dW}{dt}, \tag{2.232}$$

rather than

$$dE = \Delta Q + \Delta W, \tag{2.233}$$

An argument for writing the first law in the form (2.232) is that the first law applies to a process, which must occur over an interval of time. Here, dE/dt represents the rate of energy change, dW/dt is the rate of doing work and dQ/dt is the rate of heating. In contrast, dE in (2.233) is the infinitesimal change in internal energy, ΔW is the infinitesimal work done on the system, and ΔQ is the infinitesimal heat added. However, the meaning of an infinitesimal in this context is vague. For example, for the process shown in Figure 2.13, the energy difference $E_2 - E_1$ is arbitrarily small and hence could be represented by a differential dE, but the work and heating are not infinitesimal. However, the use of infinitesimals should not cause confusion if you understand that dy in the context $dy/dx = f(x)$ has a different meaning than in the context, $dy = f(x)\,dx$.
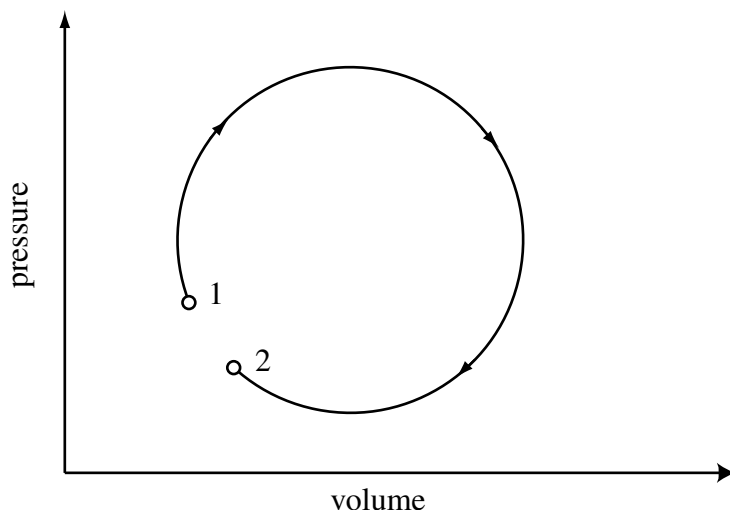
Figure 2.13: The change in internal energy can be made arbitrarily small by making the initial (1) and final (2) states arbitrarily close, but the total work done, which is the area enclosed by the nearly closed curve, is not vanishingly small. Adapted from Bohren and Albrecht.

If the use of infinitesimals is confusing to you, we encourage you to replace infinitesimals by rate equations as in (2.232).

Example 2.18. Exact and inexact differentials

Suppose that a system is descibed by two parameters, x and y and $f(x,y) = xy$ (see page 42).[31] Then

$$df = d(xy) = y dx + x dy. \tag{2.234}$$

If $f(x,y)$ changes from $(0,0)$ to $(1,1)$, the change in f is given by

$$\Delta f = \int_{0,0}^{1,1} = xy]_{0,0}^{1,1)} - (1 \times 1) - (0 \times 0) = 1. \tag{2.235}$$

This result is independent of the path because df is an exact differential.

Now consider $dg = y dx$. The change in g when (x,y) changes from $(0,0)$ to $(1,1)$ along the path shown in Figure 2.14(a) is

$$\Delta g = \int_{0,0}^{1,1} y dx = \int_0^1 x dx = 1/2. \tag{2.236}$$

Show that when the integral is along the path shown in Figure 2.14(b), the result is $\Delta g = 0$. Hence the value of Δg depends on the path and dg is an inexact differential. (Many textbooks write inexact differentials as $\bar{d}g$.)

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[30]See Bohren and Albrecht, pp. 93–99.

[31]This example is taken from Stephen J. Blundell and Katherine M. Blundell, *Thermal Physics*, Oxford University Press (2006), page 105.
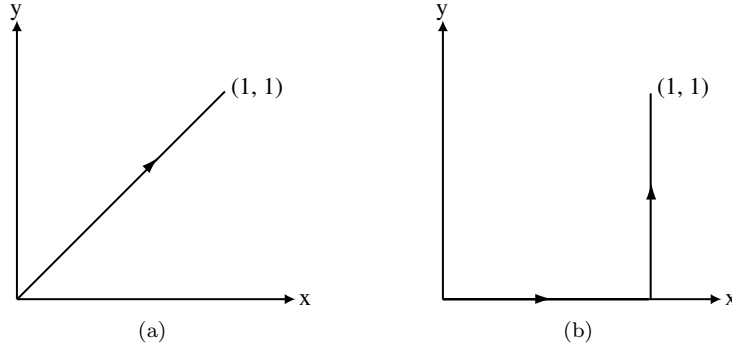
Figure 2.14: Two among many possible paths between the points x, $y) = (0, 0)$ and $(1, 1)$.

Review of partial derivatives. The basic theorem of partial differentiation states that if z is a function of two independent variables x and y, then the total change in $z(x, y)$ due to changes in x and y can be expressed as

$$dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy. \tag{2.237}$$

The cross derivatives $\partial^2 z/\partial x\,\partial y$ and $\partial^2 z/\partial y\,\partial x$ are equal, that is, the order of the two derivatives does not matter. We will use this property to derive what are known as the Maxwell relations in Section 2.23.

The *chain rule* for differentiation holds in the usual way if the *same* variables are held constant in each derivative. For example, we can write

$$\left(\frac{\partial z}{\partial x}\right)_y = \left(\frac{\partial z}{\partial w}\right)_y \left(\frac{\partial w}{\partial x}\right)_y. \tag{2.238}$$

We also can derive a relation whose form is superficially similar to (2.238) when *different* variables are held constant in each term. From (2.237) we set $dz = 0$ and obtain

$$dz = 0 = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy. \tag{2.239}$$

We divide both sides of (2.239) by dx:

$$0 = \left(\frac{\partial z}{\partial x}\right)_y + \left(\frac{\partial z}{\partial y}\right)_x \left(\frac{\partial y}{\partial x}\right)_z, \tag{2.240}$$

and rewrite (2.240) as

$$\left(\frac{\partial z}{\partial x}\right)_y = -\left(\frac{\partial z}{\partial y}\right)_x \left(\frac{\partial y}{\partial x}\right)_z. \tag{2.241}$$

Note that (2.241) involves a relation between the three possible partial derivatives which involve x, y, and z.

Problem 2.27. Consider the function

$$z(x, y) = x^2 y + 2x^4 y^6. \tag{2.242}$$

Calculate $\partial z/\partial x$, $\partial z/\partial y$, $\partial^2 z/\partial x\,\partial y$, and $\partial^2 z/\partial y\,\partial x$ and show that $\partial^2 z/\partial x\,\partial y = \partial^2 z/\partial y\,\partial x$.
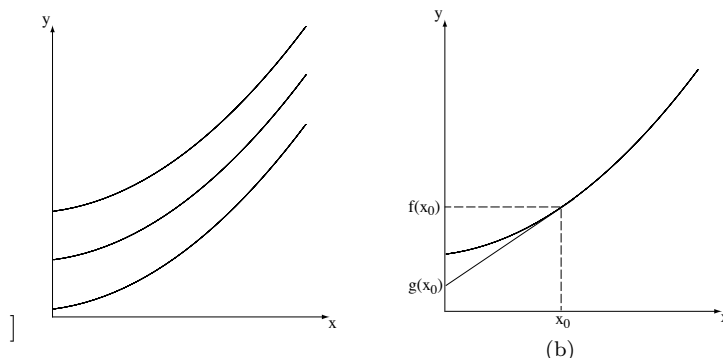
Figure 2.15: (a) The intercepts of the three curves differ. (b) Geometrical interpretation of the Legendre transformation.

2.26.2 Thermodynamic potentials and Legendre transforms

Consider a function $f(x)$ of one variable. The *Legendre transform* allows us to replace the independent variable x by the derivative $f'(x) = df/dx$ without sacrificing any of the information in the original relation. In the following we will consider functions of only one variable, but the results can be easily generalized to functions of several variables.

The derivative

$$m(x) \equiv f'(x) \tag{2.243}$$

is the slope of $f(x)$ at x. To treat m as the independent variable instead of x, we might be tempted to solve (2.243) for x in terms of m and then simply find $f(m)$. (Note that although $f(m)$ is a different function than $f(x)$, we still use the same symbol. That is, the symbol f names a quantity not a functional relationship, and the symbol f plus the argument tells us the functional relationship.) However, this procedure would lead to a loss of some of the mathematical content of the orginal function $f(x)$. That is, given f as a function of m, we would not be able to reconstruct $f(x)$.

Example 2.19. Suppose that[32] $f(x) = (1/2)e^{2x}$. Hence $m = e^{2x}$ and $f(m) = m/2$. We now try to reconstruct $f(x)$ from $f(m)$ to determine if we still have the same information. Because $m = f'(x)$, we have $f(m) = f(m(x)) = f'(x)/2$ or $f' = 2f$. The solution of the latter differential equation gives $f(x) = Ae^{2x}$, where A is not specified. So this procedure loses information. The problem is that knowing only the slope does not tell us the value of the intercept at $x = 0$.

The goal of the Legendre transformation is to find the function $g(m)$ such that $g(m)$ contains the same information as the function $f(x)$. From Figure 2.15 we see that we need to know the value of the intersection of the tangent to f at the point $(x_0, f(x_0))$ with the y-axis at $x = 0$.

Consider the tangent line that passes through the point $(x_0, f(x_0))$ with slope m and intercept

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[32]This example is adapted from Debashish Chowdhury and Dietrich Stauffer, *Principles of Equilibrium Statistical Mechanics*, Wiley-VCH (2000).

b at $y = 0$. Because the general equation for a straight line is $y = mx + b$, we can write

$$b = y - mx \tag{2.244a}$$

or

$$g(x_0) = f(x_0) - f'(x_0)x_0. \tag{2.244b}$$

The slope depends on the particular point x_0. The function $g(x)$ for an arbitrary point x is given by

$$g(x) = f(x) - xf'(x) = f(x) - xm. \tag{2.245}$$

The Legendre transform of $f(x)$ can be determined by first calculating $m(x)$ and then determining the relation $g(m)$ using (2.245). It turns out that the right-hand side of (2.245) will not depend on x. The function $g(m)$ is called the Legendre transform of $f(x)$.

To show that g depends only on the slope m, we differentiate g as given by (2.245)

$$dg = df - mdx - xdm. \tag{2.246}$$

Because $df = mdx$ (see (2.243)) we have

$$dg = -xdm. \tag{2.247}$$

Hence, g depends only on m, just as $df = mdx$ indicates that f depends only on x.

To calculate $g(m)$ explicitly we have to eliminate x in (2.245) using $m = f'(x)$. We can solve the latter for x only if there is a one-to-one relation between x and m, which holds if the function $f'(x)$ is monotonic.

Example 2.20. We again consider $f(x) = \frac{1}{2}e^{2x}$ for which $m(x) = e^{2x}$. Then $g(x)$ becomes

$$g(x) = f(x) - xm = \frac{1}{2}e^{2x} - xe^{2x}. \tag{2.248}$$

We next invert the relation $m = e^{2x}$ to solve for x in terms of m: $x = \frac{1}{2}\ln m$. Hence the Legendre transform of $f(x)$ is

$$g(m) = \frac{1}{2}m(1 - \ln m). \tag{2.249}$$

Now suppose that $g(m)$ is given. Can we construct $f(x)$? From (2.247) we have $x = -dg/dm$, which leads to $x = \frac{1}{2}\ln m$ and hence $m = e^{2x}$ for our example. Hence

$$f(m) = g(m) + xm = \frac{1}{2}m(1 - \ln m) + xm \tag{2.250a}$$

and

$$f(x) = \frac{1}{2}e^{2x}(1 - 2x) + xe^{2x} = \frac{1}{2}e^{2x}, \tag{2.250b}$$

which is our original function.

Problem 2.28. Some practice examples

(a) Calculate the Legendre transform of $f(x) = x^3$.

(b) Calculate the legendre transforms of the functions $f(x) = x$ and $f(x) = \sin x$ if they exist.

Problem 2.29. The Helmholtz free energy
Start from the function $E(S, V, N)$ and use the Legendre transform to find the function $F(T, V, N)$.

Vocabulary

thermodynamics, system, boundary, surroundings, macrostate

insulator, conductor, adiabatic wall

thermal contact, thermal equilibrium, temperature, thermodynamic equilibrium

thermometer, Celsius temperature scale, ideal gas temperature scale, thermodynamic temperature

heating, work

internal energy E, entropy S, state function, laws of thermodynamics

ideal gas, ideal gas equation of state, van der Waals equation of state

Boltzmann's constant, universal gas constant

intensive and extensive variables

heat capacity, specific heat

quasistatic, reversible, irreversible, isothermal, constant volume, adiabatic, quasistatic, and cyclic processes

heat bath, heat source, heat sink

Carnot engine, refrigerator, heat pump efficiency, coefficient of performance

thermodynamic potential, Helmholtz free energy F, Gibbs free energy G, enthalpy H, Landau potential Ω, availability A

Notation

volume V, number of particles N, thermodynamic temperature T, pressure P, chemical potential μ

total work W, total energy transferred due to a temperature difference alone Q

kelvin K, Celsius °C, Fahrenheit °F

heat capacity C, specific heat c

thermal efficiency η

Boltzmann's constant k, gas constant R

Additional Problems

Problem 2.30. Compare the notion of mechanical equilibrium and thermodynamic equilibrium.

Problem 2.31. Explain how a barometer works to measure pressure.

Problem 2.32. Is a diamond forever?

What does it mean to say that diamond is a metastable form of carbon? What is the stable form of carbon? Is it possible to apply the laws of thermodynamics to diamond?

Problem 2.33. A question of degree

Although you were probably taught how to convert between Fahrenheit and Celsius temperatures, you might not remember the details. The fact that $1°\text{C}$ equals $\frac{9}{5}°\text{F}$ is not too difficult to remember, but where does the factor of 32 go? An alternative procedure is to add 40 to the temperature in $°\text{C}$ or $°\text{F}$ and multiply by $\frac{5}{9}$ if going from $°\text{F}$ to $°\text{C}$ or by $\frac{9}{5}$ if going from $°\text{C}$ to $°\text{F}$. Then subtract 40 from the calculated temperature to obtain the desired conversion. Explain why this procedure works.

Problem 2.34. Hot and cold

It is common in everyday language to refer to temperatures as "hot" and "cold." Why is this use of language misleading? Does it make sense to say that one body is "twice as hot" as another? Does it matter whether the Celsius or kelvin temperature scale is used?

Problem 2.35. Does it make sense to talk about the amount of heat in a room?

Problem 2.36. Heat as a fluid

In what context can energy transferred by heating be treated as a fluid? Give some examples where this concept of "heat" is used in everyday life. In what context does the concept of "heat" as a fluid break down? Is it possible to isolate "heat" in a bottle or pour it from one object to another?

Problem 2.37. Why should we check the pressure in a tire when the tire is cold?

Problem 2.38. Suppose that we measure the temperature of a body and then place the body on a moving conveyer belt. Does the temperature of the body change?

Problem 2.39. Why do we use the triple point of water to calibrate thermometers? Why not use the melting point or the boiling point?

Problem 2.40. Money in the bank

In the text we discussed the analogy of the internal energy to the amount of water in a pond. The following analogy due to Dugdale might also be helpful.[33] Suppose that a student has a bank account with a certain amount of money. The student can add to this amount by either depositing or withdrawing cash and by writing or depositing checks from the accounts of others. Does the total amount of money in his account distinguish between cash and check transfers? Discuss the analogies to internal energy, work, and heating.

Problem 2.41. Common misconceptions

The following excerpt is taken from a text used by one of the author's children in the sixth grade. The title and the author of the text will remain anonymous. Find the conceptual errors in the text.

A. 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.

Scientists use a *small calorie* and a *large Calorie*. The unit used to measure the amount of heat needed to raise the temperature of 1 gram of water 1 degree centigrade is the *small calorie*. The *large calorie* is used to measure units of heat in food. For example, a glass of milk when burned in your body produces about 125 Calories.

Questions:

    1. What is heat?

    2. What two things does the amount of heat a substance has depend on?

    3. What is a calorie?

    4. Explain the following: small calorie; large calorie.

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[33]See Dugdale, pp. 21–22.

B. *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.

C. *Expansion and Contraction*

Most solids, liquids and gases *expand* when heated and *contract* when cooled. When matter is heated, its molecules move faster. As they move, they collide with their neighbors very rapidly. The collisions force the molecules to spread farther apart. The farther apart they spread, the more the matter expands.

Air, which is a mixture of gases, expands and becomes lighter when its temperature rises. Warm air rises because the cold, heavier air sinks and pushes up the lighter warm air.

What happens when solids or gases are cooled? The molecules slow down and collide less. The molecules move closer together, causing the material to contract.

Problem 2.42. Why are the terms heat capacity and specific heat poor choices of names? Suggest more appropriate names. Comment on the statement: "The heat capacity of a body is a measure of how much heat the body can hold."

Problem 2.43. The atmosphere of Mars has a pressure that is only 0.007 times that of the Earth and an average temperature of $218\,\mathrm{K}$. What is the volume of 1 mole of the Martian atmosphere?

Problem 2.44. Discuss the meaning of the statement that one of the most important contributions of 19th century thermodynamics was the development of the understanding that heat (and work) are names of *methods* not names of *things*.

Problem 2.45. Gasoline burns in an automobile engine and releases energy at the rate of $160\,\mathrm{kW}$. Energy is exhausted through the car's radiator at the rate of $51\,\mathrm{kW}$ and out the exhaust at $50\,\mathrm{kW}$. An additional $23\,\mathrm{kW}$ goes to frictional heating within the machinery of the car. What fraction of the fuel energy is available for moving the car?

Problem 2.46. Two moles of an ideal gas at $300\,\mathrm{K}$ occupying a volume of $0.10\,\mathrm{m}^3$ is compressed isothermally by a motor driven piston to a volume of $0.010\,\mathrm{m}^3$. If this process takes places in $120\,\mathrm{s}$, how powerful a motor is needed?

Problem 2.47. Give an example of a process in which a system is not heated, but its temperature increases. Also give an example of a process in which a system is heated, but its temperature is unchanged.

Problem 2.48. Expansion of gas into vacuum

(a) Suppose that a gas expands adiabatically into a vacuum. What is the work done by the gas?

(b) Suppose that the total energy of the gas is given by (see (2.26))

$$E = \frac{3}{2}NkT - N\frac{N}{V}a, \tag{2.251}$$

where a is a positive constant. Initially the gas occupies a volume V_A at a temperature T_A. The gas then expands adiabatically into a vacuum so that it occupies a total volume V_B. What is the final temperature of the gas?

Problem 2.49. Entropy as a state function

(a) Suppose that an ideal gas expands in a quasistatic adiabatic process from $P = 1\,\mathrm{Pa}$ and $V_A = 1\,\mathrm{m}^3$ to $V_B = 8\,\mathrm{m}^3$. What is the change in the pressure and the entropy of the gas?

(b) Assume that one mole of the gas is present. What are the initial and final temperatures of the gas?

(c) Show that you obtain the same answer for the change in the entropy that you found in part (a) for another path that starts at the same initial state. Consider a process at constant volume that brings the system to the temperature T_B which you found in part (b). What is the change in entropy of this process?

(d) Next increase the volume at constant temperature T_B. What is the change in the entropy in this isothermal process?

(e) Compare the total change in the entropy to the result that you found in part (a).

Problem 2.50. Calculate the work done on one mole of an ideal gas in an adiabatic quasistatic compression from volume V_A to volume V_B. The initial pressure is P_A.

Problem 2.51. Consider the following processes and calculate W, the total work done on the system and Q, the total energy absorbed by heating the system when it is brought quasistatically from A to C (see Figure 2.16). Assume that the system is an ideal gas. (This problem is adapted from Reif, p. 215.)

(a) The volume is changed quasistatically from $A \to C$ while the gas is kept thermally isolated.

(b) The system is compressed from its original volume of $V_A = 8\,\mathrm{m}^3$ to its final volume $V_C = 1\,\mathrm{m}^3$ along the path $A \to B$ and $B \to C$. The pressure is kept constant at $P_A = 1\,\mathrm{Pa}$ and the system is cooled to maintain constant pressure. The volume is then kept constant and the system is heated to increase the pressure to $P_B = 32\,\mathrm{Pa}$.

(c) $A \to D$ and $D \to C$. The two steps of the preceding process are performed in opposite order.

(d) $A \to C$. The volume is decreased and the system is heated so that the pressure is proportional to the volume.

Problem 2.52. A $0.5\,\mathrm{kg}$ copper block at $80°\mathrm{C}$ is dropped into $1\,\mathrm{kg}$ of water at $10°\mathrm{C}$. What is the final temperature? What is the change in entropy of the system? The specific heat of copper is $386\,\mathrm{J/(kg\,K)}$.

Problem 2.53. Carnot efficiencies

(a) Surface temperatures in the tropical oceans are approximately $25°\mathrm{C}$, while hundreds of meters below the surface the temperature is approximately $5°\mathrm{C}$. What would be the efficiency of a Carnot engine operating between these temperatures?

(b) What is the efficiency of a Carnot engine operating between the normal freezing and boiling points of water?
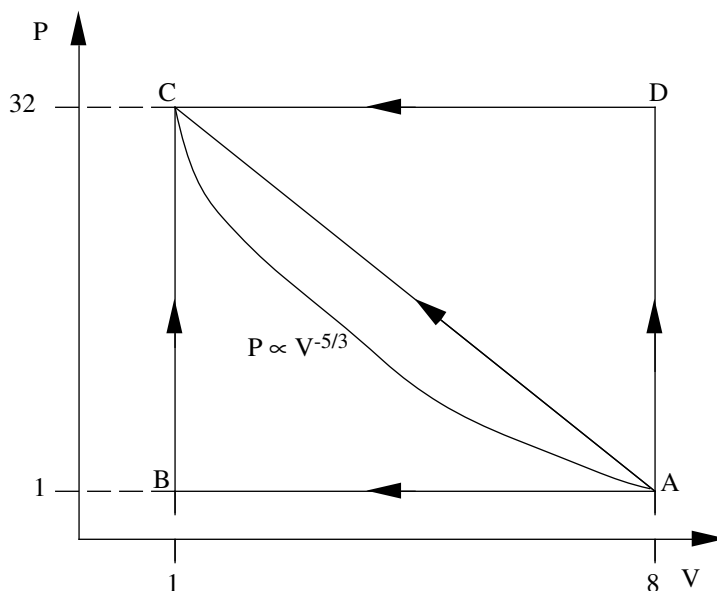
Figure 2.16: Illustration of various thermodynamic processes discussed in Problem 2.51. The units of the pressure P and the volume V are Pa and m^3, respectively.

Problem 2.54. A small sample of material is taken through a Carnot cycle between a heat source of boiling helium at 1.76 K and a heat sink at an unknown lower temperature. During the process, 7.5 mJ of energy is absorbed by heating from the helium and 0.55 mJ is rejected at the lower temperature. What is the lower temperature?

Problem 2.55. Positive change in total entropy

(a) Show that the total entropy change in Example 2.13 can be written as

$$\Delta S = Cf\left(\frac{T_2}{T_1}\right), \tag{2.252}$$

where

$$f(x) = \ln x + \frac{1}{x} - 1. \tag{2.253}$$

and $x > 1$ corresponds to heating. Calculate $f(x = 1)$ and df/dx and show that the entropy of the universe increases for a heating process.

(b) If the total entropy increases in a heating process, does the total entropy decrease in a cooling process? Use similar considerations to show that the total entropy increases in both cases.

(c) Plot $f(x)$ as a function of x and confirm that its minimum value is at $x = 1$ and that $f > 0$ for $x < 1$ and $x > 1$.

Problem 2.56. Enthalpy

Show that the enthalpy $H \equiv E + PV$ is the appropriate free energy for the case where the entropy and number of particles is fixed, but the volume can change. In this case we consider a system connected to a larger body such that the pressure of the system equals that of the large body with the constraint that the larger body and the system do not exchange energy. An example of this situation would be a gas confined to a glass container with a movable piston.

Problem 2.57. Landau potential

Find the Landau potential for the case where the temperature is fixed by a heat bath, the volume is fixed, and particles can move between the systems and the heat bath. You will need to extend the definition of the availability to allow for the number of particles to vary within the system. Use the same argument about extensive variables to show that the Landau potential equals $-PV$.

Problem 2.58. One kilogram of water at $50°C$ is brought into contact with a heat bath at $0°C$. What is the change of entropy of the water, the bath, and the combined system consisting of both the water and the heat bath? Given that the total entropy increased in Example 2.13, should the entropy increase or decrease in this case?

Problem 2.59. Changes in entropy

Calculate the changes in entropy due to various methods of heating:

(a) One kilogram of water at $0°C$ is brought into contact with a heat bath at $90°C$. What is the change in entropy of the water? What is the change in entropy of the bath? What is the change in entropy of the entire system consisting of both water and heat bath? (The specific heat of water is approximately $4184\,\text{J/kg K}$.)

(b) The water is heated from $0°C$ to $90°C$ by first bringing it into contact with a heat bath at $45°C$ and then with a heat bath at $90°C$. What is the change in entropy of the entire system?

(c) Discuss how the water can be heated from $0°C$ to $90°C$ without any change in entropy of the entire system.

Problem 2.60. If S is expressed as a function of T, V or T, P, then it is no longer a thermodynamic potential. That is, the maximum thermodynamic information is contained in S as a function of E and V (for fixed N). Why?

Problem 2.61. Refrigerators

A refrigerator cools a body by heating the hotter room surrounding the body. According to the second law of thermodynamics, work must be done by an external body. Suppose that we cool the cold body by the amount Q_{cold} at temperature T_{cold} and heat the room by the amount Q_{hot} at temperature T_{hot}. The external work supplied is W (see Figure 2.17). The work W supplied is frequently electrical work, the refrigerator interior is cooled (Q_{cold} extracted), and Q_{hot} is given to the room. We define the *coefficient of performance* (COP) as

$$\text{COP} = \frac{\text{what you get}}{\text{what you pay for}} = \frac{Q_{\text{cold}}}{W}. \tag{2.254}$$

Show that the maximum value of the COP corresponds to a reversible refrigerator and is given by

$$\text{COP} = \frac{T_{\text{cold}}}{T_{\text{hot}} - T_{\text{cold}}}. \tag{2.255}$$

Note that a refrigerator is more efficient for smaller temperature differences.
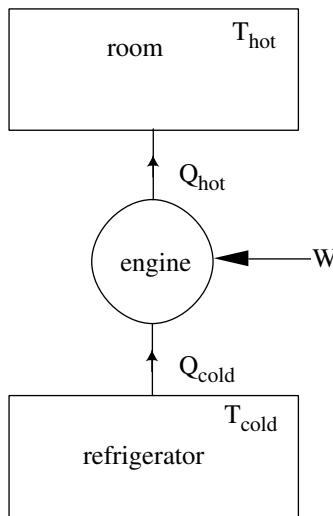
Figure 2.17: The transfer of energy in an idealized refrigerator.

Problem 2.62. Heat pumps

A heat pump works on the same principle as a refrigerator, but the object is to heat a room by cooling its cooler surroundings. For example, we could heat a building by cooling a nearby body of water. If we extract energy Q_{cold} from the surroundings at T_{cold}, do work W, and deliver Q_{hot} to the room at T_{hot}, the coefficient of performance is given by

$$\text{COP} = \frac{\text{what you get}}{\text{what you pay for}} = \frac{Q_{\text{hot}}}{W}. \tag{2.256}$$

What is the maximum value of COP for a heat pump in terms of T_{cold} and T_{hot}? What is the COP when the outside temperature is 0°C and the interior temperature is 23°C? Is it more effective to operate a heat pump during the winters in New England where the winters are cold or in the Pacific Northwest where the winters are relatively mild? (It is too bad that the maximum efficiency of a heat pump occurs when it is needed least.)

Problem 2.63. Use (2.137) to derive the relation (2.49) between V and T for an ideal gas in a quasistatic adiabatic process.

Problem 2.64. The Otto cycle

The Otto cycle is the idealized prototype of most present-day internal combustion engines. The cycle was first described by Beau de Rochas in 1862. Nicholas Otto independently conceived of

the same cycle in 1876 and then constructed an engine to implement it. The idealization makes two basic assumptions. One is that the working substance is taken to be air rather than a mixture of gases and vapor whose composition changes during the cycle. For simplicity, we assume that C_V and C_P are constant and that $\gamma = C_P/C_V = 1.4$, the value for air. The more important approximation is that the changes are assumed to be quasistatic. An idealized cycle that represents the six parts of this cycle is known as the air standard Otto cycle and is illustrated in Figure 2.18.

$5 \rightarrow 1$. *Intake stroke.* The mixture of gasoline and air is drawn into the cylinder through the intake valve by the movement of the piston. Idealization: A quasistatic isobaric intake of air at pressure P_0 to a volume V_1.

$1 \rightarrow 2$. *Compression stroke.* The intake valve closes and air-fuel mixture is rapidly compressed in the cylinder. The compression is nearly adiabatic and the temperature rises. Idealization: A quasistatic adiabatic compression from V_1 to V_2; the temperature rises from T_1 to T_2.

$2 \rightarrow 3$. *Explosion.* The mixture explodes such that the volume remains unchanged and a very high temperature and pressure is reached. Idealization: A quasistatic and constant volume increase of temperature and pressure due to the absorption of energy from a series of heat baths between T_2 and T_3.

$3 \rightarrow 4$. *Power stroke.* The hot combustion products expand and do work on the piston. The pressure and temperature decrease considerably. Idealization: A quasistatic adiabatic expansion produces a decrease in temperature.

$4 \rightarrow 1$. *Valve exhaust.* At the end of the power stroke the exhaust valve opens and the combustion products are exhausted to the atmosphere. There is a sudden decrease in pressure. Idealization: A quasistatic constant volume decrease in temperature to T_1 and pressure P_0 due to a exchange of energy with a series of heat baths between T_4 and T_1.

$1 \rightarrow 5$. *Exhaust stroke.* The piston forces the remaining gases into the atmosphere. The exhaust valve then closes and the intake valve opens for the next intake stroke. Idealization: A quasistatic isobaric expulsion of the air.

Show that the efficiency of the Otto cycle is

$$\eta = 1 - \left(\frac{V_2}{V_1}\right)^{\gamma-1}. \tag{2.257}$$

A compression ratio of about ten can be used without causing knocking. Estimate the theoretical maximum efficiency. In a real engine, the efficiency is about half of this value.

Suggestions for Further Reading

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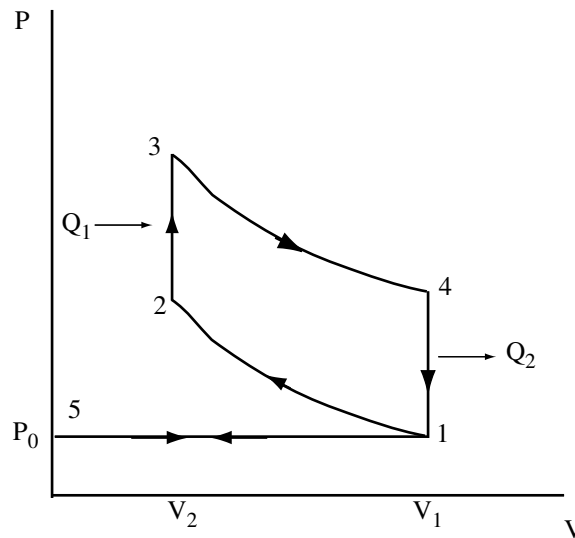
Figure 2.18: The air standard Otto cycle.

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Chapter 3

Concepts of Probability

We introduce the basic concepts of probability and apply them to simple physical systems and everyday life. We will discover the universal nature of the central limit theorem and the Gaussian distribution for the sum of a large number of random variables and discuss its relation to why thermodynamics is possible. Because of the importance of probability in many contexts and the relatively little time it will take us to consider more advanced topics, our discussion goes beyond what we will need for the applications of statistical mechanics in these notes.

3.1 Probability in Everyday Life

One of our goals, which we will consider in Chapter 4 and subsequent chapters, is to relate the behavior of various macroscopic quantities to the underlying microscopic behavior of the individual atoms or other constituents. To do so, we will need to introduce some ideas from probability.

We all use the ideas of probability in everyday life. For example, every morning many of us decide what to wear based on the probability of rain. We cross streets knowing that the probability of being hit by a car is small. We can even make a rough estimate of the probability of being hit by a car. It must be less that one in a thousand, because you have crossed streets thousands of times and hopefully you have not been hit. You might be hit tomorrow, or you might have been hit the first time you tried to cross a street. These comments illustrate that we have some intuitive sense of probability, and because it is a useful concept for survival, we know how to estimate it. As expressed by Laplace (1819),

Probability theory is nothing but common sense reduced to calculation.

Another interesting thought is due to Maxwell (1850): The true logic of this world is the calculus of probabilities . . . That is, probability is a natural language for describing real world phenomena.

However, our intuition only takes us so far. Consider airplane travel. Is it safe to fly? Suppose that there is a one chance in 100,000 of a plane crashing on a given flight and that there are a 1000 flights a day. Then every 100 days or so there would be a reasonable likelihood of a plane crash.

This estimate is in rough accord with what we read. For a given flight, your chances of crashing are approximately one part in 10^5, and if you fly five times a year for 100 years, it seems that flying is not too much of a risk. Suppose that instead of living 100 years, you could live 20,000 years. In this case you would take 100,000 flights, and it would be much more risky to fly if you wished to live your full 20,000 years. Although this last statement seems reasonable, can you explain why?

Much of the motivation for the mathematical formulation of probability arose from the proficiency of professional gamblers in estimating betting odds and their desire to have more quantitative measures. Although games of chance have been played since history has been recorded, the first steps toward a mathematical formulation of games of chance began in the middle of the 17th century. Some of the important contributors over the following 150 years include Pascal, Fermat, Descartes, Leibnitz, Newton, Bernoulli, and Laplace, names that are probably familiar to you.

Given the long history of games of chance and the interest in estimating probability in a variety of contexts, it is remarkable that the theory of probability took so long to develop. One reason is that the idea of probability is subtle and is capable of many interpretations. An understanding of probability is elusive due in part to the fact that the probably depends on the status of the information that we have (a fact well known to poker players). Although the rules of probability are defined by simple mathematical rules, an understanding of probability is greatly aided by experience with real data and concrete problems. To test your current understanding of probability, try to solve Problems 3.1–3.6 before reading the rest of this chapter. Then in Problem 3.7 formulate the laws of probability as best as you can based on your solutions to these problems.

Problem 3.1. Marbles in a jar

A jar contains 2 orange, 5 blue, 3 red, and 4 yellow marbles. A marble is drawn at random from the jar. Find the probability that

(a) the marble is orange;

(b) the marble is red;

(c) the marble is orange or blue.

Problem 3.2. Piggy bank

A piggy bank contains one penny, one nickel, one dime, and one quarter. It is shaken until two coins fall out at random. What is the probability that at least $0.30 falls out?

Problem 3.3. Two dice

A girl tosses a pair of dice at the same time. Find the probability that

(a) both dice show the same number;

(b) both dice show a number less than 5;

(c) both dice show an even number;

(d) the product of the numbers is 12.

Problem 3.4. Free throws

A boy hits 16 free throws out of 25 attempts. What is the probability that he will make a free throw on his next attempt?

Problem 3.5. Toss of a die

Consider an experiment in which a die is tossed 150 times and the number of times each face is observed is counted. The value of A, the number of dots on the face of the die and the number of times that it appeared is shown in Table 3.1.

(a) What is the predicted average value of A assuming a fair die?

(b) What is the average value of A observed in this experiment?

value of A	frequency
1	23
2	28
3	30
4	21
5	23
6	25

Table 3.1: The number of times face A appeared in 150 tosses.

Problem 3.6. What's in your purse?

A coin is taken at random from a purse that contains one penny, two nickels, four dimes, and three quarters. If x equals the value of the coin, find the average value of x.

Problem 3.7. Rules of probability

Based on your solutions to the above problems, state the rules of probability as you understand them at this time.

The following problems are related to the use of probability in everyday life.

Problem 3.8. Choices

Suppose that you are offered the following choice:

(a) A certain prize of $50.

(b) You flip a (fair) coin and win $100 if you get a head, but $0 if you get a tail. Which choice would you make? Explain your reasoning. Would your choice change if the certain prize was $40?

Problem 3.9. More choices

Suppose that you are offered the following choices:

(a) A prize of $100 is awarded for each head found in ten flips of a coin, or

(b) a certain prize of $400. What choice would you make? Explain your reasoning.

Problem 3.10. Thinking about probability

(a) Suppose that you were to judge an event to be 99.9999% probable. Would you be willing to bet $999 999 against $1 that the event would occur? Discuss why probability assessments should be kept separate from decision issues.

(b) Suppose that someone gives you a dollar to play the lottery. What sequence of six numbers between 1 and 36 would you choose?

(c) Suppose you toss a coin 8 times and obtain heads each time. Estimate the probability that you will obtain heads on your ninth toss.

(d) What is the probability that it will rain tomorrow? What is the probability that the Dow Jones industrial average will increase tomorrow?

(e) Give several examples of the use of probability in everyday life. Distinguish between various types of probability.

3.2 The Rules of Probability

We now summarize the basic rules and ideas of probability.[1] Suppose that there is an operation or a process that has several distinct possible *outcomes*. The process might be the flip of a coin or the roll of a six-sided die.[2] We call each flip a *trial*. The list of all the possible *events* or *outcomes* is called the *sample space*. We assume that the events are *mutually exclusive*, that is, the occurrence of one event implies that the others cannot happen at the same time. We let n represent the number of events, and label the events by the index i which varies from 1 to n. For now we assume that the sample space is finite and discrete. For example, the flip of a coin results in one of two events that we refer to as heads and tails and the role of a die yields one of six possible events.

For each event i, we assign a probability $P(i)$ that satisfies the conditions

$$P(i) \geq 0, \tag{3.1}$$

and

$$\sum_i P(i) = 1. \tag{3.2}$$

$P(i) = 0$ implies that the event cannot occur, and $P(i) = 1$ implies that the event must occur. The normalization condition (3.2) says that the sum of the probabilities of all possible mutually exclusive outcomes is unity.

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[1] In 1933 the Russian mathematician A. N. Kolmogorov formulated a complete set of axioms for the mathematical definition of probability.

[2] The earliest known six-sided dice have been found in the Middle East. A die made of baked clay was found in excavations of ancient Mesopotamia. The history of games of chance is discussed by Deborah J. Bennett, *Randomness*, Harvard University Press (1998).

Example 3.1. Let x be the number of points on the face of a die. What is the sample space of x?

Solution. The sample space or set of possible events is $x_i = \{1, 2, 3, 4, 5, 6\}$. These six outcomes are mutually exclusive.

The rules of probability will be summarized further in (3.3) and (3.5). These abstract rules must be supplemented by an *interpretation* of the term probability. As we will see, there are many different interpretations of probability because any interpretation that satisfies the rules of probability may be regarded as a kind of probability.

An interpretation of probability that is relatively easy to understand is based on *symmetry*. Suppose that we have a two-sided coin that shows heads and tails. Then there are two possible mutually exclusive outcomes, and if the coin is perfect, each outcome is equally likely.[3] If a die with six distinct faces (see Figure 3.1) is perfect, we can use symmetry arguments to argue that each outcome should be counted equally and $P(i) = 1/6$ for each of the six faces. For an actual die, we can estimate the probability *a posteriori*, that is, by the observation of the outcome of many throws. As is usual in physics, our intuition will lead us to the concepts.
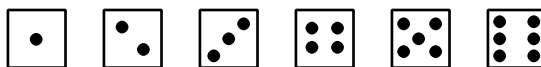
Figure 3.1: The six possible outcomes of the toss of a die.

Suppose that we know that the probability of rolling any face of a die in one throw is equal to 1/6, and we want to find the probability of finding face 3 *or* face 6 in one throw. In this case we wish to know the probability of a trial that is a combination of more elementary operations for which the probabilities are already known. That is, we want to know the probability of the outcome, *i or j*, where i is distinct from j. According to the rules of probability, the probability of event *i or j* is given by

$$P(i \text{ or } j) = P(i) + P(j). \qquad \text{(addition rule)} \tag{3.3}$$

The relation (3.3) is generalizable to more than two events. An important consequence of (3.3) is that if $P(i)$ is the probability of event i, then the probability of event i not occurring is $1 - P(i)$.

Example 3.2. What is the probability of throwing a three or a six with one throw of a die?

Solution. The probability that the face exhibits either 3 or 6 is $\frac{1}{6} + \frac{1}{6} = \frac{1}{3}$.

Example 3.3. What is the probability of *not* throwing a six with one throw of die?

Solution. The answer is the probability of either "1 or 2 or 3 or 4 or 5." The addition rule gives that the probability $P(\text{not six})$ is

$$P(\text{not six}) = P(1) + P(2) + P(3) + P(4) + P(5) \tag{3.4a}$$

$$= 1 - P(6) = \frac{5}{6}, \tag{3.4b}$$

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[3]Is the outcome of a coin toss really random? It appears that the randomness in a coin toss is introduced by sloppy humans. Each human-generated flip has a different height and speed and is caught at a different angle, giving different outcomes. See the references at the end of the chapter.

where the last relation follows from the fact that the sum of the probabilities for all outcomes sums to unity. It is very useful to take advantage of this property when solving many probability problems.

Another simple rule is for the probability of the joint occurrence of independent events. These events might be the probability of throwing a 3 on one die *and* the probability of throwing a 4 on a second die. If two events are independent, then the probability of both events occurring is the product of their probabilities

$$P(i \text{ and } j) = P(j)\,P(j). \qquad \text{(multiplication rule)} \tag{3.5}$$

Events are independent if the occurrence of one event does not change the probability for the occurrence of the other.

To understand the applicability of (3.5) and the meaning of the independence of events, consider the problem of determining the probability that a person chosen at random is a female over six feet tall. Suppose that we know that the probability of a person to be over six feet tall is $P(6^+) = \frac{1}{5}$, and the probability of being female is $P(\text{female}) = \frac{1}{2}$. We might conclude that the probability of being a tall female is $P(\text{female})P(6^+) = \frac{1}{2} \times \frac{1}{5} = \frac{1}{10}$. The same probability would hold for a tall male. However, this reasoning is incorrect, because the probability of being a tall female differs from the probability of being a tall male. The problem is that the two events – being over six feet tall and being female – are not independent. On the other hand, consider the probability that a person chosen at random is female and was born on September 6. We can reasonably assume equal likelihood of birthdays for all days of the year, and it is correct to conclude that this probability is $\frac{1}{2} \times \frac{1}{365}$ (not counting leap years). Being a woman and being born on September 6 are independent events.

Problem 3.11. Give an example from your solutions to Problems 3.1–3.6 where you used the addition rule or the multiplication rule or both.

Example 3.4. What is the probability of throwing an even number with one throw of a die?

Solution. We can use the addition rule to find that

$$P(\text{even}) = P(2) + P(4) + P(6) = \frac{1}{6} + \frac{1}{6} + \frac{1}{6} = \frac{1}{2}. \tag{3.6}$$

Example 3.5. What is the probability of the same face appearing on two successive throws of a die?

Solution. We know that the probability of any specific combination of outcomes, for example, (1,1), (2,2), … (6,6) is $\frac{1}{6} \times \frac{1}{6} = \frac{1}{36}$. Hence, by the addition rule

$$P(\text{same face}) = P(1,1) + P(2,2) + \ldots + P(6,6) = 6 \times \frac{1}{36} = \frac{1}{6}. \tag{3.7}$$

Example 3.6. What is the probability that in two throws of a die at least one six appears?

Solution. We have already established that

$$P(6) = \frac{1}{6} \qquad P(\text{not } 6) = \frac{5}{6}. \tag{3.8}$$

There are four possible outcomes $(6, 6)$, $(6, \text{not } 6)$, $(\text{not } 6, 6)$, $(\text{not } 6, \text{not } 6)$ with the probabilities

$$P(6, 6) = \frac{1}{6} \times \frac{1}{6} = \frac{1}{36} \tag{3.9a}$$

$$P(6, \text{not } 6) = P(\text{not } 6, 6) = \frac{1}{6} \times \frac{5}{6} = \frac{5}{36} \tag{3.9b}$$

$$P(\text{not } 6, \text{not } 6) = \frac{5}{6} \times \frac{5}{6} = \frac{25}{36}. \tag{3.9c}$$

All outcomes except the last have at least one six. Hence, the probability of obtaining at least one six is

$$P(\text{at least one } 6) = P(6, 6) + P(6, \text{not } 6) + P(\text{not } 6, 6) \tag{3.10a}$$

$$= \frac{1}{36} + \frac{5}{36} + \frac{5}{36} = \frac{11}{36}. \tag{3.10b}$$

A more direct way of obtaining this result is to use the normalization condition. That is,

$$P(\text{at least one six}) = 1 - P(\text{not } 6, \text{not } 6) = 1 - \frac{25}{36} = \frac{11}{36}. \tag{3.10c}$$

Example 3.7. What is the probability of obtaining at least one six in four throws of a die?

Solution. We know that in one throw of a die, there are two outcomes with $P(6) = \frac{1}{6}$ and $P(\text{not } 6) = \frac{5}{6}$. Hence, in four throws of a die there are sixteen possible outcomes, only one of which has no six. That is, in the fifteen mutually exclusive outcomes, there is at least one six. We can use the multiplication rule (3.3) to find that

$$P(\text{not } 6, \text{not } 6, \text{not } 6, \text{not } 6) = P(\text{not } 6)^4 = \left(\frac{5}{6} \right)^4, \tag{3.11}$$

and hence

$$P(\text{at least one six}) = 1 - P(\text{not } 6, \text{not } 6, \text{not } 6, \text{not } 6) \tag{3.12a}$$

$$= 1 - \left(\frac{5}{6} \right)^4 = \frac{671}{1296} \approx 0.517. \tag{3.12b}$$

Frequently we know the probabilities only up to a constant factor. For example, we might know $P(1) = 2P(2)$, but not $P(1)$ or $P(2)$ separately. Suppose we know that $P(i)$ is proportional to $f(i)$, where $f(i)$ is a known function. To obtain the normalized probabilities, we divide each function $f(i)$ by the sum of all the unnormalized probabilities. That is, if $P(i) \propto f(i)$ and $Z = \sum f(i)$, then $P(i) = f(i)/Z$. This procedure is called *normalization*.

Example 3.8. Suppose that in a given class it is three times as likely to receive a C as an A, twice as likely to obtain a B as an A, one-fourth as likely to be assigned a D as an A, and nobody fails the class. What are the probabilities of getting each grade?

Solution. We first assign the unnormalized probability of receiving an A as $f(A) = 1$. Then $f(B) = 2$, $f(C) = 3$, and $f(D) = 0.25$. Then $Z = \sum_i f(i) = 1 + 2 + 3 + 0.25 = 6.25$. Hence, $P(A) = f(A)/Z = 1/6.25 = 0.16$, $P(B) = 2/6.25 = 0.32$, $P(C) = 3/6.25 = 0.48$, and $P(D) = 0.25/6.25 = 0.04$.

The normalization procedure arises again and again in different contexts. We will see that much of the mathematics of statistical mechanics can be formulated in terms of the calculation of normalization constants.

Problem 3.12. Find the probability distribution $P(n)$ for throwing a sum n with two dice and plot $P(n)$ as a function of n.

Problem 3.13. What is the probability of obtaining at least one double six in twenty-four throws of a pair of dice?

Problem 3.14. Suppose that three dice are thrown at the same time. What is the probability that the sum of the three faces is 10 compared to 9?

Problem 3.15. What is the probability that the total number of spots shown on three dice thrown at the same time is 11? What is the probability that the total is 12? What is the fallacy in the following argument? The number 11 occurs in six ways: (1,4,6), (2,3,6), (1,5,5), (2,4,5), (3,3,5), (3,4,4). The number 12 also occurs in six ways: (1,5,6), (2,4,6), (3,3,6), (2,5,5), (3,4,5), (4,4,4) and hence the two numbers should be equally probable.

3.3 Mean Values

The specification of the *probability distribution* $P(1)$, $P(2)$, ... $P(n)$ for the n possible values of the variable x constitutes the most complete statistical description of the system. However, in many cases it is more convenient to describe the distribution of the possible values of x in a less detailed way. The most familiar way is to specify the *average* or *mean* value of x, which we will denote as $\overline{x}$. The definition of the mean value of x is

$$\overline{x} \equiv x_1 P(1) + x_2 P(2) + \ldots + x_n P(n) \tag{3.13a}$$

$$= \sum_{i=1}^{n} x_i P(i), \tag{3.13b}$$

where $P(i)$ is the probability of x_i. If $f(x)$ is a function of x, then the mean value of $f(x)$ is defined by

$$\overline{f(x)} = \sum_{i=1}^{n} f(x_i) P(i). \tag{3.14}$$

Example 3.9. Expected value

Lets reconsider the choices in Problem 3.8: A certain \$50 or \$100 if you flip a coin and get a head and \$0 if you get a tail. The *expected value* is

$$\text{expected value} = \sum_{i} P_i \times (\text{value of } i), \tag{3.15}$$

where the sum is over the expected outcomes and P_i is the probability of outcome i. In this case the expected value is $1/2 \times \$100 + 1/2 \times \$0 = \$50$. We see that the two choices are equivalent, and that the expected value is the same as the mean or average value. (Most people prefer the first choice because the outcome is "certain.")

If $f(x)$ and $g(x)$ are any two functions of x, then

$$\overline{f(x) + g(x)} = \sum_{i=1}^{n} [f(x_i) + g(x_i)] P(i) \tag{3.16a}$$

$$= \sum_{i=1}^{n} f(x_i) P(i) + \sum_{i=1}^{n} g(x_i) P(i), \tag{3.16b}$$

or

$$\overline{f(x) + g(x)} = \overline{f(x)} + \overline{g(x)}. \tag{3.16c}$$

Problem 3.16. Show that if c is a constant, then

$$\overline{cf(x)} = c\overline{f(x)}. \tag{3.17}$$

In general, we can define the mth *moment* of the probability distribution P as

$$\overline{x^m} \equiv \sum_{i=1}^{n} x_i{}^m P(i), \tag{3.18}$$

where we have let $f(x) = x^m$. The mean of x is the first moment of the probability distribution.

Problem 3.17. Suppose that the variable x takes on the values -2, -1, 0, 1, and 2 with probabilities $1/16$, $4/16$, $6/16$, $4/16$, and $1/16$, respectively. Calculate the first two moments of x.

The mean value of x is a measure of the central value of x about which the various values of x_i are distributed. If we measure x from its mean, we have that

$$\Delta x \equiv x - \overline{x}, \tag{3.19}$$

and

$$\overline{\Delta x} = \overline{(x - \overline{x})} = \overline{x} - \overline{x} = 0. \tag{3.20}$$

That is, the average value of the deviation of x from its mean vanishes.

If only one outcome j were possible, we would have $P(i) = 1$ for $i = j$ and zero otherwise, that is, the probability distribution would have zero width. In general, there is more than one outcome and a possible measure of the width of the probability distribution is given by

$$\overline{\Delta x^2} \equiv \overline{(x - \overline{x})^2}. \tag{3.21}$$

The quantity $\overline{\Delta x^2}$ is known as the *dispersion* or *variance* and its square root is called the *standard deviation*. It is easy to see that the larger the spread of values of x about $\overline{x}$, the larger the variance. The use of the square of $x - \overline{x}$ ensures that the contribution of x values that are smaller and larger than $\overline{x}$ enter with the same sign. A useful form for the variance can be found by letting

$$\overline{(x - \overline{x})^2} = \overline{(x^2 - 2x\overline{x} + \overline{x}^2)} \tag{3.22a}$$

$$= \overline{x^2} - 2\overline{x}\,\overline{x} + \overline{x}^2, \tag{3.22b}$$

or

$$\overline{(x - \overline{x})^2} = \overline{x^2} - \overline{x}^2. \tag{3.23}$$

Because $\overline{\Delta x^2}$ is always nonnegative, it follows that $\overline{x^2} \geq \overline{x}^2$.

The variance is the mean value of $(x - \overline{x})^2$ and represents the square of a width. We will find that it is useful to interpret the width of the probability distribution in terms of the standard deviation σ, which is defined as the square root of the variance. The standard deviation of the probability distribution $P(x)$ is given by

$$\sigma_x = \sqrt{\overline{\Delta x^2}} = \sqrt{\left(\overline{x^2} - \overline{x}^2\right)}. \tag{3.24}$$

Example 3.10. Find the mean value $\overline{x}$, the variance $\overline{\Delta x^2}$, and the standard deviation σ_x for the value of a single throw of a die.

Solution. Because $P(i) = \frac{1}{6}$ for $i = 1, \ldots, 6$, we have that

$$\overline{x} = \frac{1}{6}(1 + 2 + 3 + 4 + 5 + 6) = \frac{7}{2} = 3.5 \tag{3.25a}$$

$$\overline{x^2} = \frac{1}{6}(1 + 4 + 9 + 16 + 25 + 36) = \frac{46}{3} \tag{3.25b}$$

$$\overline{\Delta x^2} = \overline{x^2} - \overline{x}^2 = \frac{46}{3} - \frac{49}{4} = \frac{37}{12} \approx 3.08 \tag{3.25c}$$

$$\sigma_x \approx \sqrt{3.08} = 1.76 \tag{3.25d}$$

Example 3.11. On the average, how many times must a die be thrown until a 6 appears?

Solution. Although it might seem obvious that the answer is six, it is instructive to confirm this answer. Let p be the probability of a six on a given throw. The probability of success for the first time on trial i is given in Table 3.2.

trial	probability of success on trial i
1	p
2	qp
3	$q^2 p$
4	$q^3 p$

Table 3.2: Probability of a head for the first time on trial i ($q = 1 - p$).

The sum of the probabilities is $p + qp + q^2p + \cdots = p(1 + q + q^2 + \cdots) = p/(1 - q) = p/p = 1$. The mean number of trials m is

$$m = p + 2pq + 3pq^2 + 4pq^3 + \cdots \tag{3.26a}$$

$$= p(1 + 2q + 3q^2 + \cdots) \tag{3.26b}$$

$$= p\frac{d}{dq}\left(1 + q + q^2 + q^3 + \cdots\right) \tag{3.26c}$$

$$= p\frac{d}{dq}\frac{1}{1 - q} = \frac{p}{(1 - q)^2} = \frac{1}{p} \tag{3.26d}$$

Another way to obtain this result is to note that if the first toss is a failure, then the mean number of tosses required is $1 + m$, and if the first toss is a success, the mean number is 1. Hence, $m = q(1 + m) + p(1)$ or $m = 1/p$.

3.4 The Meaning of Probability

How can we assign the probabilities of the various events? If we say that event E_1 is more probable than event E_2 ($P(E_1) > P(E_2)$), we mean that E_1 is more likely to occur than E_2. This statement of our intuitive understanding of probability illustrates that probability is a way of classifying the plausibility of events under conditions of uncertainty. Probability is related to our degree of belief in the occurrence of an event.

This definition of probability is not bound to a single evaluation rule and there are many ways to obtain $P(E_i)$. For example, we could use symmetry considerations as we have done, past frequencies, simulations, theoretical calculations, or as we will learn in Section 3.4.2, Bayesian inference. Probability assessments depend on who does the evaluation and the status of the information the evaluator has at the moment of the assessment. We always evaluate the conditional probability, that is, the probability of an event E given the information I, $P(E|I)$. Consequently, several people can have simultaneously different degrees of belief about the same event, as is well known to investors in the stock market.

If rational people have access to the same information, they should come to the same conclusion about the probability of an event. The idea of a *coherent bet* forces us to make probability assessments that correspond to our belief in the occurrence of an event. If we consider an event to be 50% probable, then we should be ready to place an even bet on the occurrence of the event or on its opposite. However, if someone wishes to place the bet in one direction but not in the other, it means that this person thinks that the preferred event is more probable than the other. In this case the 50% probability assessment is *incoherent* and this person's wish does not correspond to his or her belief.

A coherent bet has to be considered *virtual*. For example, a person might judge an event to be 99.9999% probable, but nevertheless refuse to bet $999999 against $1, if $999999 is much more than the person's resources. Nevertheless, the person might be convinced that this bet would be fair if he/she had an infinite budget. Probability assessments should be kept separate from decision issues. Decisions depend not only on the probability of the event, but also on the subjective importance of a given amount of money (see for example, Problems 3.10 and 3.92).

Our discussion of probability as the degree of belief that an event will occur shows the inadequacy of the frequency definition of probability, which *defines* probability as the ratio of the number of desired outcomes to the total number of possible outcomes. This definition is inadequate because we would have to specify that each outcome has equal probability. Thus we would have to use the term probability in its own definition. If we do an experiment to measure the frequencies of various outcomes, then we need to make an additional assumption that the measured frequencies will be the same in the future as they were in the past. Also we have to make a large number of measurements to insure accuracy, and we have no way of knowing a priori how many measurements are sufficient. Thus, the definition of probability as a frequency really turns out to be a method for estimating probabilities with some hidden assumptions.

Our definition of probability as a measure of the degree of belief in the occurrence of an outcome implies that probability depends on our prior knowledge, because belief depends on prior knowledge. For example, if we toss a coin and obtain 100 tails in a row, we might use this knowledge as evidence that the coin or toss is biased, and thus estimate that the probability of throwing another tail is very high. However, if a careful physical analysis shows that there is no bias, then we would stick to our estimate of 1/2. The probability depends on what knowledge we bring to the problem. If we have no knowledge other than the possible outcomes, then the best estimate is to assume equal probability for all events. However, this assumption is not a definition, but an example of belief. As an example of the importance of prior knowledge, consider the following problem.

Problem 3.18. A couple with two children

(a) A couple has two children. What is the probability that at least one child is a girl?

(b) Suppose that you know that at least one child is a girl. What is the probability that the other child is a girl?

(c) Instead suppose that we know that the oldest child is a girl. What is the probability that the youngest is a girl?

We know that we can estimate probabilities empirically by sampling, that is, by making repeated measurements of the outcome of independent events. Intuitively we believe that if we perform more and more measurements, the calculated average will approach the exact mean of the quantity of interest. This idea is called *the law of large numbers.*

As an example, suppose that we flip a single coin M times and count the number of heads. Our result for the number of heads is shown in Table 3.3. We see that the fraction of heads approaches 1/2 as the number of measurements becomes larger.

Problem 3.19. Use the applet/application at <stp.clarku.edu/simulations/cointoss> to simulate multiple tosses of a single coin. What is the correspondence between this simulation of a coin being tossed many times and the actual physical tossing of a coin? If the coin is "fair," what do you think the ratio of the number of heads to the total number of tosses will be? Do you obtain this number after 100 tosses? 10,000 tosses?

Another way of estimating the probability is to perform a single measurement on many copies or replicas of the system of interest. For example, instead of flipping a single coin 100 times in succession, we collect 100 coins and flip all of them at the same time. The fraction of coins that show heads is an estimate of the probability of that event. The collection of identically prepared systems is called an *ensemble* and the probability of occurrence of a single event is estimated with respect to this ensemble. The ensemble consists of a large number M of identical systems, that is, systems that satisfy the same known conditions.

If the system of interest is not changing in time, it is reasonable to assume that an estimate of the probability by either a series of measurements on a single system at different times or similar measurements on many identical systems at the same time would give consistent results.

Note that we have *estimated* various probabilities by a frequency, but have not *defined* probability in terms of a frequency. As emphasized by D'Agostini, past frequency is experimental data.

heads	tosses	fraction of heads
4	10	0.4
29	50	0.58
49	100	0.49
101	200	0.505
235	500	0.470
518	1,000	0.518
4997	10,000	0.4997
50021	100,000	0.50021
249946	500,000	0.49999
500416	1,000,000	0.50042

Table 3.3: The number and fraction of heads in M tosses of a coin. We did not really toss a coin in the air 10^6 times. Instead we used a computer to generate a sequence of random numbers to simulate the tossing of a coin. Because you might not be familiar with such sequences, imagine a robot that can write the positive integers between 1 and 2^{31} on pieces of paper. Place these pieces in a hat, shake the hat, and then chose the pieces at random. If the number chosen is less than $\frac{1}{2} \times 2^{31}$, then we say that we found a head. Each piece is placed back in the hat after it is read.

This data happened with certainty so the concept of probability no longer applies. Probability is how much we believe that an event will occur taking into account all available information including past frequencies. Because probability quantifies the degree of belief at a given time, it is not measurable. If we make further measurements, they can only influence future assessments of the probability.

3.4.1   Information and uncertainty

Consider an experiment that has two outcomes E_1 and E_2 with probabilities P_1 and P_2. For example, the experiment could correspond to the toss of a coin. For one coin the probabilities are $P_1 = P_2 = 1/2$ and for the other (a bent coin) $P_1 = 1/5$ and $P_2 = 4/5$. Intuitively, we would say that the result of the first experiment is more uncertain.

Consider two additional experiments. In the third experiment there are four outcomes with $P_1 = P_2 = P_3 = P_4 = 1/4$ and in the fourth experiment there are six outcomes with $P_1 = P_2 = P_3 = P_4 = P_5 = P_6 = 1/6$. Intuitively the fourth experiment is the most uncertain because there are more outcomes and the first experiment is the least uncertain. You are probably not clear about how to rank the second and third experiments.

We will now introduce a mathematical measure that is consistent with our intuitive sense of uncertainty. Let us define the uncertainty function $S(P_1, P_2, \ldots, P_i, \ldots)$ where P_i is the probability of event i. We first consider the case where all the probabilities P_i are equal. Then $P_1 = P_2 = \ldots = P_i = 1/\Omega$, where Ω is the total number of outcomes. In this case we have $S = S(1/\Omega, 1/\Omega, \ldots)$ or simply $S(\Omega)$.

It is easy to see that $S(\Omega)$ has to satisfy some simple conditions. For only one outcome, $\Omega = 1$

and there is no uncertainty. Hence we must have

$$S(\Omega = 1) = 0. \tag{3.27}$$

We also have that

$$S(\Omega_1) > S(\Omega_2) \text{ if } \Omega_1 > \Omega_2. \tag{3.28}$$

That is, $S(\Omega)$ is a increasing function of Ω.

We next consider multiple events. For example, suppose that we throw a die with Ω_1 outcomes and flip a coin with Ω_2 equally probable outcomes. The total number of outcomes is $\Omega = \Omega_1 \Omega_2$. If the result of the die is known, the uncertainty associated with the die is reduced to zero, but there still is uncertainty associated with the toss of the coin. Similarly, we can reduce the uncertainty in the reverse order, but the total uncertainty is still nonzero. These considerations suggest that

$$S(\Omega_1 \Omega_2) = S(\Omega_1) + S(\Omega_2). \tag{3.29}$$

It is remarkable that there is an unique functional form that satisfies the three conditions (3.27)–(3.29). We can find this form by writing (3.29) in the form

$$S(xy) = S(x) + S(y), \tag{3.30}$$

and taking the variables x and y to be continuous. (The analysis can be done assuming that x and y are discrete variables, but the analysis is simpler if we assume that x and y are continuous. Given this assumption the functional form of S might already be clear.) This generalization is consistent with $S(\Omega)$ being a increasing function of Ω. First we take the partial derivative of $S(xy)$ with respect to x and then with respect to y. We let $z = xy$ and obtain

$$\frac{\partial S(z)}{\partial x} = \frac{\partial z}{\partial x}\frac{dS(z)}{dz} = y\frac{dS(z)}{dz} \tag{3.31a}$$

$$\frac{\partial S(z)}{\partial y} = \frac{\partial z}{\partial y}\frac{dS(z)}{dz} = x\frac{dS(z)}{dz}. \tag{3.31b}$$

From (3.30) we have

$$\frac{\partial S(z)}{\partial x} = \frac{dS(x)}{dx} \tag{3.32a}$$

$$\frac{\partial S(z)}{\partial y} = \frac{dS(y)}{dy}. \tag{3.32b}$$

By comparing the right-hand side of (3.31) and (3.32), we have

$$\frac{dS}{dx} = y\frac{dS}{dz} \tag{3.33a}$$

$$\frac{dS}{dy} = x\frac{dS}{dz}. \tag{3.33b}$$

If we multiply (3.33a) by x and (3.33b) by y, we obtain

$$x\frac{dS(x)}{dx} = y\frac{dS(y)}{dy} = z\frac{dS(z)}{dz}. \tag{3.34}$$

Note that the first term in (3.34) depends only on x and the second term depends only on y. Because x and y are independent variables, the three terms in (3.34) must be equal to a constant. Hence we have the desired condition

$$x\frac{dS(x)}{dx} = y\frac{dS(y)}{dy} = A,\tag{3.35}$$

where A is a constant. The differential equation in (3.35) can be integrated to give

$$S(x) = A\ln x + B.\tag{3.36}$$

The integration constant B must be equal to zero to satisfy the condition (3.27). The constant A is arbitrary so we choose $A = 1$. Hence for equal probabilities we have that

$$S(\Omega) = \ln \Omega.\tag{3.37}$$

What about the case where the probabilities for the various events are unequal? We will show in Section 3.12.1 that the general form of the uncertainty S is

$$S = -\sum_i P_i \ln P_i.\tag{3.38}$$

Note that if all the probabilities are equal, then

$$P_i = \frac{1}{\Omega}\tag{3.39}$$

for all i. In this case

$$S = -\sum_i \frac{1}{\Omega} \ln \frac{1}{\Omega} = \Omega\frac{1}{\Omega}\ln\Omega = \ln\Omega,\tag{3.40}$$

because there are Ω equal terms in the sum. Hence (3.38) reduces to (3.37) as required. We also see that if outcome j is certain, $P_j = 1$ and $P_i = 0$ if $i \neq j$ and $S = -1\ln 1 = 0$. That is, if the outcome is certain, the uncertainty is zero and there is no missing information.

We have shown that if the P_i are known, then the uncertainty or missing information S can be calculated. Usually the problem is the other way around, and we want to determine the probabilities. Suppose we flip a perfect coin for which there are two possibilities. We know intuitively that $P_1(\text{heads}) = P_2(\text{tails}) = 1/2$. That is, we would not assign a different probability to each outcome unless we had information to justify it. Intuitively we have adopted the principle of *least bias* or *maximum uncertainty*. Lets reconsider the toss of a coin. In this case S is given by

$$S = -\sum_i P_i \ln P_i = -(P_1 \ln P_1 + P_2 \ln P_2)\tag{3.41a}$$

$$= -(P_1 \ln P_1 + (1 - P_1)\ln(1 - P_1)),\tag{3.41b}$$

where we have used the fact that $P_1 + P_2 = 1$. To maximize S we take the derivative with respect to P_1:[4]

$$\frac{dS}{dP_1} = -[\ln P_1 + 1 - \ln(1 - P_1) - 1] = -\ln\frac{P_1}{1 - P_1} = 0.\tag{3.42}$$

---

[4]We have used the fact that $d(\ln x)/dx = 1/x$.

The solution of (3.42) satisfies

$$\frac{P_1}{1 - P_1} = 1, \tag{3.43}$$

which is satisfied by $P_1 = 1/2$. We can check that this solution is a maximum by calculating the second derivative.

$$\frac{\partial^2 S}{\partial P_1^2} = -\left[\frac{1}{P_1} + \frac{1}{1 - P_1}\right] = -4 < 0, \tag{3.44}$$

which is less then zero.

Problem 3.20. Uncertainty

(a) Consider the toss of a coin for which $P_1 = P_2 = 1/2$ for the two outcomes. What is the uncertainty in this case?

(b) What is the uncertainty for $P_1 = 1/3$ and $P_2 = 2/3$? How does the uncertainty in this case compare to that in part (a)?

(c) On page 113 we discussed four experiments with various outcomes. Compare the uncertainty S of the third and fourth experiments.

Example 3.12. The toss of a three-sided die yields events E_1, E_2, and E_3 with a face of one, two, and three points. As a result of tossing many dice, we learn that the mean number of points is $f = 1.9$, but we do not know the individual probabilities. What are the values of P_1, P_2, and P_3 that maximize the uncertainty?

Solution. We have

$$S = -\left[P_1 \ln P_1 + P_2 \ln P_2 + P_3 \ln P_3\right]. \tag{3.45}$$

We also know that

$$f = 1P_1 + 2P_2 + 3P_3, \tag{3.46}$$

and $P_1 + P_2 + P_3 = 1$. We use the latter condition to eliminate P_3 using $P_3 = 1 - P_1 - P_2$, and rewrite (3.46) as

$$f = P_1 + 2P_2 + 3(1 - P_1 - P_2) = 3 - 2P_1 - P_2. \tag{3.47}$$

We then use (3.47) to eliminate P_2 and P_3 from (3.45) using $P_2 = 3 - f - 2P_1$ and $P_3 = f - 2 + P_1$:

$$S = -[P_1 \ln P_1 + (3 - f - 2P_1) \ln(3 - f - 2P_1) + (f - 2 + P_1) \ln(f - 2 + P_1)]. \tag{3.48}$$

Because S in (3.48) depends on only P_1, we can differentiate S with respect P_1 to find its maximum value:

$$\frac{dS}{dP_1} = -\left[\ln P_1 - 1 - 2[\ln(3 - f - 2P_1) - 1] + [\ln(f - 2 + P_1) - 1]\right] \tag{3.49a}$$

$$= \ln \frac{P_1(f - 2 + P_1)}{(3 - f - 2P_1)^2} = 0. \tag{3.49b}$$

We see that for dS/dP_1 to be equal to zero, the argument of the logarithm must be one. The result is a quadratic equation for P_1 (see Problem 3.21).

Problem 3.21. Fill in the missing steps in Example 3.12 and solve for P_1, P_2, and P_3.

In Section 3.12.2 we maximize the uncertainty for a case for which there are more than three outcomes.

3.4.2   *Bayesian inference

Conditional probabilities are not especially important for the development of equilibrium statistical mechanics, so this section may be omitted for now. However, conditional probability and Bayes' theorem are very important for the analysis of data including spam filters for email, and in the more general context of statistical physics. Bayes' theorem gives us a way of understanding how the probability that a hypothesis is true is affected by new evidence.

Let us define $P(A|B)$ as the probability of A occurring given that we know that B has occurred. We know that

$$P(A) = P(A|B) + P(A|-B), \tag{3.50}$$

where $-B$ means that B did not occur. We also know that

$$P(A \text{ and } B) = P(A|B)P(B) = P(B|A)P(A). \tag{3.51}$$

Equation (3.51) means that the probability that A and B occur equals the probability that A occurs given B times the probability that B occurs, which is the same as the probability that B occurs given A times the probability A that occurs. Note that $P(A \text{ and } B)$ is the same as $P(B \text{ and } A)$, but $P(A|B)$ does not have the same meaning as $P(B|A)$.

We can rearrange (3.51) to obtain Bayes' theorem

$$\boxed{P(A|B) = \frac{P(B|A)P(A)}{P(B)}.} \qquad \text{(Bayes' theorem)} \tag{3.52}$$

We can generalize (3.52) for the case of multiple possible outcomes A_i for the same B. We rewrite (3.52) as

$$P(A_i|B) = \frac{P(B|A_i)P(A_i)}{P(B)}. \tag{3.53}$$

If all the A_i are mutually exclusive and if at least one of the A_i must occur, then we can also write

$$P(B) = \sum_i P(B|A_i)P(A_i). \tag{3.54}$$

If we substitute (3.54) for $P(B)$ into (3.53), we obtain

$$P(A_i|B) = \frac{P(B|A_i)P(A_i)}{\sum_i P(B|A_i)P(A_i)}. \tag{3.55}$$

Bayes' theorem is very useful for finding the most probable explanation of a given data set. In this context A_i represents the possible explanation and B represents the data. As more data becomes available, the probabilities $P(B|A_i)P(A_i)$ change.

Example 3.13. A chess program has two modes, expert (E) and novice (N). The expert mode beats you 75% of the time and the novice mode wins 50% of the time. You close your eyes and randomly choose one of the modes and play two games. The computer wins (W) both times. What is the probability that you chose the novice mode?

Solution. The probability of interest is $P(N|WW)$, which is difficult to calculate directly. Bayes theorem lets you use the easy to calculate probability $P(WW|N)$ to determine $P(N|WW)$. We use (3.52) to write

$$P(N|WW) = \frac{P(WW|N)P(N)}{P(WW)}. \tag{3.56}$$

We know that $P(N) = 1/2$ and $P(WW|N) = (1/2)^2 = 1/4$.

We next have to calculate $P(WW)$. There are two ways that the program won the two games: (1) You chose the novice mode and it won twice, or (2) you chose the expert mode and it won twice. Because N and E are mutually exculsive, we have $P(WW) = P(N \text{ and } WW) + P(E \text{ and } WW)$. From (3.51) we have

$$P(WW) = P(WW|N)P(N) + P(WW|E)P(E) \tag{3.57a}$$

$$= (1/2 \times 1/2 \times 1/2) + (3/4 \times 3/4 \times 1/2) = \frac{13}{32}. \tag{3.57b}$$

Hence

$$P(N|WW) = \frac{P(WW|N)P(N)}{P(WW)} = \frac{(1/4 \times 1/2)}{\frac{13}{32}} = \frac{4}{13} \approx 0.31. \tag{3.58}$$

Note that the probability of choosing the novice mode has decreased from 50% to about 31% because you have the additional information that you lost twice and thus are more likely to have chosen the expert mode.

Example 3.14. Alice plants two types of flowers in her garden: 30% of type A and 70% of type B. Both types yield either red or yellow flowers, with $P(\text{red}|A) = 0.4$ and $P(\text{red}|B) = 0.3$.

(a) What is the percentage of red flowers that Alice will obtain?

Solution. We can use the total probability law (3.51) to write

$$P(\text{red}) = P(\text{red}|A)P(A) + P(\text{red}|B)P(B) \tag{3.59a}$$
$$= (0.4 \times 0.3) + (0.3 \times 0.7) = 33/100. \tag{3.59b}$$

So Alice will find that one of three flowers will be red.

(b) Suppose a red flower is picked at random from Alice's garden. What is the probability of the flower being type A?

Solution. We apply Bayes' theorem and obtain

$$P(A|\text{red}) = \frac{P(\text{red}|A)P(A)}{P(\text{red}|A)P(A) + P(\text{red}|B)P(B)} \tag{3.60a}$$

$$= \frac{0.4 \times 0.3}{(0.4 \times 0.3) + (0.3 \times 0.7)} = \frac{12}{33} = \frac{4}{11} \approx 0.36. \tag{3.60b}$$

We find that given that the flower is red, its probability of being type A increases to 0.36 because type A has a higher probability than type B of yielding red flowers.

Example 3.15. Do you have a fair coin?

Suppose that there are four coins of the same type in a bag. Three of them are fair, but the fourth is double-headed. You choose one coin at random from the bag and toss it five times. It comes up heads each time. What is the probability that you have chosen the double-headed coin?

Solution. If the coin were fair, the probability of five heads in a row (5H) would be $(1/2)^5 = 1/32 \approx 0.03$. This probability is small, so you would probably decide that you have not chosen a fair coin. But because you have more information, you can determine a better estimate of the probability.

We have

$$P(\text{H5}) = P(5\text{H}|\text{fair})P(\text{fair}) + P(5\text{H}|\text{not fair})P(\text{not fair}) \tag{3.61a}$$

$$= [(1/2)^5 \times 3/4] + [1 \times 1/4] = 35/128 \approx 0.27. \tag{3.61b}$$

$$P(\text{fair coin}|5\text{H}) = P(5\text{H}|\text{fair coin})P(\text{fair coin})/P(5H) \tag{3.61c}$$

$$= \frac{[(1/2)^5 \times 3/4]}{35/128} = 3/35 = 0.12. \tag{3.61d}$$

Thus the probability that the coin was fair is about a factor of four greater given that you tossed a coin five times.

Problem 3.22. More on choosing a fair coin

Suppose that you have two coins that look and feel identical, but one is double-headed and one is fair. The two coins are placed in a box and you choose one at random.

(a) What is the probability that you have chosen the fair coin?

(b) Suppose that you toss the chosen coin twice and obtain heads both times. What is the probability that you have chosen the fair coin? Why is this probability different than in part (a)?

(c) Suppose that you toss the chosen coin four times and obtain four heads. What is the probability that you have chosen the fair coin?

(d) Suppose that there are ten coins in the box with nine fair and one double-headed. You toss the chosen twice and obtain two heads. What is the probability that you have chosen the fair coin?

(e) Now suppose that the biased coin is not double-headed, but has a probability of 0.98 of coming up heads. Also suppose that the probability of choosing the biased coin is 1 in 10^4. What is the probability of choosing the biased coin given that the first toss yields heads?

Example 3.16. Monty Hall problem

Consider the quandary known as the Monty Hall problem. In this former television show a contestant is shown three doors. Behind one door is an expensive prize such as a car and behind the other two doors are inexpensive gifts such as a tie. The contestant chooses a door. Suppose she chooses door 1. Then the host opens door 2 containing the tie knowing that the car is not behind

door 2. The contestant now has a choice – should she stay with her original choice or switch to door 3? What would you do?[5]

Let us use Bayes' theorem to determine her best course of action. We want to calculate

$$P(A_1|B) = P(\text{car behind door 1}|\text{door 2 open after door 1 chosen}), \tag{3.62a}$$

and

$$P(A_3|B) = P(\text{car behind door 3}|\text{door 2 open after door 1 chosen}), \tag{3.62b}$$

where A_i denotes car behind door i. We know that all the $P(A_i)$ equal 1/3, because with no information we assume that the probability that the car is behind each door is the same. Because the host can open door 2 or 3 if the car is behind door 1, but can only open door 2 if the car is behind door 3 we have

$$P(\text{door 2 open after door 1 chosen}|\text{car behind 1}) = \frac{1}{2} \tag{3.63a}$$

$$P(\text{door 2 open after door 1 chosen}|\text{car behind 2}) = 0 \tag{3.63b}$$

$$P(\text{door 2 open after door 1 chosen}|\text{car behind 3}) = 1. \tag{3.63c}$$

From Bayes' theorem we have

$$P(\text{car behind 1}|\text{door 2 open after door 1 chosen}) = \frac{\frac{1}{2} \times \frac{1}{3}}{(\frac{1}{2} \times \frac{1}{3}) + (0 \times \frac{1}{3}) + (1 \times \frac{1}{3})} = \frac{1}{3} \tag{3.64a}$$

$$P(\text{car behind 3}|\text{door 2 open after door 1 chosen}) = \frac{1 \times \frac{1}{3}}{(\frac{1}{2} \times \frac{1}{3}) + (0 \times \frac{1}{3}) + (1 \times \frac{1}{3})} = \frac{2}{3}. \tag{3.64b}$$

The results in (3.64) suggest the contestant has a higher probability of winning the car if she switches doors and chooses door 3. The same logic suggests that she should always switch doors independently of which door she originally chose.[6]

Problem 3.23. What does the host know?

The point of Bayesian statistics is that it approaches a given data set with a particular model in mind. In the Monte Hall problem the model we have used is that the host knows where the car is.

(a) Suppose that the host doesn't know where the car is, but chooses door 2 at random and there is no car. What is the probability that the car is behind door 1?

(b) Is the probability that you found in part (a) the same as found in Example 3.16? Why or why not? Discuss why the probability that the car is behind door 1 depends on what the host knows.

Example 3.17. Bayes theorem and the problem of false positives

Even though you have no symptoms, your doctor wishes to test you for a rare disease that only 1 in 10,000 people of your age contract. The test is 98% accurate, which means that if you have the

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[5]This question was posed on the TV game show, "Let's Make A Deal," hosted by Monty Hall.

[6]A search for Monty Hall will bring many sites, including <en.wikipedia.org/wiki/Monty_Hall_problem>, that discuss the problem in detail.

disease, 98% of the times the test will come out positive, and 2% negative. We also assume that if you do not have the disease, the test will come out negative 98% of the time and positive 2% of the time. You take the test and it comes out positive. What is the probability that you have the disease?

Solution. Let $P(p|D) = 0.98$ represent the probability of testing positive and having the disease, $-D$ represent the probability of not having the disease, and n represent testing negative. Then we are given that $P(n|D) = 0.02$, $P(n|-D) = 0.98$, $P(p|-D) = 0.02$, $P(D) = 0.0001$, and $P(-D) = 0.9999$. From Bayes' theorem we have

$$P(D|p) = \frac{P(p|D)P(D)}{P(p|D)P(D) + P(p|-D)P(-D)} \tag{3.65a}$$

$$= \frac{(0.98)(0.0001)}{(0.98)(0.0001) + (0.02)(0.9999)} \tag{3.65b}$$

$$= 0.0047 = 0.47\%. \tag{3.65c}$$

Is this test useful?

Because of the problem of false positives, some tests might actually reduce your life span and thus are not recommended. Suppose that a certain type of cancer occurs in 1 in 1000 people who are less than 50 years old. The death rate from this cancer is 25% in 10 years. The probability of having cancer if the test is positive is 1 in 20. Because people who test positive become worried, 90% of the patients who test positive have surgery to remove the cancer. As a result of surgery, 2% die due to complications, and the rest are cured.

We have that

$$P(\text{death rate due to cancer}) = P(\text{death}|\text{cancer})P(\text{cancer}) \tag{3.66a}$$

$$= 0.25 \times 0.001 = 0.00025 \tag{3.66b}$$

$$P(\text{death due to test}) = P(\text{die}|\text{surgery})P(\text{surgery}|\text{positive})P(\text{test}|\text{posiive}) \tag{3.66c}$$

$$= 0.02 \times 0.90 \times 0.02 = 0.00036. \tag{3.66d}$$

Hence, the probability of dring from surgery is greater than dying from the cancer.

Problem 3.24. Imagine that you have a sack of 3 balls that can be either red or green. There are four hypotheses for the distribution of colors for the balls: (1) all are red, (2) 2 are red, (3) 1 is red, and (4) all are green. Initially, you have no information about which hypothesis is correct, and thus you assume that they are equally probable. Suppose that you pick one ball out of the sack and it is green. Use Bayes' theorem to determine the new probabilities for each hypothesis.

Problem 3.25. Make a table that determines the accuracy necessary for a test to give the probability of having a disease if tested positive equal to at least 50% for diseases that occur in 1 in 100, 1 in 1000, 1 in 10,000, and 1 in 100,000 people.

We have emphasized that the definition of probability as a frequency is inadequate. If you are interesting in learning more about Bayesian inference, see in particular the paper by D'Agostini.

3.5   Bernoulli Processes and the Binomial Distribution

Because most physicists spend little time gambling,[7] we will have to develop our intuitive under-standing of probability in other ways. Our strategy will be to first consider some physical systems for which we can calculate the probability distribution by analytical methods. Then we will use the computer to generate more data to analyze.

Noninteracting magnetic moments

Consider a system of N noninteracting magnetic moments of spin $\frac{1}{2}$, each having a magnetic moment μ in an external magnetic field B. The field B is in the up $(+z)$ direction. Spin $\frac{1}{2}$ implies that a spin can point either up (parallel to B) or down (antiparallel to B). The energy of interaction of each spin with the magnetic field is $E = \mp\mu B$, according to the orientation of the magnetic moment. As discussed in Section 1.10, this model is a simplification of more realistic magnetic systems.

We will take p to be the probability that the spin (magnetic moment) is up and q the probability that the spin is down. Because there are no other possible outcomes,we have $p+q = 1$ or $q = 1-p$. If $B = 0$, there is no preferred spatial direction and $p = q = 1/2$. For $B \neq 0$ we do not yet know how to calculate p and for now we will assume that p is a known parameter. In Section 4.8 we will learn how to calculate p and q when the system is in equilibrium at temperature T.

We associate with each spin a random variable s_i which has the values ± 1 with probability p and q, respectively. One of the quantities of interest is the magnetization M, which is the net magnetic moment of the system. For a system of N spins the magnetization is given by

$$M = \mu(s_1 + s_2 + \ldots + s_N) = \mu\sum_{i=1}^{N} s_i. \tag{3.67}$$

In the following, we will take $\mu = 1$ for convenience whenever it will not cause confusion. Alternatively, we can interpret M as the net number of up spins.

We will first calculate the mean value of M, then its variance, and finally the probability distribution $P(M)$ that the system has magnetization M. To compute the mean value of M, we need to take the mean values of both sides of (3.67). If we use (3.16c), we can interchange the sum and the average and write

$$\overline{M} = \overline{\Big(\sum_{i=1}^{N} s_i\Big)} = \sum_{i=1}^{N} \overline{s}_i. \tag{3.68}$$

Because the probability that any spin has the value ± 1 is the same for each spin, the mean value of each spin is the same, that is, $\overline{s}_1 = \overline{s}_2 = \ldots = \overline{s}_N \equiv \overline{s}$. Therefore the sum in (3.68) consists of N equal terms and can be written as

$$\overline{M} = N\overline{s}. \tag{3.69}$$

The meaning of (3.69) is that the mean magnetization is N times the mean magnetization of a single spin. Because $\overline{s} = (1 \times p) + (-1 \times q) = p - q$, we have that

$$\overline{M} = N(p - q). \tag{3.70}$$

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[7]After a Las Vegas hotel hosted a meeting of the American Physical Society in March, 1986, the physicists were asked never to return.

Now let us calculate the variance of M, that is, $\overline{(M - \overline{M})^2}$. We write

$$\Delta M = M - \overline{M} = \sum_{i=1}^{N} \Delta s_i, \tag{3.71}$$

where

$$\Delta s_i \equiv s_i - \overline{s}. \tag{3.72}$$

As an example, let us calculate $\overline{(\Delta M)^2}$ for $N = 3$ spins. In this case $(\Delta M)^2$ is given by

$$(\Delta M)^2 = (\Delta s_1 + \Delta s_2 + \Delta s_3)(\Delta s_1 + \Delta s_2 + \Delta s_3) \tag{3.73a}$$

$$= \left[(\Delta s_1)^2 + (\Delta s_2)^2 + (\Delta s_3)^2\right] + 2\left[\Delta s_1 \Delta s_2 + \Delta s_1 \Delta s_3 + \Delta s_2 \Delta s_3\right]. \tag{3.73b}$$

We take the mean value of (3.73b), interchange the order of the sums and averages, and write

$$\overline{(\Delta M)^2} = \left[\overline{(\Delta s_1)^2} + \overline{(\Delta s_2)^2} + \overline{(\Delta s_3)^2}\right] + 2\left[\overline{\Delta s_1 \Delta s_2} + \overline{\Delta s_1 \Delta s_3} + \overline{\Delta s_2 \Delta s_3}\right]. \tag{3.74}$$

The first term on the right of (3.74) represents the three terms in the sum that are multiplied by themselves. The second term represents all the cross terms arising from different terms in the sum, that is, the products in the second sum refer to different spins. Because different spins are statistically independent (the spins do not interact), we have that

$$\overline{\Delta s_i \, \Delta s_j} = \overline{\Delta s_i} \, \overline{\Delta s_j} = 0, \qquad (i \neq j) \tag{3.75}$$

because $\overline{\Delta s_i} = 0$. That is, each cross term vanishes on the average. Hence (3.75) reduces to a sum of squared terms

$$\overline{(\Delta M)^2} = \left[\overline{(\Delta s_1)^2} + \overline{(\Delta s_2)^2} + \overline{(\Delta s_3)^2}\right]. \tag{3.76}$$

Because each spin is equivalent on the average, each term in (3.76) is equal. Hence, we obtain the desired result

$$\overline{(\Delta M)^2} = 3\overline{(\Delta s)^2}. \tag{3.77}$$

The variance of M is 3 times the variance of a single spin, that is, the variance is additive.

We can evaluate $\overline{(\Delta M)^2}$ further by finding an explicit expression for $\overline{(\Delta s)^2}$. We have that $\overline{s^2} = [1^2 \times p] + [(-1)^2 \times q] = p + q = 1$. Hence, we have

$$\overline{(\Delta s)^2} = \overline{s^2} - \overline{s}^2 = 1 - (p - q)^2 = 1 - (2p - 1)^2 \tag{3.78a}$$

$$= 1 - 4p^2 + 4p - 1 = 4p(1 - p) = 4pq, \tag{3.78b}$$

and our desired result for $\overline{(\Delta M)^2}$ is

$$\overline{(\Delta M)^2} = 3(4pq). \tag{3.79}$$

Problem 3.26. Use similar considerations to show that for $N = 3$ that

$$\overline{n} = 3p \tag{3.80}$$

and

$$\overline{(n - \overline{n})^2} = 3pq, \tag{3.81}$$

where n is the number of up spins. Explain the difference between (3.70) and (3.80) for $N = 3$, and the difference between (3.79) and (3.81).
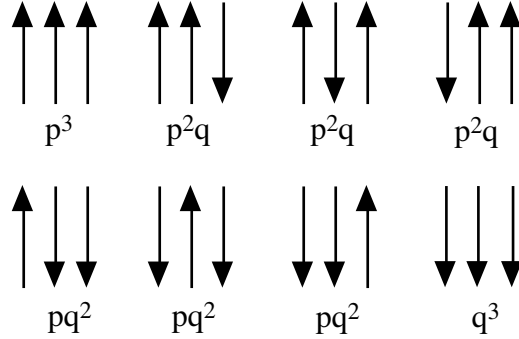
Figure 3.2: An ensemble of $N = 3$ spins. The arrow indicates the direction of the magnetic moment of a spin. The probability of each member of the ensemble is shown.

Problem 3.27. In the text we showed that $\overline{(\Delta M)^2} = 3\overline{(\Delta s)^2}$ for $N = 3$ spins (see (3.77) and (3.79)). Use similar considerations for N noninteracting spins to show that

$$\overline{(\Delta M)^2} = N(4pq). \tag{3.82}$$

Because of the simplicity of a system of noninteracting spins, we can calculate the probability distribution itself and not just the first few moments. As an example, let us consider the statistical properties of a system of $N = 3$ noninteracting spins. Because each spin can be in one of two states, there are $2^{N=3} = 8$ distinct outcomes (see Figure 3.2). Because each spin is independent of the other spins, we can use the multiplication rule (3.5) to calculate the probabilities of each outcome as shown in Figure 3.2. Although each outcome is distinct, several of the configurations have the same number of up spins. One quantity of interest is the probability $P_N(n)$ that n spins are up out a total of N spins. For example, there are three states with $n = 2$, each with probability $p^2 q$ so the probability that two spins are up is equal to $3p^2 q$. For $N = 3$ we see from Figure 3.2 that

$$P_3(n = 3) = p^3 \tag{3.83a}$$

$$P_3(n = 2) = 3p^2 q \tag{3.83b}$$

$$P_3(n = 1) = 3pq^2 \tag{3.83c}$$

$$P_3(n = 0) = q^3. \tag{3.83d}$$

Example 3.18. Find the first two moments of $P_3(n)$.

Solution. The first moment $\overline{n}$ of the distribution is given by

$$\overline{n} = 0 \times q^3 + 1 \times 3pq^2 + 2 \times 3p^2 q + 3 \times p^3 \tag{3.84a}$$

$$= 3p\,(q^2 + 2pq + p^2) = 3p\,(q + p)^2 = 3p. \tag{3.84b}$$

Similarly, the second moment $\overline{n^2}$ of the distribution is given by

$$\overline{n^2} = 0 \times q^3 + 1 \times 3pq^2 + 4 \times 3p^2q + 9 \times p^3 \tag{3.84c}$$

$$= 3p\left(q^2 + 4pq + 3p^2\right) = 3p(q + 3p)(q + p) \tag{3.84d}$$

$$= 3p\left(q + 3p\right) = (3p)^2 + 3pq. \tag{3.84e}$$

Hence

$$\overline{(n - \overline{n})^2} = \overline{n^2} - \overline{n}^2 = 3pq. \tag{3.84f}$$

The mean magnetization M or the mean of the net number of up spins is given by the difference between the mean number of spins pointing up minus the mean number of spins pointing down: $\overline{M} = [\overline{n} - (3 - \overline{n}]$, or $\overline{M} = 3(2p - 1) = 3(p - q)$.

Problem 3.28. Coins and random walks

The outcome of N coins is identical to N noninteracting spins, if we associate the number of coins with N, the number of heads with n, and the number of tails with $N - n$. For a fair coin the probability p of a head is $p = \frac{1}{2}$ and the probability of a tail is $q = 1 - p = \frac{1}{2}$. What is the probability that in three tosses of a coin, there will be two heads?

Problem 3.29. One-dimensional random walk

The original statement of the *random walk* problem was posed by Pearson in 1905. If a drunkard begins at a lamp post and takes N steps of equal length in random directions, how far will the drunkard be from the lamp post? We will consider an idealized example of a random walk for which the steps of the walker are restricted to a line (a one-dimensional random walk). Each step is of equal length a, and at each interval of time, the walker either takes a step to the right with probability p or a step to the left with probability $q = 1 - p$. The direction of each step is independent of the preceding one. Let n be the number of steps to the right, and n' the number of steps to the left. The total number of steps $N = n + n'$. What is the probability that a random walker in one dimension has taken three steps to the right out of four steps?

From the above examples and problems, we see that the probability distributions of noninteracting magnetic moments, the flip of a coin, and a random walk are identical. These examples have two characteristics in common. First, in each trial there are only *two* outcomes, for example, up or down, heads or tails, and right or left. Second, the result of each trial is independent of all previous trials, for example, the drunken sailor has no memory of his or her previous steps. This type of process is called a *Bernoulli* process (after the mathematician Jacob Bernoulli, 1654–1705).

Because of the importance of magnetic systems, we will cast our discussion of Bernoulli processes in terms of the noninteracting magnetic moments of spin $\frac{1}{2}$. The main quantity of interest is the probability $P_N(n)$ which we now calculate for arbitrary N and n. We know that a particular outcome with n up spins and n' down spins occurs with probability $p^n q^{n'}$. We write the probability $P_N(n)$ as

$$P_N(n) = W_N(n, n')s\, p^n q^{n'}, \tag{3.85}$$

where $n' = N - n$ and $W_N(n, n')$ is the number of distinct configurations of N spins with n up spins and n' down spins. From our discussion of $N = 3$ noninteracting spins, we already know the first several values of $W_N(n, n')$.

We can determine the general form of $W_N(n, n')$ by obtaining a recursion relation between W_N and W_{N-1}. A total of n up spins and n' down spins out of N total spins can be found by adding one spin to $N - 1$ spins. The additional spin is either
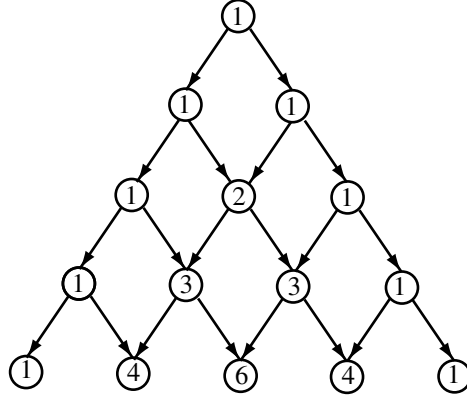
Figure 3.3: The values of the first few coefficients $W_N(n, n')$. Each number is the sum of the two numbers to the left and right above it. This construction is called a Pascal triangle.

(a) up if there are $(n-1)$ up spins and n' down spins, or

(b) down if there are n up spins and n' down spins.

Because there are $W_N(n-1, n')$ ways of reaching the first case and $W_N(n, n'-1)$ ways in the second case, we obtain the recursion relation

$$W_N(n, n') = W_{N-1}(n-1, n') + W_{N-1}(n, n'-1). \tag{3.86}$$

If we begin with the known values $W_0(0, 0) = 1$, $W_1(1, 0) = W_1(0, 1) = 1$, we can use the recursion relation (3.86) to construct $W_N(n, n')$ for any desired N. For example,

$$W_2(2, 0) = W_1(1, 0) + W_1(2, -1) = 1 + 0 = 1. \tag{3.87a}$$
$$W_2(1, 1) = W_1(0, 1) + W_1(1, 0) = 1 + 1 = 2. \tag{3.87b}$$
$$W_2(0, 2) = W_1(-1, 2) + W_1(0, 1) = 0 + 1. \tag{3.87c}$$

In Figure 3.3 we show that $W_N(n, n')$ forms a pyramid or (a Pascal) triangle.

It is straightforward to show by induction that the expression

$$W_N(n, n') = \frac{N!}{n!\, n'!} = \frac{N!}{n!(N-n)!} \tag{3.88}$$

satisfies the relation (3.86). Note the convention $0! = 1$. We can combine (3.85) and (3.88) to find the desired result

$$\boxed{P_N(n) = \frac{N!}{n!\,(N-n)!}\, p^n q^{N-n}.} \qquad \text{(binomial distribution)} \tag{3.89}$$

The form (3.89) is called the *binomial distribution*. Note that for $p = q = 1/2$, $P_N(n)$ reduces to

$$P_N(n) = \frac{N!}{n!\,(N-n)!} 2^{-N}. \tag{3.90}$$
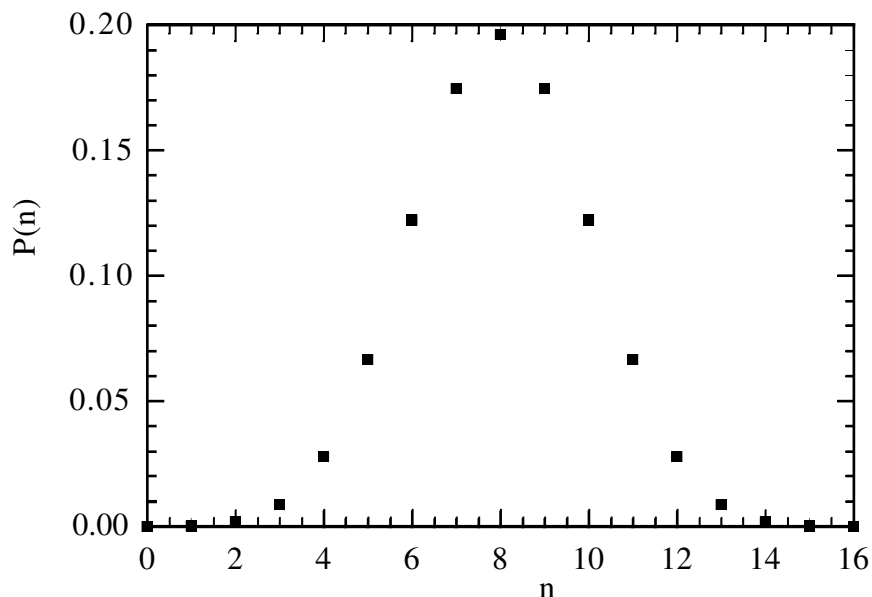
Figure 3.4: The binomial distribution $P_{16}(n)$ for $p = q = 1/2$ and $N = 16$. What is your visual estimate for the width of the distribution?

The probability $P_N(n)$ is shown in Figure 3.4 for $N = 16$.

Problem 3.30. Binomial distribution

(a) Calculate the distribution $P_N(n)$ that n spins are up out of a total of N for $N = 4$ and $N = 16$ and put your results in the form of a table. Calculate the mean values of n and n^2 using your tabulated values of $P_N(n)$. It is possible to do the calculation for general p and q, but choose $p = q = 1/2$ if necessary. Although it is better to first do the calculation of $P_N(n)$ by hand, you can use the applet/application at `<stp.clarku.edu/simulations/binomial>`.

(b) Plot your tabulated results for $P_N(n)$ (see Figure 3.4) or use the applet mentioned in part (a). Assume that $p = q = 1/2$. Visually estimate the width of the distribution for each value of N. Then use the applet/application for larger values of N. What is the qualitative dependence of the width on N? Also compare the relative heights of the maximum of P_N.

(c) Plot $P_N(n)$ as a function of $n/\overline{n}$ for $N = 4$ and $N = 16$ on the same graph as in part (b). Visually estimate the relative width of the distribution for each value of N.

(d) The applet/application plots $P_N(n)$ for various values of N in the same size window. Does the width of the distribution appear to become larger or smaller as N is increased?

(e) Plot $\ln P_N(n)$ versus $n/\overline{n}$ for $N = 16$. (Choose Log Axes under the Views menu.) Describe the behavior of $\ln P_N(n)$. Can $\ln P_N(n)$ be fitted to a parabola of the form $A + B(n - \overline{n})^2$, where A and B are fit parameters?

Problem 3.31. Asymmetrical distribution

(a) Plot $P_N(n)$ versus n for $N = 16$ and $p = 2/3$. For what value of n is $P_N(n)$ a maximum? How does the width of the distribution compare to what you found in Problem 3.30?

(b) For what value of p and q do you think the width is a maximum for a given N?

Example 3.19. Show that the expression (3.89) for $P_N(n)$ satisfies the normalization condition (3.2).

Solution. The reason that (3.89) is called the binomial distribution is that its form represents a typical term in the expansion of $(p + q)^N$. By the binomial theorem we have

$$(p + q)^N = \sum_{n=0}^{N} \frac{N!}{n! \, (N - n)!} \, p^n \, q^{N-n}. \tag{3.91}$$

We use (3.89) and write

$$\sum_{n=0}^{N} P_N(n) = \sum_{n=0}^{N} \frac{N!}{n! \, (N - n)!} \, p^n q^{N-n} = (p + q)^N = 1^N = 1, \tag{3.92}$$

where we have used (3.91) and the fact that $p + q = 1$.

Problem 3.32. Monte Carlo simulation of a one-dimensional random walk

The applet/application at `<stp.clarku.edu/simulations/randomwalks/fixedlength1d.html>` simulates a random walk in one dimension. As described in the text, a walker starts at the origin and takes N steps. At each step the walker goes to the right with probability p or to the left with probability $(1 - p)$. Each step is the same length and independent of the previous steps. What is the displacement of the walker after N steps? Are some displacements more likely than others?

We can simulate a N-step walk by the following pseudocode:

```
do istep = 1,N
  if (rnd <= p) then
    x = x + 1
  else
    x = x - 1
  end if
end do
```

The function `rnd` generates a random number between zero and one. The quantity x is the net displacement assuming that the steps are of unit length.

We average over many walkers (trials), where each trial consists of a N step walk and construct a histogram for the number of times that the displacement x is found for a given number of walkers. The probability that the walker is a distance x from the origin after N steps is proportional to the corresponding value of the histogram. This procedure is called *Monte Carlo* sampling.[8]

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[8]The name "Monte Carlo" was coined by Nicolas Metropolis in 1949.

(a) Is the value of x for one trial of any interest? Why do we have to average over many trials?

(b) Will we obtain the exact answer for the probability distribution?

(c) Choose $N = 4$ and $p = 1/2$. How does the histogram change, if at all, as the number of walk increases for fixed N?

(d) Describe the qualitative changes of the histogram for larger values of N and $p = 1/2$.

(e) What is the most probable value of x for $p = 1/2$ and $N = 16$ and $N = 32$? What is the approximate width of the distribution? Define the width visually. One way to do so is to determine the value of x at which the value of the histogram is one-half of its maximum value. How does the width change as a function of N for fixed p?

Calculation of the mean value

We now find an analytical expression for the dependence of $\bar{n}$ on N and p. From the definition (3.13) and (3.89) we have

$$\bar{n} = \sum_{n=0}^{N} n \, P_N(n) = \sum_{n=0}^{N} n \, \frac{N!}{n! \, (N-n)!} \, p^n q^{N-n}. \tag{3.93}$$

We evaluate the sum in (3.93) by using a technique that is useful in a variety of contexts.[9] The technique is based on the fact that

$$p \, \frac{d}{dp} p^n = n p^n. \tag{3.94}$$

We use (3.94) to rewrite (3.93) as

$$\bar{n} = \sum_{n=0}^{N} n \frac{N!}{n! \, (N-n)!} \, p^n q^{N-n} \tag{3.95a}$$

$$= \sum_{n=0}^{N} \frac{N!}{n! \, (N-n)!} \left(p \frac{\partial}{\partial p} p^n \right) q^{N-n}. \tag{3.95b}$$

We have used a partial derivative in (3.95b) to remind us that the derivative operator does not act on q. We interchange the order of summation and differentiation in (3.95b) and write

$$\bar{n} = p \frac{\partial}{\partial p} \left[\sum_{n=0}^{N} \frac{N!}{n! \, (N-n)!} \, p^n q^{N-n} \right] \tag{3.96a}$$

$$= p \frac{\partial}{\partial p} (p+q)^N, \tag{3.96b}$$

where we have temporarily assumed that p and q are independent variables. Because the operator acts only on p, we have

$$\bar{n} = pN(p+q)^{N-1}. \tag{3.97}$$

---

[9]The integral $\int_0^\infty x^n \, e^{-ax^2}$ for $a > 0$ is evaluated in Appendix A using a similar technique.

The result (3.97) is valid for arbitrary p and q, and hence it is applicable for $p + q = 1$. Thus our desired result is

$$\overline{n} = pN. \tag{3.98}$$

The dependence of $\overline{n}$ on N and p should be intuitively clear. Compare the general result (3.98) to the result (3.84b) for $N = 3$. What is the dependence of $\overline{n'}$ on N and p?

Calculation of the relative fluctuations

To determine $\overline{\Delta n^2}$ we need to know $\overline{n^2}$ (see the relation (3.23)). The average value of n^2 can be calculated in a manner similar to that for $\overline{n}$. We write

$$\overline{n^2} = \sum_{n=0}^{N} n^2 \frac{N!}{n!\,(N-n)!}\, p^n q^{N-n} \tag{3.99a}$$

$$= \sum_{n=0}^{N} \frac{N!}{n!\,(N-n)!} \left(p \frac{\partial}{\partial p}\right)^2 p^n q^{N-n} \tag{3.99b}$$

$$= \left(p \frac{\partial}{\partial p}\right)^2 \sum_{n=0}^{N} \frac{N!}{n!\,(N-n)!}\, p^n q^{N-n} = \left(p \frac{\partial}{\partial p}\right)^2 (p + q)^N \tag{3.99c}$$

$$= \left(p \frac{\partial}{\partial p}\right) \left[pN(p+q)^{N-1}\right] \tag{3.99d}$$

$$= p\left[N(p+q)^{N-1} + pN(N-1)(p+q)^{N-2}\right]. \tag{3.99e}$$

Because we are interested in the case $p + q = 1$, we have

$$\overline{n^2} = p\left[N + pN(N-1)\right] \tag{3.100a}$$

$$= p\left[pN^2 + N(1-p)\right] = (pN)^2 + p\,(1-p)N \tag{3.100b}$$

$$= \overline{n}^2 + pqN, \tag{3.100c}$$

where we have used (3.98) and let $q = 1 - p$. Hence, from (3.100c) we find that the variance of n is given by

$$\sigma_n{}^2 = \overline{(\Delta n)^2} = \overline{n^2} - \overline{n}^2 = pqN. \tag{3.101}$$

Problem 3.33. Compare the calculated values of σ_n from (3.101) with your estimates in Problem 3.30 and to the exact result (3.84f) for $N = 3$.

The relative width of the probability distribution of n is given by (3.98) and (3.101)

$$\frac{\sigma_n}{\overline{n}} = \frac{\sqrt{pqN}}{pN} = \left(\frac{q}{p}\right)^{1/2} \frac{1}{\sqrt{N}}. \tag{3.102}$$

We see that the relative width goes to zero as $1/\sqrt{N}$.

Frequently we need to evaluate $\ln N!$ for $N \gg 1$. A simple approximation for $\ln N!$ known as *Stirling's approximation* is

$$\ln N! \approx N \ln N - N. \qquad \text{(Stirling's approximation)} \tag{3.103}$$

A more accurate approximation is given by

$$\ln N! \approx N \ln N - N + \frac{1}{2} \ln(2\pi N). \tag{3.104}$$

A simple derivation of Stirling's approximation is given in Appendix A.

Problem 3.34. Applicability of Stirling's approximation

(a) What is the largest value of $\ln N!$ that you can calculate exactly using a typical hand calculator?

(b) Compare the approximations (3.103) and (3.104) to each other and to the exact value of $\ln N!$ for $N = 5$, 10, 20, and 50. If necessary, compute $\ln N!$ directly using the relation

$$\ln N! = \sum_{m=1}^{N} \ln m. \tag{3.105}$$

(c) Use the simple form of Stirling's approximation to show that

$$\frac{d}{dx} \ln x! = \ln x \text{ for } x \gg 1. \tag{3.106}$$

Problem 3.35. Consider the binomial distribution $P_N(n)$ for $N = 16$ and $p = q = 1/2$. What is the value of $P_N(n)$ for $n = \sigma_n/2$? What is the value of the product $P_N(n = \overline{n})\sigma_n$?

Problem 3.36. Density fluctuations
A container of volume V contains N molecules of a gas. We assume that the gas is dilute so that the position of any one molecule is independent of all other molecules. Although the density will be uniform on the average, there are fluctuations in the density. Divide the volume V into two parts V_1 and V_2, where $V = V_1 + V_2$.

(a) What is the probability p that a particular molecule is in each part?

(b) What is the probability that N_1 molecules are in V_1 and N_2 molecules are in V_2?

(c) What is the average number of molecules in each part?

(d) What are the relative fluctuations of the number of particles in each part?

Problem 3.37. Random walk
Suppose that a random walker takes n steps to the right and n' steps to the left. Each step is of equal length a and the probability of a step to the right is p. Denote x as the net displacement of a walker. What is the mean value $\overline{x}$ for a N-step random walk? What is the analogous expression for the variance $\overline{(\Delta x)^2}$?
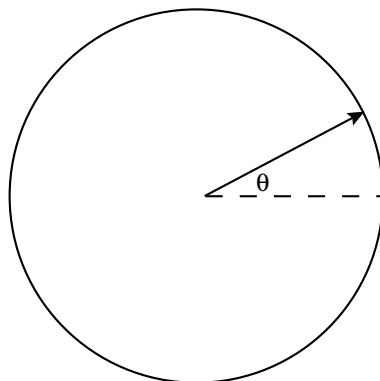
Figure 3.5: The angle θ is an example of a continuous random variable.

3.6   Continuous Probability Distributions

In many cases of physical interest the random variables have continuous values. Examples of continuous variables are the position of the holes in a dart board, the position and velocity of a classical particle, and the angle of a compass needle.

As an example, consider a spinner, the equivalent of a wheel of fortune,[10] with an arrow that spins around and stops at some angle at random (see Figure 3.5). In this case the variable θ is a continuous random variable that takes all values in the interval $[0, 2\pi]$. What is the probability that θ has a particular value? Because there are an infinite number of possible values of θ in the interval $[0, 2\pi]$, the probability of obtaining any particular value of θ is zero. We say that the values of θ are not countable. Instead, we have to reformulate the question and ask for the probability that the value of θ is between θ and $\theta + \Delta theta$. In other words, we have to ask for the probability that θ is in a particular bin of width $d\theta$. For example, the probability that θ is between 0 and π is $1/2$ and the probability that θ is between 0 and $\pi/2$ is $1/4$.

Another example of a continuous random variable is the displacement from the origin of a one-dimensional random walker that steps at random to the right with probability p, but with a step length that is chosen at random between zero and the maximum step length a. The continuous nature of the step length means that the displacement x of the walker is a continuous variable. If we do a simulation of this random walk, we can record the number of times $H(x)$ that the displacement of the walker from the origin after N steps is in a bin of width Δx between x and $x + \Delta x$. A plot of $H(x)$ as a function of x for a given bin width Δx is shown in Figure 3.6). If the number of walkers that is sampled is sufficiently large, we would find that $H(x)$ is proportional to the estimated probability that a walker is in a bin of width Δx a distance x from the origin after N steps. To obtain the probability, we divide $H(x)$ by the total number of walkers.

In practice, the choice of the bin width is a compromise. If Δx is too big, the features of the histogram would be lost. If Δx is too small, many of the bins would be empty for a given number of walkers, and our estimate of the number of walkers in each bin would be less accurate.

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[10]The Wheel of Fortune is an American television game show that involves three contestants. The name of the show comes from the large spinning wheel that determines the dollar amounts and prizes won by the contestants.
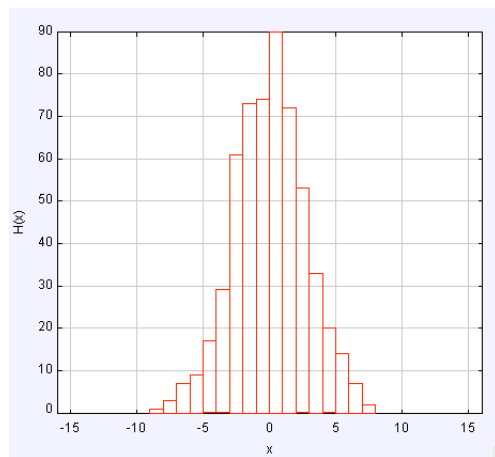
Figure 3.6: Histogram of the number of times that the displacement of a one-dimensional random walker is between x and $x + \Delta x$ after $N = 16$ steps. The data was generated by simulating 565 walkers, a relatively small number in this case. The length of each step was chosen at random between zero and unity and the bin width is $\Delta x = 1$.
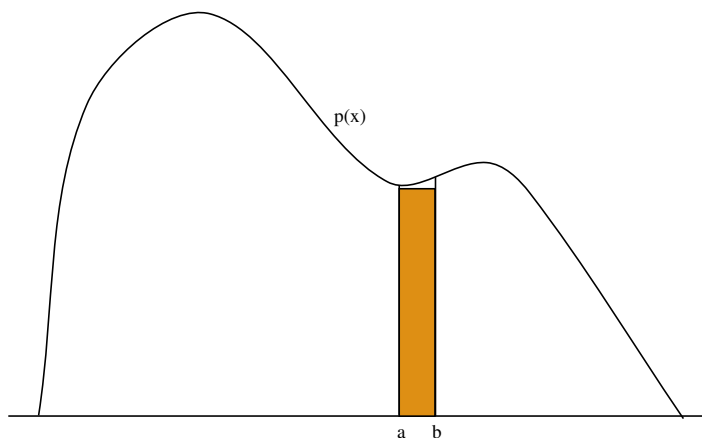
Figure 3.7: The probability that x is between a and b is equal to the shaded area.

Because we expect the number of walkers in a particular bin to be proportional to the width of the bin, we can write $H(x) = p(x)\Delta x$. The quantity $p(x)$ is called the *probability density*. In the limit that $\Delta x \to 0$, $H(x)$ becomes a continuous function of x, and we can write the probability that the displacement of the walker is between a and b as (see Figure 3.7).

$$P(a \text{ to } b) = \int_a^b p(x)\, dx. \tag{3.107}$$

Note that the probability density $p(x)$ is nonnegative and has units of one over the dimension of x.

The formal properties of the probability density $p(x)$ can be generalized from the discrete case. For example, the normalization condition is given by

$$\int_{-\infty}^{\infty} p(x)\, dx = 1. \tag{3.108}$$

The mean value of the function $f(x)$ in the interval a to b is given by

$$\overline{f} = \int_{a}^{b} f(x)\, p(x)\, dx. \tag{3.109}$$

Problem 3.38. Simulation of a one-dimensional random walk with variable step length

The applet/application at `<stp.clarku.edu/simulations/randomwalks/continuous1d.html>` simulates a random walk in one dimension with a variable jump length.

(a) The simulation uses a step length with a uniform probability between 0 and 1. Calculate the mean step length and its variance.

(b) How does the variance found in the simulation depend on the variance of the step length that you calculated in part (a)?

(c) Does the qualitative features of the histogram change as the number of walkers increases?

(d) Explore how the histogram changes with the bin width. What is a reasonable choice of the bin width for $N = 100$?

Problem 3.39. Exponential probability density

The random variable x has the probability density

$$p(x) = \begin{cases} A\, e^{-\lambda x} & \text{if } 0 \leq x \leq \infty \\ 0 & x < 0. \end{cases} \tag{3.110}$$

(a) Determine the normalization constant A in terms of λ.

(b) What is the mean value of x? What is the most probable value of x?

(c) What is the mean value of x^2?

(d) Choose $\lambda = 1$ and determine the probability that a measurement of x yields a value between 1 and 2.

(e) Choose $\lambda = 1$ and determine the probability that a measurement of x yields a value less than 0.3.

Problem 3.40. Probability density for velocity

Consider the probability density function $p(\mathbf{v}) = (a/\pi)^{3/2}\, e^{-av^2}$ for the velocity $\mathbf{v}$ of a particle, where $\mathbf{v} = |\mathbf{v}|$ and $v^2 = v_x^2 + v_y^2 + v_z^2$. Each of the three velocity components can range from $-\infty$ to $+\infty$ and a is a constant.

(a) What is the probability that a particle has a velocity between v_x and $v_x + dv_x$, v_y and $v_y + dv_y$, and v_z and $v_z + dv_z$?

(b) Show that $p(\mathbf{v})$ is normalized to unity. Use the fact that

$$\int_0^\infty e^{-au^2}\,du = \frac{1}{2}\sqrt{\frac{\pi}{a}}. \tag{3.111}$$

Note that this calculation involves doing three similar integrals that can be evaluated separately.

(c) What is the probability that $v_x \geq 0$, $v_y \geq 0$, $v_z \geq 0$ simultaneously?

Problem 3.41. Gaussian probability density

(a) Find the first four moments of the Gaussian probability density

$$p(x) = (2\pi)^{-\frac{1}{2}} e^{-x^2/2}. \qquad (-\infty < x < \infty) \tag{3.112}$$

Guess the dependence of the kth moment on k for k even. What are the odd moments of $p(x)$?

(b) Calculate the value of C_4, the fourth-order cumulant, defined by

$$C_4 = \overline{x^4} - 4\overline{x^3}\,\overline{x} - 3\overline{x^2}^2 + 12\,\overline{x^2}\,\overline{x}^2 - 6\,\overline{x}^4. \tag{3.113}$$

Problem 3.42. Uniform probability distribution

Consider the probability density given by

$$p(x) = \begin{cases} (2a)^{-1} & \text{for } |x| \leq a \\ 0 & \text{for } |x| > a \end{cases} \tag{3.114}$$

(a) Sketch the dependence of $p(x)$ on x.

(b) Find the first four moments of $p(x)$.

(c) Calculate the value of the fourth-order cumulant C_4 defined in (3.113)). What is C_4 for the probability density in (3.114)? Compare your result to the corresponding result for C_4 for the Gaussian distribution.

Problem 3.43. Cauchy probability distribution

Not all probability densities have a finite variance.

(a) Sketch the *Lorentz* or *Cauchy distribution* given by

$$p(x) = \frac{1}{\pi}\frac{\gamma}{(x-a)^2 + \gamma^2}. \qquad (-\infty < x < \infty) \tag{3.115}$$

Choose $a = 0$ and $\gamma = 1$ and compare the form of $p(x)$ in (3.115) to the Gaussian distribution given by (3.112).

(b) Give a simple argument for the existence of the first moment of the Lorentz distribution. Does the second moment exist?

3.7 The Gaussian Distribution as a Limit of the Binomial Distribution

In Problem 3.30 we found that for large N, the binomial distribution has a well-defined maximum at $n = pN$ and can be approximated by a smooth, continuous function even though only integer values of n are physically possible. We now find the form of this function of n.

The first step is to realize that for $N \gg 1$, $P_N(n)$ is a rapidly varying function of n near $n = pN$, and for this reason we do not want to approximate $P_N(n)$ directly. Because the logarithm of $P_N(n)$ is a slowly varying function (see Problem 3.30), we expect that the power series expansion of $\ln P_N(n)$ to converge. Hence, we expand $\ln P_N(n)$ in a Taylor series about the value of $n = \tilde{n}$ at which $\ln P_N(n)$ reaches its maximum value. We will write $p(n)$ instead of $P_N(n)$ because we will treat n as a continuous variable and hence $p(n)$ is a probability density. We find

$$\ln p(n) = \ln p(n = \tilde{n}) + (n - \tilde{n})\frac{d\ln p(n)}{dn}\Big|_{n=\tilde{n}} + \frac{1}{2}(n - \tilde{n})^2\frac{d^2\ln p(n)}{d^2n}\Big|_{n=\tilde{n}} + \cdots \qquad (3.116)$$

Because we have assumed that the expansion (3.116) is about the maximum $n = \tilde{n}$, the first derivative $d\ln p(n)/dn\big|_{n=\tilde{n}}$ must be zero. For the same reason the second derivative $d^2\ln p(n)/dn^2\big|_{n=\tilde{n}}$ must be negative. We assume that the higher terms in (3.116) can be neglected and adopt the notation

$$\ln A = \ln p(n = \tilde{n}), \qquad (3.117)$$

and

$$B = -\frac{d^2\ln p(n)}{dn^2}\Big|_{n=\tilde{n}}. \qquad (3.118)$$

The approximation (3.116) and the notation in (3.117) and (3.118) allows us to write

$$\ln p(n) \approx \ln A - \frac{1}{2}B(n - \tilde{n})^2, \qquad (3.119)$$

or

$$p(n) \approx A\, e^{-\frac{1}{2}B(n-\tilde{n})^2}. \qquad (3.120)$$

We next use Stirling's approximation to evaluate the first two derivatives of $\ln p(n)$ and the value of $\ln p(n)$ at its maximum to find the parameters A, B, and $\tilde{n}$. We write

$$\ln p(n) = \ln N! - \ln n! - \ln(N - n)! + n\ln p + (N - n)\ln q. \qquad (3.121)$$

It is straightforward to use the relation (3.106) to obtain

$$\frac{d(\ln p(n))}{dn} = -\ln n + \ln(N - n) + \ln p - \ln q. \qquad (3.122)$$

The most probable value of n is found by finding the value of n that satisfies the condition $d\ln p/dn = 0$. We find

$$\frac{N - \tilde{n}}{\tilde{n}} = \frac{q}{p}, \qquad (3.123)$$

or $(N - \tilde{n})p = \tilde{n}q$. If we use the relation $p + q = 1$, we obtain

$$\tilde{n} = pN. \tag{3.124}$$

Note that $\tilde{n} = \overline{n}$, that is, the value of n for which $p(n)$ is a maximum is also the mean value of n.

The second derivative can be found from (3.122). We have

$$\frac{d^2(\ln p(n))}{dn^2} = -\frac{1}{n} - \frac{1}{N - n}. \tag{3.125}$$

Hence, the coefficient B defined in (3.118) is given by

$$B = -\frac{d^2 \ln p(n)}{dn^2}\Big|_{n=\tilde{n}} = \frac{1}{\tilde{n}} + \frac{1}{N - \tilde{n}} = \frac{1}{Npq}. \tag{3.126}$$

From the relation (3.101) we see that

$$B = \frac{1}{\sigma^2}, \tag{3.127}$$

where σ^2 is the variance of n.

If we use the simple form of Stirling's approximation (3.103) to find the normalization constant A from the relation $\ln A = \ln p(n = \tilde{n})$, we would find that $\ln A = 0$. Instead, we have to use the more accurate form of Stirling's approximation (3.104). The result is

$$A = \frac{1}{(2\pi Npq)^{1/2}} = \frac{1}{(2\pi\sigma^2)^{1/2}}. \tag{3.128}$$

Problem 3.44. Derive (3.128) using the more accurate form of Stirling's approximation (3.104) with $n = pN$ and $N - n = qN$.

If we substitute our results for $\tilde{n}$, B, and A into (3.120), we find the standard form for the Gaussian probability distribution

$$\boxed{p(n) = \frac{1}{\sqrt{2\pi\sigma^2}} e^{-(n-\overline{n})^2/2\sigma^2}}. \qquad \text{(Gaussian probability density)} \tag{3.129}$$

An alternative derivation of the parameters A, B, and $\tilde{n}$ is given in Problem 3.75.

From our derivation we see that (3.129) is valid for large values of N and for values of n near $\overline{n}$. Even for relatively small values of N, the Gaussian approximation is a good approximation for most values of n. A comparison of the Gaussian approximation to the binomial distribution is given in Table 3.4.

The most important feature of the Gaussian probability distribution is that its relative width, $\sigma_n/\overline{n}$, decreases as $N^{-1/2}$. Of course, the binomial distribution shares this feature.

n	$P_{10}(n)$	Gaussian approximation
0	0.000977	0.001700
1	0.009766	0.010285
2	0.043945	0.041707
3	0.117188	0.113372
4	0.205078	0.206577
5	0.246094	0.252313

Table 3.4: Comparison of the exact values of $P_{10}(n)$ with the Gaussian probability distribution (3.129) for $p = q = 1/2$.

3.8 The Central Limit Theorem or Why is Thermodynamics Possible?

We have discussed how to estimate probabilities empirically by sampling, that is, by making repeated measurements of the outcome of independent events. Intuitively we believe that if we perform more and more measurements, the calculated average will approach the exact mean of the quantity of interest. This idea is called *the law of large numbers*. However, we can go further and find the form of the probability distribution that a particular measurement differs from the exact mean. The form of this probability distribution is given by the *central limit theorem*. We first illustrate this theorem by considering a simple measurement.

Suppose that we wish to estimate the probability of obtaining face 1 in one throw of a die. The answer of $\frac{1}{6}$ means that if we perform N measurements, face 1 will appear approximately $N/6$ times. What is the meaning of approximately? Let S be the total number of times that face one appears in N measurements. We write

$$S = \sum_{i=1}^{N} s_i, \tag{3.130}$$

where

$$s_i = \begin{cases} 1, & \text{if the } i\text{th throw gives 1} \\ 0 & \text{otherwise.} \end{cases} \tag{3.131}$$

If N is large, then S/N approaches $1/6$. How does this ratio approach the limit? We can empirically answer this question by repeating the measurement M times. (Each measurement of S consists of N throws of a die.) Because S itself is a random variable, we know that the measured values of S will not be identical. In Figure 3.8 we show the results of $M = 10,000$ measurements of S for $N = 100$ and $N = 800$. We see that the approximate form of the distribution of values of S is a Gaussian. In Problem 3.45 we calculate the absolute and relative width of the distributions.

Problem 3.45. Estimate the absolute width and the relative width of the distributions shown in Figure 3.8 for $N = 100$ and $N = 800$. Does the error of any one measurement of S decreases with increasing N as expected? How would the plot change if M were increased to $M = 10,000$?

In Section 3.12.3 we show that in the limit of large N, the probability density $p(S)$ is given
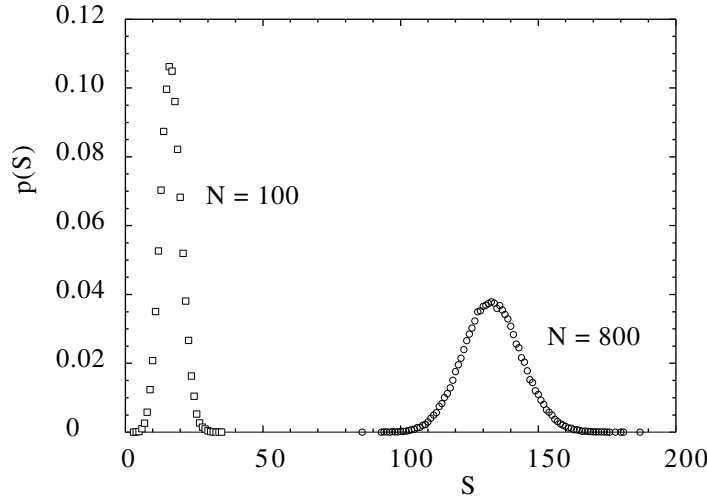
Figure 3.8: The distribution of the measured values of $M = 10,000$ different measurements of the sum S for $N = 100$ and $N = 800$ terms in the sum. The quantity S is the number of times that face 1 appears in N throws of a die. For $N = 100$, the measured values are $\overline{S} = 16.67$, $\overline{S^2} = 291.96$, and $\sigma_S = 3.74$. For $N = 800$, the measured values are $\overline{S} = 133.31$, $\overline{S^2} = 17881.2$, and $\sigma_S = 10.52$. What are the estimated values of the relative width for each case?

by

$$p(S) = \frac{1}{\sqrt{2\pi\sigma_S^2}}e^{-(S-\overline{S})^2/2\sigma_S^2}, \tag{3.132}$$

where

$$\overline{S} = N\overline{s} \tag{3.133}$$

$$\sigma_S^2 = N\sigma^2, \tag{3.134}$$

with $\sigma^2 = \overline{s^2} - \overline{s}^2$. The quantity $p(S)\Delta S$ is the probability that the value of $\sum_{i=1}^{N} s_i$ is between S and $S + \Delta S$. Equation (3.132) is equivalent to the central limit theorem. Note that the Gaussian form in (3.132) holds only for large N and for values of S near its most probable (mean) value. The latter restriction is the reason that the theorem is called the *central* limit theorem; the requirement that N be large is the reason for the term *limit*.

The central limit theorem is one of the most remarkable results of the theory of probability. In its simplest form, the theorem states that the probability o the sum of a large number of random variables approximates a Gaussian distribution. Moreover, the approximation steadily improves as the number of variables in the sum increases.

For the throw of a die, $\overline{s} = \frac{1}{6}$, $\overline{s^2} = \frac{1}{6}$, and $\sigma^2 = \overline{s^2} - \overline{s}^2 = \frac{1}{6} - \frac{1}{36} = \frac{5}{36}$. For N throws of a die, we have $\overline{S} = N/6$ and $\sigma_S^2 = 5N/36$. Hence, we see that in this case the most probable relative error in any one measurement of S decreases as $\sigma_S/\overline{S} = \sqrt{5/N}$.

Note that if we let S represent the displacement of a walker after N steps, and let σ^2 equal the mean square displacement for a single step, then the result (3.132)–(3.134) is equivalent to

our results for random walks in the limit of large N. Or we can let S represent the magnetization of a system of noninteracting spins and obtain similar results. That is, a random walk and its equivalents are examples of an *additive* random process.

The central limit theorem shows why the Gaussian probability density is ubiquitous in nature. If a random process is related to a sum of a large number of microscopic processes, the sum will be distributed according to the Gaussian distribution *independently* of the nature of the distribution of the microscopic processes.

The central limit theorem implies that macroscopic bodies have well defined macroscopic properties even though their constituent parts are changing rapidly. For example in a gas or liquid, the particle positions and velocities are continuously changing at a rate much faster than a typical measurement time. For this reason we expect that during a measurement of the pressure of a gas or a liquid, there are many collisions with the wall and hence the pressure has a well defined average. We also expect that the probability that the measured pressure deviates from its average value is proportional to $N^{-1/2}$, where N is the number of particles. Similarly, the vibrations of the molecules in a solid have a time scale much smaller than that of macroscopic measurements, and hence the pressure of a solid also is a well-defined quantity.

Problem 3.46. Random walks and the central limit theorem Use the central limit theorem to show that the probability that a one-dimensional random walker has a displacement between x and $x + dx$. (There is no need to derive the central limit theorem.)

Problem 3.47. Central limit theorem

Use the applet/application at `<stp.clarku.edu/simulations/centralLimitTheorem.html>` to test the applicability of the central limit theorem.

(a) First assume that the variable s_i is uniformly distributed between 0 and 1. Calculate the mean and standard deviation of s and compare your numerical results with your analytical calculation.

(b) Use the default value of N, the number of terms in the sum, and describe the qualitative form of $p(S)$, where $p(S)\Delta S$ is the probability that the sum S is between S and $S + \Delta S$. Does the qualitative form of $p(S)$ change as the number of measurements (trials) of S is increased for a given value of N?

(c) What is the approximate width of $p(S)$ for $N = 12$? Describe the changes, if any, of the width of $p(S)$ as N is increased. Increase N by at least a factor of 4. Do your results depend strongly on the number of measurements?

(d) To determine the generality of your results, consider the probability density $f(s) = e^{-s}$ for $s \geq 0$ and answer the same questions as in parts (a)–(c).

(e) Consider the Lorentz distribution $f(s) = (1/\pi)(1/(s^2 + 1))$, where $-\infty \leq s \leq \infty$. What is the mean value and variance of s? Is the form of $p(S)$ consistent with the results that you found in parts (b)–(d)?

(f) Each value of S can be considered to be a measurement. The sample variance $\tilde{\sigma}_S^2$ is a measure of the square of the differences of the result of each measurement and is given by

$$\tilde{\sigma}_S^2 = \frac{1}{N-1} \sum_{i=1}^{N} (S_i - \overline{S})^2. \tag{3.135}$$

The reason for the factor of $N-1$ rather than N in the definition of $\tilde{\sigma}_S^2$ is that to compute it, we need to use the N values of s to compute the mean of S, and thus, loosely speaking, we have only $N-1$ independent values of s remaining to calculate $\tilde{\sigma}_S^2$. Show that if $N \gg 1$, then $\tilde{\sigma}_S \approx \sigma_S$, where the standard deviation σ_S is given by $\sigma_S^2 = \overline{S^2} - \overline{S}^2$.

(g) The quantity $\tilde{\sigma}_S$ is known as the standard deviation of the means. That is, $\tilde{\sigma}_S$ is a measure of how much variation we expect to find if we make repeated measurements of S. How does the value of $\tilde{\sigma}_S$ compare to your estimated width of the probability density $p(S)$?

3.9 The Poisson distribution and Should You Fly in Airplanes?

We now return to the question of whether or not it is safe to fly. If the probability of a plane crashing is $p = 10^{-5}$, then $1 - p$ is the probability of surviving a single flight. The probability of surviving N flights is then $P_N = (1-p)^N$. For $N = 400$, $P_N \approx 0.996$, and for $N = 10^5$, $P_N \approx 0.365$. Thus, our intuition is verified that if we took 400 flights, we would have only a small chance of crashing.

This type of reasoning is typical when the probability of an individual event is small, but there are very many attempts. Suppose we are interested in the probability of the occurrence of n events out of N attempts given that the probability p of the event for each attempt is very small. The resulting probability is called the *Poisson distribution*, a distribution that is important in the analysis of experimental data. We discuss it here because of its intrinsic interest.

To derive the Poisson distribution, we begin with the binomial distribution:

$$P(n) = \frac{N!}{n!\,(N-n)!}\, p^n (1-p)^{N-n}. \tag{3.136}$$

(As before, we suppress the N dependence of P.) As in Section (3.7, we will approximate $\ln P(n)$ rather than $P(n)$ directly. We first use Stirling's approximation to write

$$\ln \frac{N!}{(N-n)!} = \ln N! - \ln(N-n)! \tag{3.137a}$$

$$\approx N \ln N - (N-n) \ln(N-n) \tag{3.137b}$$

$$\approx N \ln N - (N-n) \ln N \tag{3.137c}$$

$$= N \ln N - N \ln N + n \ln N \tag{3.137d}$$

$$= n \ln N. \tag{3.137e}$$

From (3.137e) we obtain

$$\frac{N!}{(N-n)!} \approx e^{n \ln N} = N^n. \tag{3.138}$$

For $p \ll 1$, we have $\ln(1-p) \approx -p$, $e^{\ln(1-p)} = 1 - p \approx e^{-p}$, and $(1-p)^{N-n} \approx e^{-p(N-n)} \approx e^{-pN}$. If we use the above approximations, we find

$$P(n) \approx \frac{N^n}{n!} p^n e^{-pN} = \frac{(Np)^n}{n!} e^{-pN}, \tag{3.139}$$

or

$$\boxed{P(n) = \frac{\overline{n}^n}{n!} e^{-\overline{n}}}, \qquad \text{(Poisson distribution)} \tag{3.140}$$

where $\overline{n} = pN$. The form (3.140) is the Poisson distribution.

Let us apply the Poisson distribution to the airplane survival problem. We want to know the probability of never crashing, that is, $P(n = 0)$. The mean $\overline{N} = pN$ equals $10^{-5} \times 400 = 0.004$ for $N = 400$ flights and $\overline{N} = 1$ for $N = 10^5$ flights. Thus, the survival probability is $P(0) = e^{-\overline{N}} \approx 0.996$ for $N = 400$ and $P(0) \approx 0.368$ for $N = 10^5$ as we calculated previously. We see that if we fly 100,000 times, we have a much larger probability of dying in a plane crash.

Problem 3.48. Poisson distribution

(a) Show that the Poisson distribution is properly normalized, and calculate the mean and variance of n. Because $P(n)$ for $n > N$ is negligibly small, you can sum $P(n)$ from $n = 0$ to $n = \infty$ even though the maximum value of n is N.

(b) Plot the Poisson distribution $P(n)$ as a function of n for $p = 0.01$ and $N = 100$.

3.10   *Traffic Flow and the Exponential Distribution

The Poisson distribution is closely related to the exponential distribution as we will see in the following. Consider a sequence of similar random events and let t_1, t_2, ... be the time at which each successive event occurs. Examples of such sequences are the successive times when a phone call is received and the times when a Geiger counter registers a decay of a radioactive nucleus. Suppose that we determine the sequence over a very long time T that is much greater than any of the intervals $t_i - t_{i-1}$. We also suppose that the average number of events is λ per unit time so that in a time interval t, the mean number of events is λt.

Assume that the events occur at random and are independent of each other. Given λ, the mean number of events per unit time, we wish to find the probability distribution $w(t)$ of the interval t between the events. We know that if an event occurred at time $t = 0$, the probability that another event occurs within the interval $[0, t]$ is

$$\int_0^t w(t) \Delta t, \tag{3.141}$$

and the probability that no event occurs in the interval t is

$$1 - \int_0^t w(t)\Delta t. \tag{3.142}$$

Thus the probability that the duration of the interval between the two events is between t and $t + \Delta t$ is given by

$$w(t)\Delta t = \text{probability that no event occurs in the interval } [0, t]$$
$$\times \text{ probability that an event occurs in interval } [t, t + \Delta t]$$
$$= \Big[1 - \int_0^t w(t)dt\Big]\lambda\Delta t. \tag{3.143}$$

If we cancel Δt from each side of (3.143) and differentiate both sides with respect to t, we find

$$\frac{dw}{dt} = -\lambda w, \tag{3.144}$$

so that

$$w(t) = Ae^{-\lambda t}. \tag{3.145}$$

The constant of integration A is determined from the normalization condition:

$$\int_0^\infty w(t)\, dt = 1 = A \int_0^\infty e^{-\lambda t}dt = A/\lambda. \tag{3.146}$$

Hence, $w(t)$ is the exponential function

$$w(t) = \lambda e^{-\lambda t}. \tag{3.147}$$

These results for the exponential distribution lead naturally to the Poisson distribution. Let us divide a long time interval T into n smaller intervals $t = T/n$. What is the probability that 0, 1, 2, 3, ... events occur in the time interval t, given λ, the mean number of events per unit time? We will show that the probability that n events occur in the time interval t is given by the Poisson distribution:

$$P_n(t) = \frac{(\lambda t)^n}{n!}e^{-\lambda t}. \tag{3.148}$$

We first consider the case $n = 0$. If $n = 0$, the probability that no event occurs in the interval t is (see (3.143))

$$P_{n=0}(t) = 1 - \lambda\int_0^t e^{-\lambda t'}dt' = e^{-\lambda t}. \tag{3.149}$$

For the case $n = 1$, there is exactly one event in time interval t. This event must occur at some time t' which may occur with equal probability in the interval $[0, t]$. Because no event can occur in the interval $[t', t]$, we have

$$P_{n=1}(t) = \int_0^t \lambda e^{-\lambda t'}e^{-\lambda(t'-t)}dt', \tag{3.150}$$

where we have used (3.149) with $t \to (t' - t)$. Hence,

$$P_{n=1}(t) = \int_0^t \lambda e^{-\lambda t} dt = (\lambda t) e^{-\lambda t}. \tag{3.151}$$

In general, if n events are to occur in the interval $[0, t]$, the first must occur at some time t' and exactly $(n-1)$ must occur in the time $(t - t')$. Hence,

$$P_n(t) = \int_0^t \lambda e^{-\lambda t'} P_{n-1}(t - t'). \tag{3.152}$$

Equation (3.152) is a recurrence formula that can be used to derive (3.148) by induction. It is easy to see that (3.148) satisfies (3.152) for $n = 0$ and 1. As is usual when solving recursion formula by induction, we assume that (3.148) is correct for $(n-1)$. We substitute this result into (3.152) and find

$$P_n(t) = \lambda^n e^{-\lambda t} \int_0^t (t - t')^{n-1} dt' / (n-1)! = \frac{(\lambda t)^b}{n!} e^{-\lambda t}. \tag{3.153}$$

An application of the Poisson distribution is given in Problem 3.49.

N	frequency
0	1
1	7
2	14
2	25
4	31
5	26
6	27
7	14
8	8
9	3
10	4
11	3
12	1
13	0
14	1
> 15	0

Table 3.5: Observed distribution of vehicles passing a marker on a highway in thirty second intervals. The data was taken from page 98 of Montroll and Badger.

*Problem 3.49.** Analysis of traffic data

In Table 3.5 we show the number of vehicles passing a marker during a thirty second interval. The observations were made on a single lane of a six lane divided highway. Assume that the traffic density is so low that passing occurs easily and no platoons of cars develop.

(a) Is the distribution of the number of vehicles consistent with the Poisson distribution? If so, what is the value of the parameter λ?

(b) As the traffic density increases, the flow reaches a regime where the vehicles are very close to one another so that they are no longer mutually independent. Make arguments for the form of the probability distribution of the number of vehicles passing a given point in this regime.

3.11 *Are All Probability Distributions Gaussian?

We have discussed the properties of *random additive processes* and found that the probability distribution for their sum is a Gaussian for a sufficiently large number of terms. As an example of such a process, we discussed a one-dimensional random walk on a lattice for which the displacement x is the sum of N random steps.

We now discuss *random multiplicative processes*. Examples of such processes include the distributions of incomes, rainfall, and fragment sizes in rock crushing processes.[11] Consider the latter for which we begin with a rock of size w. We strike the rock with a hammer and generate two fragments whose sizes are pw and qw, where $q = 1 - p$. In the next step the possible sizes of the fragments are $p^2 w$, pqw, qpw, and $q^2 w$. What is the distribution of the fragment sizes after N blows of the hammer?

To answer this question, we consider a binary sequence in which the numbers x_1 and x_2 appear independently with probabilities p and q respectively. If there are N elements in the product Π, we can ask what is $\overline{\Pi}$, the mean value of Π? To calculate $\overline{\Pi}$ we define $P(n)$ to be the probability that the product of N independent factors of x_1 and x_2 has the value $x_1{}^n x_2{}^{N-n}$. This probability is given by the number of sequences where x_1 appears n times multiplied by the probability of choosing a specific sequence with x_1 appearing n times. This probability is the familiar binomial distribution:

$$P_N(n) = \frac{N!}{n!\,(N-n)!} p^n q^{N-n}. \tag{3.154}$$

We average over all possible outcomes of the product to obtain its mean value

$$\overline{\Pi} = \sum_{n=0}^{N} P(n) x_1{}^n x_2{}^{N-n} = (px_1 + qx_2)^N. \tag{3.155}$$

The most probable event in the product contains Np factors of x_1 and Nq factors of x_2. Hence, the most probable value of the product is

$$\widetilde{\Pi} = (x_1{}^p x_2{}^q)^N. \tag{3.156}$$

To obtain a better feeling for these results, we first consider some special cases. For $x_1 = 2$, $x_2 = 1/2$, and $p = q = 1/2$ we have $\overline{\Pi} = (1/4)[x_2^2 + 2x_1 x_2 + x_2^2] = (1/4)[4 + 2 + 1/4] = 25/16$ for $N = 2$; for general N we have $\overline{\Pi} = (5/4)^N$. In contrast, the most probable value for $N = 2$ is given by $\widetilde{\Pi} = 2^{1/2} \times (1/2)^{1/2} = 1$; the same result holds for any N. For $p = 1/3$ and $q = 2/3$ and the same values of x_1 and x_2 we find $\overline{\Pi} = 1$ for all N and $\widetilde{\Pi} = (\frac{1}{2} \times \frac{1}{2} \times 2)^{2/3} = 2^{-2/3}$ for $N = 2$ and $2^{-N/3}$ for any N. We see that $\widetilde{\Pi} \neq \overline{\Pi}$ for a random multiplicative process. In contrast, the

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[11]The following discussion is based on an article by Sidney Redner (see references).

most probable event is a good approximation to the mean value of the sum orf a random additive process (and is identical for $p = q$).

The reason for the large discrepancy between $\overline{\overline{\Pi}}$ and $\widetilde{\Pi}$ is the important role played by rare events. For example, a sequence of N factors of $x_1 = 2$ occurs with a very small probability, but the value of this product is very large in comparison to the most probable value. Hence, this extreme event makes a finite contribution to $\overline{\overline{\Pi}}$ and a dominant contribution to the higher moments $\overline{\overline{\Pi^m}}$.

*__Problem 3.50.__ (a) Confirm the general result in (3.155) for $N = 4$ by showing explicitly all the possible values of the product.

(b) Consider the case $x_1 = 2$, $x_2 = 1/2$, $p = 1/4$, and $q = 3/4$, and calculate $\overline{\overline{\Pi}}$ and $\widetilde{\Pi}$.

(c) Show that $\overline{\overline{\Pi^m}}$, the mean value of the mth moment, reduces to $(px_1^m)^N$ as $m \to \infty$. This result implies that the mth moment is determined solely by the most extreme event for $m \gg 1$.

(d) Based on the Gaussian approximation for the probability of a random additive process, what is a reasonable guess for the continuum approximation to the probability of a random multiplicative process? Such a distribution is called the *log-normal* distribution. Discuss why or why not you expect the log-normal distribution to be a good approximation for $N \gg 1$.

*__Problem 3.51.__ Simulation of multiplicative process

(a) Run the applet/application at `<stp.clarku.edu/simulations/productprocess.html>` which simulates the distribution of values of the product $x_1{}^n x_2{}^{N-n}$. Choose $x_1 = 2$, $x_2 = 1/2$, and $p = q = 1/2$. First choose $N = 4$ and estimate $\overline{\overline{\Pi}}$ and $\widetilde{\Pi}$. Do your estimated values converge more or less uniformly to the analytical values as the number of measurements becomes large? Do a similar simulation for $N = 40$. Compare your results with a similar simulation of a random walk and discuss the importance of extreme events for random multiplicative processes.

(b) The true average value of a product of random variables is governed by rare events that are at the tail of the distribution. However, the most probable events will likely dominate in a simulation of a multiplicative process. As the number of trials increase, there will be an increase in the number of rare events that are sampled, and we expect that the observed averages will fluctuate greatly. As the number of trials is increased still further, the number of rare events will be more accurately sampled, and the observed averages will eventually converge to their true values. Redner has estimated that the minimum number of trials for this crossover to occur is given by

$$\ln T^* = \frac{N}{2pq}\left(p - \frac{pq(x_1/x_2)^m}{q + p(x_1/x_2)^m}\right)^2, \tag{3.157}$$

where T is the number of trials and m is the moment of the distribution that we wish to estimate. How does the estimate of T^* in (3.157) compare with the results you observe in the simulation?

3.12   *Supplementary Notes

3.12.1   The uncertainty for unequal probabilities

Consider a loaded die for which the probabilities P_j are not equal. We wish to motivate the form (3.38) for S. Imagine that we roll the die a large number of times N. Then each outcome would occur $N_j = NP_j$ times and there would be $N_j = NP_1$ outcomes of face 1, NP_2 outcomes of face 2, ... These outcomes could occur in many different orders. Thus the original uncertainty about the outcome of one roll of a die is converted into an uncertainty about order. Because all the possible orders that can occur in an experiment of N rolls are equally likely, we can use (3.37) for the associated uncertainty S_N:

$$S_N = \ln \Omega = \ln \Big[\frac{N!}{\prod_j N_j!} \Big], \tag{3.158}$$

The right-hand side of (3.158) equals the total number of possible sequences.

To understand the form (3.158) suppose that we know that if we toss a coin four times, we will obtain 2 heads and 2 tails. What we don't know is the sequence. In Table 3.6 we show the six possible sequences. It is easy to see that this number is given by

$$M = \frac{N!}{\prod_j N_j} = \frac{4!}{2!\,2!} = 6. \tag{3.159}$$

H	H	T	T
H	T	H	T
H	T	T	H
T	T	H	H
T	H	T	H
T	H	H	T

Table 3.6: Possible sequences of tossing a coin four times such that two heads and two tails are obtained.

Now that we understand the form of S_N in (3.158), we can find the desired form of S. The uncertainty S_N in (3.158) is the uncertainty associated with all N rolls. The uncertainty associated with one roll is

$$S = \lim_{N \to \infty} \frac{1}{N} S_N = \lim_{N \to \infty} \frac{1}{N} \ln \Big[\frac{N!}{\prod_j N_j!} \Big] = \lim_{N \to \infty} \frac{1}{N} \Big[\ln N! - \sum_j \ln N_j! \Big]. \tag{3.160}$$

We can reduce (3.160) to a simpler form by using Stirling's approximation, $\ln N! \approx N \ln N - N$

for large N and substituting $N_j = NP_j$:

$$S = \lim_{N \to \infty} \frac{1}{N} \Big[N \ln N - N - \sum_j (NP_j) \ln(NP_j) + \sum_j (NP_j) \Big] \tag{3.161a}$$

$$= \lim_{N \to \infty} \frac{1}{N} \Big[N \ln N - N - N \ln N \sum_j P_j - N \sum_j P_j \ln P_j + N \sum_j P_j \Big] \tag{3.161b}$$

$$= - \sum_j P_j \ln P_j, \tag{3.161c}$$

where we used the fact that $\sum_j P_j = 1$.

3.12.2 Method of undetermined multipliers

Suppose that we want to maximize the function $f(x, y) = xy^2$ subject to the constraint that $x^2 + y^2 = 1$. One way would be to substitute $y^2 = 1 - x^2$ and maximize $f(x) = x(1 - x^2)$. However, this approach works only if f can be reduced to a function of one variable. However we first consider this simple case as a way of introducing the general method of undetermined multipliers.

We wish to maximize $f(x, y)$ subject to the constraint that $g(x, y) = x^2 + y^2 - 1 = 0$. In the method of undetermined multipliers, this problem can be reduced to solving the equation

$$df - \lambda dg = 0, \tag{3.162}$$

where $df = y^2 dx + 2xy dy = 0$ at the maximum of f and $dg = 2x dx + 2y dy = 0$. If we substitute df and dg in (3.162), we have

$$(y^2 - 2\lambda x)dx + 2(xy - \lambda y)dy = 0. \tag{3.163}$$

We can choose $\lambda = y^2/2x$ so that the first term is zero. Because this term is zero, the second term must also be zero; that is, $x = \lambda = y^2/2x$, so $x = \pm y/\sqrt{2}$. Hence, from the constraint $g(x, y) = 0$, we obtain $x = \sqrt{1/3}$ and $\lambda = 2$.

In general, we wish to maximize the function $f(x_1, x_2, \ldots, x_N)$ subject to the constraints $g_j(x_1, x_2, \ldots, x_N) = 0$ where $j = 1, 2, \ldots, M$ with $M < N$. The maximum of f is given by

$$df = \sum_{i=1}^{N} \Big(\frac{\partial f}{\partial x_i} \Big) dx_i = 0, \tag{3.164}$$

and the constraint can be expressed as

$$dg = \sum_{i=1}^{N} \Big(\frac{\partial g_j}{\partial x_i} \Big) dx_i = 0. \tag{3.165}$$

As in our example, we can combine (3.164) and (3.165) and write $df - \sum_{j=1}^{M} \lambda_j dg_j = 0$ or

$$\sum_{i=1}^{N} \Big[\Big(\frac{\partial f}{\partial x_i} \Big) - \sum_{i=1}^{M} \lambda_j \Big(\frac{\partial g_j}{\partial x_i} \Big) \Big] dx_i = 0. \tag{3.166}$$

We are free to choose all M values of α_j such that the first M terms in the square brackets are zero. For the remaining $N - M$ terms, the dx_i can be independently varied because the constraints have been satisfied. Hence, the remaining terms in square brackets must be independently zero and we are left with $N - M$ equations of the form

$$\left(\frac{\partial f}{\partial x_i}\right) - \sum_{i=1}^{M} \lambda_j \left(\frac{\partial g_j}{\partial x_i}\right) = 0. \tag{3.167}$$

In Example 3.12 we were able to obtain the probabilities by reducing the uncertainty S to a function of a single variable P_1 and then maximizing $S(P_1)$. We now consider a more general problem where there are more outcomes, the case of a loaded die for which there are six outcomes. Suppose that we know that the average number of points on the face of a die if f. Then we wish to determine P_1, P_2, ..., P_6 subject to the constraints

$$\sum_{j=1}^{6} P_j = 1, \tag{3.168}$$

$$\sum_{j=1}^{6} j P_j = f. \tag{3.169}$$

For a perfect die $f = 3.5$. Equation (3.167) becomes

$$\sum_{j=1}^{6} \Big[(1 + \ln P_j) + \alpha + \beta j \Big] dP_j = 0, \tag{3.170}$$

where we have used $dS = -\sum_{j=1}^{6} d(P_j \ln P_j) = -\sum_{j=1}^{6} (1 + \ln P_j) dP_j$; α and β are the undetermined (Lagrange) multipliers. We choose α and β so that the first two terms in the brackets (with $j = 1$ and $j = 2$ are independently zero. We write

$$\alpha = \ln P_2 - 2 \ln P_1 - 1 \tag{3.171a}$$
$$\beta = \ln P_1 - \ln P_2. \tag{3.171b}$$

We can solve (3.171b) for $\ln P_2 = \ln P_1 - \beta$ and use (3.171a) to find $\ln P_1 = -1 - \alpha - \beta$ and use this result to write $P_2 = -1 - \alpha - \beta 2$. We can independently vary $dP_3, \ldots dP_6$ because the two constraints are satisfied by the values of P_1 and P_2. We let

$$\ln P_j = -1 - \alpha - j\beta, \tag{3.172}$$

or

$$P_j = e^{-1-\alpha} e^{-\beta j}. \tag{3.173}$$

We can eliminate the constant α by the normalization condition (3.168):

$$P_j = \frac{e^{-\beta j}}{\sum_j e^{-\beta j}}. \tag{3.174}$$

The constant β is determined by the constraint (3.47):

$$f = \frac{e^{-\beta} + 2e^{-\beta 2} + 3e^{-\beta 3} + 4e^{-\beta 4} + 5e^{-\beta 5} + 6e^{-\beta 6}}{e^{-\beta} + e^{-\beta 2} + e^{-\beta 3} + e^{-\beta 4} + e^{-\beta 5} + e^{-\beta 6}}. \tag{3.175}$$

In general, (3.175) must be solved numerically.

Problem 3.52. Show that the solution to (3.175) is $\beta = 0$ for $f = 7/2$, $\beta = +\infty$ for $f = 2$, $\beta = -\infty$ for $f = 6$, and $\beta = -0.1746$ for $f = 4$.

3.12.3 Derivation of the central limit theorem

To discuss the derivation of the central limit theorem, it is convenient to introduce the *characteristic function* $\phi(k)$ of the probability density $p(x)$. The main utility of the characteristic function is that it simplifies the analysis of the sums of independent random variables. We define $\phi(k)$ as the Fourier transform of $p(x)$:

$$\phi(k) = \overline{e^{ikx}} = \int_{-\infty}^{\infty} dx\, e^{ikx} p(x). \tag{3.176}$$

Because $p(x)$ is normalized, it follows that $\phi(k = 0) = 1$. The main property of the Fourier transform that we need is that if $\phi(k)$ is known, we can find $p(x)$ by calculating the inverse Fourier transform:

$$p(x) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dk\, e^{-ikx} \phi(k). \tag{3.177}$$

Problem 3.53. Calculate the characteristic function of the Gaussian probability density.

One useful property of $\phi(k)$ is that its power series expansion yields the moments of $p(x)$:

$$\phi(k) = \sum_{n=0}^{\infty} \frac{k^n}{n!} \frac{d^n \phi(k)}{dk^n}\Big|_{k=0}, \tag{3.178}$$

$$= \overline{e^{ikx}} = \sum_{n=0}^{\infty} \frac{(ik)^n \overline{x^n}}{n!}. \tag{3.179}$$

By comparing coefficients of k^n in (3.178) and (3.179), we see that

$$\overline{x} = -i \frac{d\phi}{dk}\Big|_{k=0}. \tag{3.180}$$

In Problem 3.54 we show that

$$\overline{x^2} - \overline{x}^2 = -\frac{d^2}{dk^2} \ln \phi(k)\Big|_{k=0} \tag{3.181}$$

and that certain convenient combinations of the moments are related to the power series expansion of the logarithm of the characteristic function.

Problem 3.54. The characteristic function generates the *cumulants* C_m defined by

$$\ln \phi(k) = \sum_{m=1}^{\infty} \frac{(ik)^m}{m!} C_m. \tag{3.182}$$

Show that the cumulants are combinations of the moments of x and are given by

$$C_1 = \overline{x} \tag{3.183a}$$

$$C_2 = \sigma^2 = \overline{x^2} - \overline{x}^2 \tag{3.183b}$$

$$C_3 = \overline{x^3} - 3\,\overline{x^2}\overline{x} + 2\,\overline{x}^3 \tag{3.183c}$$

$$C_4 = \overline{x^4} - 4\,\overline{x^3}\,\overline{x} - 3\,\overline{x^2}^2 + 12\,\overline{x^2}\,\overline{x}^2 - 6\,\overline{x}^4. \tag{3.183d}$$

Now let us consider the properties of the characteristic function for the sums of independent variables. For example, let $p_1(x)$ be the probability density for the weight x of adult males and let $p_2(y)$ be the probability density for the weight of adult females. If we assume that people marry one another independently of weight, what is the probability density $p(z)$ for the weight z of an adult couple? We have that

$$z = x + y. \tag{3.184}$$

How do the probability densities combine? The answer is

$$p(z) = \int dx\, dy\, p_1(x) p_2(y)\, \delta(z - x - y). \tag{3.185}$$

The integral in (3.185) represents all the possible ways of obtaining the combined weight z as determined by the probability density $p_1(x)p_2(y)$ for the combination of x and y that sums to z. The form (3.185) of the integrand is known as a *convolution*. An important property of a convolution is that its Fourier transform is a simple product. We have

$$\phi_z(k) = \int dz\, e^{ikz} p(z) \tag{3.186a}$$

$$= \int dz \int dx \int dy\, e^{ikz} p_1(x) p_2(y)\, \delta(z - x - y) \tag{3.186b}$$

$$= \int dx\, e^{ikx} p_1(x) \int dy\, e^{iky} p_2(y) \tag{3.186c}$$

$$= \phi_1(k)\phi_2(k). \tag{3.186d}$$

It is straightforward to generalize this result to a sum of N random variables. We write

$$z = x_1 + x_2 + \ldots + x_N. \tag{3.187}$$

Then

$$\phi_z(k) = \prod_{i=1}^{N} \phi_i(k). \tag{3.188}$$

That is, *for independent variables the characteristic function of the sum is the product of the individual characteristic functions.* If we take the logarithm of both sides of (3.188), we obtain

$$\ln \phi_z(k) = \sum_{i=1}^{N} \ln \phi_i(k). \tag{3.189}$$

Each side of (3.189) can be expanded as a power series and compared order by order in powers of ik. The result is that when random variables are added, their associated cumulants also add. That is, the nth order cumulants satisfy the relation:

$$C_n^z = C_n^1 + C_n^2 + \ldots + C_n^N. \tag{3.190}$$

We conclude see that if the random variables x_i are independent (uncorrelated), their cumulants and in particular, their variances, add.

If we denote the mean and standard deviation of the weight of an adult male as $\overline{x}$ and σ respectively, then from (3.183a) and (3.190) we find that the mean weight of N adult males is given by $N\overline{x}$. Similarly from (3.183b) we see that the standard deviation of the weight of N adult males is given by $\sigma_N^2 = N\sigma^2$, or $\sigma_N = \sqrt{N}\sigma$. Hence, we find the now familiar result that the sum of N random variables scales as N while the standard deviation scales as $\sqrt{N}$.

We are now in a position to derive the central limit theorem. Let x_1, x_2, ..., x_N be N mutually independent variables. For simplicity, we assume that each variable has the same probability density $p(x)$. The only condition is that the variance σ_x^2 of the probability density $p(x)$ must be finite. For simplicity, we make the additional assumption that $\overline{x} = 0$, a condition that always can be satisfied by measuring x from its mean. The central limit theorem states that the sum S has the probability density

$$p(S) = \frac{1}{\sqrt{2\pi N\sigma_x^2}} \, e^{-S^2/2N\sigma_x^2} \tag{3.191}$$

From (3.183b) we see that $\overline{S^2} = N\sigma_x^2$, and hence the variance of S grows linearly with N. However, the distribution of the values of the arithmetic mean S/N becomes narrower with increasing N:

$$\overline{\left(\frac{x_1 + x_2 + \ldots x_N}{N}\right)^2} = \frac{N\sigma_x^2}{N^2} = \frac{\sigma_x^2}{N}. \tag{3.192}$$

From (3.192) we see that it is useful to define a scaled sum:

$$z = \frac{1}{\sqrt{N}}(x_1 + x_2 + \ldots + x_N), \tag{3.193}$$

and to write the central limit theorem in the form

$$p(z) = \frac{1}{\sqrt{2\pi\sigma^2}} e^{-z^2/2\sigma^2}. \tag{3.194}$$

To obtain the result (3.194), we write the characteristic function of z as

$$\phi_z(k) = \int dx \, e^{ikz} \int dx_1 \int dx_2 \cdots \int dx_N \, \delta\big(z - \big[\frac{x_1 + x_2 + \ldots + x_N}{N^{1/2}}\big]\big) \tag{3.195a}$$

$$\times \ p(x_1) \, p(x_2) \ldots p(x_N) \tag{3.195b}$$

$$= \int dx_1 \int dx_2 \ldots \int dx_N \, e^{ik(x_1 + x_2 + \ldots x_N)/N^{1/2}} p(x_1) \, p(x_2) \ldots p(x_N) \tag{3.195c}$$

$$= \phi\big(\frac{k}{N^{1/2}}\big)^N. \tag{3.195d}$$

We next take the logarithm of both sides of (3.195d) and expand the right-hand side in powers of k to find

$$\ln \phi_z(k) = \sum_{m=2}^{\infty} \frac{(ik)^m}{m!} N^{1-m/2} C_m. \tag{3.196}$$

The $m = 1$ term does not contribute in (3.196) because we have assumed that $\bar{x} = 0$. More importantly, note that as $N \to \infty$, the higher-order terms are suppressed so that

$$\ln \phi_z(k) \to -\frac{k^2}{2} C_2, \tag{3.197}$$

or

$$\phi_z(k) \to e^{-k^2 \sigma^2/2} + \ldots \tag{3.198}$$

Because the inverse Fourier transform of a Gaussian is also a Gaussian, we find that

$$p(z) = \frac{1}{\sqrt{2\pi\sigma^2}} e^{-z^2/2\sigma^2}. \tag{3.199}$$

The leading correction to $\phi(k)$ in (3.199) gives rise to a term of order $N^{-1/2}$, and therefore does not contribute in the limit $N \to \infty$.

The only requirements for the applicability of the central limit theorem are that the various x_i be statistically independent and that the second moment of $p(x)$ exists. Not all probabilities satisfy this latter requirement as demonstrated by the Lorentz distribution (see Problem 3.43). It is not necessary that all the x_i have the same distribution.

Vocabulary

sample space, events, outcome

uncertainty, principle of least bias or maximum uncertainty

probability distribution, probability density

mean value, moments, variance, standard deviation

conditional probability, Bayes' theorem

binomial distribution, Gaussian distribution, Poisson distribution

random walk, random additive processes, central limit theorem

Stirling's approximation

Monte Carlo sampling

Rare or extreme events

Notation

probability distribution $P(i)$, mean value $\overline{f(x)}$, variance $\overline{\Delta x^2}$, standard deviation σ

conditional probability $P(A|B)$, probability density $p(x)$

Additional problems

Listing of inline problems.

Problem 3.55. In Figure 3.9 we show a square lattice of 16^2 sites each of which is occupied with probability p. Estimate the probability that a site in the lattice is occupied.
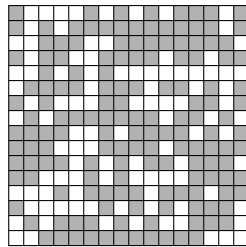
Figure 3.9: Representation of a square lattice of 16×16 sites. The sites are represented by squares and are either occupied (shaded) with probability p or are empty (white) with probability $1 - p$.

Problem 3.56. Three coins (in a fountain)

Three coins are tossed in succession. Assume that the simple events are equiprobable. Find the probabilities of the following:

(a) the first coin is heads;

(b) exactly two heads have occurred;

(c) not more than two heads have occurred.

Problem 3.57. Fallacious reasoning

A student tries to solve Problem 3.13 by using the following reasoning. The probability of a double six is 1/36. Hence the probability of finding at least one double six in 24 throws is 24/36. What is wrong with this reasoning? If you have trouble understanding the error in this reason, try solving the problem of finding the probability of at least one double six in two throws of a pair of dice. What are the possible outcomes? Is each outcome equally probable?

Problem 3.58. d'Alembert's fallacious reasoning

In two tosses of a single coin, what is the probability that heads will appear at least once? Use the rules of probability to show that the answer is $\frac{3}{4}$. However, d'Alembert, a distinguished French mathematician of the eighteenth century, reasoned that there are only 3 possible outcomes: heads on the first throw, heads on the second throw, and no heads at all. The first two of these three outcomes is favorable. Therefore the probability that heads will appear at least once is $\frac{2}{3}$. What is the fallacy in his reasoning? Even eminent mathematicians (and physicists) have been lead astray by the subtle nature of probability.

Problem 3.59. False positives

A diagnostic test for the presence of the AIDS virus has a probability of 0.005 of producing a false positive. If 200 patients are tested at a clinic, what is the probability that at least one false positive occurs?

Problem 3.60. Number of fish in a pond

A farmer wants to estimate how many fish are in her pond. She takes out 200 fish and tags them and returns them to the pond. After sufficient time to allow the tagged fish to mix with the others, she removes 250 fish at random and finds that 25 of them are tagged. Estimate the number of fish in the pond.

	x_i, y_i		x_i, y_i
1	0.984, 0.246	6	0.637, 0.581
2	0.860, 0.132	7	0.779, 0.218
3	0.316, 0.028	8	0.276, 0.238
4	0.523, 0.542	9	0.081, 0.484
5	0.349, 0.623	10	0.289, 0.032

Table 3.7: A sequence of ten random pairs of numbers.

Problem 3.61. Estimating the area of a pond

A farmer owns a field that is $10\,\text{m} \times 10\,\text{m}$. In the midst of this field is a pond of unknown area. Suppose that the farmer is able to throw 100 stones at random into the field and finds that 40 of the stones make a splash. How can the farmer use this information to estimate the area of the pond?

Problem 3.62. Monte Carlo integration

Consider the ten pairs of numbers, (x_i, y_i), given in Table 3.7. The numbers are all are in the range $0 < x_i, y_i \leq 1$. Imagine that these numbers were generated by counting the clicks generated by a Geiger counter of radioactive decays, and hence they can be considered to be a part of a sequence of random numbers. Use this sequence to estimate the magnitude of the integral

$$F = \int_0^1 dx \sqrt{(1 - x^2)}. \tag{3.200}$$

If you have been successful in estimating the integral in this way, you have found a simple version of a general method known as *Monte Carlo integration*.[12] An applet for estimating integrals by Monte Carlo integration can be found at `<stp.clarku.edu/simulations/estimate>`.

Problem 3.63. Bullseyes

A person playing darts hits a bullseye 20% of the time on the average. Why is the probability of b bullseyes in N attempts a binomial distribution? What are the values of p and q? Find the probability that the person hits a bullseye

(a) once in five throws;

(b) twice in ten throws. Why are these probabilities not identical?

Problem 3.64. There are 10 children in a given family. Assuming that a boy is as likely to be born as a girl, find the probability of the family having

(a) 5 boys and 5 girls;

(b) 3 boys and 7 girls.

Problem 3.65. What is the probability that five children produced by the same couple will consist of the following:

---

[12]Monte Carlo methods were first developed to estimate integrals that could not be performed by other ways.

(a) three sons and two daughters?

(b) alternating sexes?

(c) alternating sexes starting with a son?

(d) all daughters? Assume that the probability of giving birth to a boy and a girl is the same.

Problem 3.66. Probability in baseball

A good hitter in baseball has a batting average of 300 or more, which means that the hitter will be successful 3 times out of 10 tries on the average. Assume that on average a hitter gets three hits for each 10 times at bat and that he has 4 times at bat per game.

(a) What is the probability that he gets zero hits in one game?

(b) What is the probability that he will get two hits or less in a three game series?

(c) What is the probability that he will get five or more hits in a three game series? Baseball fans might want to think about the significance of "slumps" and "streaks" in baseball.

Problem 3.67. Playoff winners

In the World Series in baseball and in the playoffs in the National Basketball Association and the National Hockey Association, the winner is determined by a best of seven series. That is, the first team that wins four games wins the series and is the champion. Do a simple statistical calculation assuming that the two teams are evenly matched and the winner of any game might as well be determined by a coin flip and show that a seven game series should occur 31.25% of the time. What is the probability that the series lasts n games? More information can be found at <www.mste.uiuc.edu/hill/ev/seriesprob.html> and at <www.aip.org/isns/reports/2003/080.html>.

Problem 3.68. Galton board

The Galton board (named after Francis Galton (1822–1911)), is a triangular array of pegs. The rows are numbered $0, 1, \ldots$ from the top row down such that row n has $n+1$ pegs. Suppose that a ball is dropped from above the top peg. Each time the ball hits a peg, it bounces to the right with probability p and to the left with probability $1-p$, independently from peg to peg. Suppose that N balls are dropped successively such that the balls do not encounter one another. How will the balls be distributed at the bottom of the board? Links to applets that simulate the Galton board can be found in the references.

Problem 3.69. The birthday problem

What if somebody offered to bet that at least two people in your physics class had the same birthday? Would you take the bet?

(a) What are the chances that at least two people in your class have the same birthday? Assume that the number of students is 25.

(b) What are the chances that at least one other person in your class has the same birthday as you? Explain why the chances are less in the second case.

Problem 3.70. A random walk down Wall Street

Many analysts attempt to select stocks by looking for correlations in the stock market as a whole or for patterns for particular companies. Such an analysis is based on the belief that there are repetitive patterns in stock prices. To understand one reason for the persistence of this belief do the following experiment. Construct a stock chart (a plot of stock price versus time) showing the movements of a hypothetical stock initially selling at $50 per share. On each successive day the closing stock price is determined by the flip of a coin. If the coin toss is a head, the stock closes 1/2 point ($0.50) higher than the preceding close. If the toss is a tail, the price is down by 1/2 point. Construct the stock chart for a long enough time to see "cycles" and other patterns appear. The moral of the charts is that a sequence of numbers produced in this manner is identical to a random walk, yet the sequence frequently appears to be correlated.

Problem 3.71. Suppose that a random walker takes N steps of unit length with probability p of a step to the right. The displacement m of the walker from the origin is given by $m = n - n'$, where n is the number of steps to the right and n' is the number of steps to the left. Show that $\overline{m} = (p - q)N$ and $\sigma_m^2 = \overline{(m - \overline{m})^2} = 4Npq$.

Problem 3.72. The result (3.79) for $\overline{(\Delta M)^2}$ differs by a factor of four from the result for σ_n^2 in (3.101). Why? Compare (3.79) to the result of Problem 3.37.

Problem 3.73. Size of the airways in the mammalian lung

The geometry of branched structures such as blood vessels or airways are important factors in determining the efficiency of physiological processes. The airways of the bronchial tree of mammalian lungs branch at regular intervals with a systematic reduction of their diameter. In the human lung the conducting airway tree ends at about 2^{17} divisions.

In this problem we consider a simplified model of how the average diameter of the airways in the mammalian lung change down the bronchial tree. Assume that the diameter at the $n = 0$ branch (the trachea) is one. Suppose that the airways branch into two nearly equal parts of width p and q. (In this case p and q are not probabilities and hence $p + q$ is not necessarily unity.) After the first division, the average diameter is $L(1) = (p + q)/2$; after two divisions (generations), the average diameter is $L(2) = (p^2 + 2pq + q^2)/4$. Show that the average diameter of the bronchial tube after n generations is given by

$$L(n) = (p + q)^n/2^n = e^{-n/n_0}, \tag{3.201}$$

where $n_0^{-1} = |\ln[(p + q)/2]|$. What is the behavior of $L(n)$ for $p = q = 1/3$? This exponential behavior of $L(n)$ is observed for $n \leq 10$. To explain the behavior of $L(n)$ for larger N, it is necessary to assume that the division is not precisely given by p and q, but is only p and q on the average.

Problem 3.74. Watching a drunkard

A random walker is observed to take a total of N steps, n of which are to the right.

(a) Suppose that a curious observer finds that on ten successive nights the walker takes $N = 20$ steps and that the values of n are given successively by 14, 13, 11, 12, 11, 12, 16, 16, 14, 8. Compute $\overline{n}$, $\overline{n^2}$, and σ_n. Use this information to estimate p. If your reasoning gives different values for p, which estimate is likely to be the most accurate?

(b) Suppose that on another ten successive nights the same walker takes $N = 100$ steps and that the values of n are given by 58, 69, 71, 58, 63, 53, 64, 66, 65, 50. Compute the same quantities as in part (a) and estimate p. How does the ratio of σ_n to $\overline{n}$ compare for the two values of N? Explain your results.

(c) Compute $\overline{m}$ and σ_m, where $m = n - n'$ is the net displacement of the walker. This problem inspired an article by Zia and Schmittmann (see the references).

Problem 3.75. Alternative derivation of the Gaussian distribution

In Section 3.7 we evaluated the derivatives of $P(n)$ to determine the parameters A, B, and $\tilde{n}$ in (3.120). Another way to determine these parameters is to assume that the binomial distribution can be approximated by a Gaussian and require that the first several moments of the Gaussian and binomial distribution be equal. We write

$$P(n) = Ae^{-\frac{1}{2}B(n-\tilde{n})^2}, \tag{3.202}$$

and require that

$$\int_0^N P(n)\,dn = 1. \tag{3.203}$$

Because $P(n)$ depends on the difference $n - \tilde{n}$, it is convenient to change the variable of integration in (3.203) to $x = n - \tilde{n}$. We have

$$\int_{-\tilde{n}}^{N-\tilde{n}} P(x)\,dx = 1, \tag{3.204}$$

where

$$P(x) = Ae^{-\frac{1}{2}Bx^2}. \tag{3.205}$$

In the limit of large N, we can extend the upper and lower limits of integration in (3.204) and write

$$\int_{-\infty}^{\infty} P(x)\,dx = 1, \tag{3.206}$$

The first moment of $P(n)$ is given by

$$\overline{n} = \int_0^N nP(n)\,dn = pN. \tag{3.207}$$

Make a change of variables and show that

$$\int_{-\infty}^{\infty} xP(x)\,dx = \overline{n} - \tilde{n}. \tag{3.208}$$

Because the integral in (3.208) is zero, we can conclude that $\tilde{n} = \overline{n}$. We also have that

$$\overline{(n-\overline{n})^2} = \int_0^N (n-\overline{n})^2\,P(n)\,dn = pqN. \tag{3.209}$$

Do the integrals in (3.209) and (3.206) (see (A.17) and (A.21)) and confirm that the values of B and A are given by (3.126) and (3.128), respectively. The generality of the arguments leading to the Gaussian distribution suggests that it occurs frequently in probability when large numbers are involved. Note that the Gaussian distribution is characterized completely by its mean value and its width.
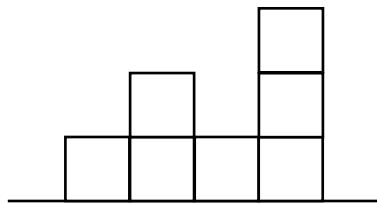
Figure 3.10: Example of a castle wall as explained in Problem 3.76.

Problem 3.76. Consider a two-dimensional 'wall constructed from N squares as shown in Figure 3.10. The base row of the cluster must be continuous, but higher rows can have gaps. Each column must be continuous and self-supporting. Determine the total number W_N of different N-site clusters, that is, the number of possible arrangements of N squares consistent with the above rules. Assume that the squares are identical.

Problem 3.77. First passage time

Suppose that a one-dimensional unbiased random walker starts out at the origin $x = 0$ at $t = 0$. How many steps will it take for the walker to reach a site at $x = 4$? This quantity, known as the *first passage time*, is a random variable because it is different for different possible realizations of the walk. Possible quantities of interest are the probability distribution of the first passage time and the mean first passage time, τ. Write a computer program to estimate $\tau(x)$ and then determine its analytical dependence on x. Why is it more difficult to estimate τ for $x = 8$ than for $x = 4$?

Problem 3.78. Heads you win

Two people take turns tossing a coin. The first person to obtain heads is the winner. Find the probabilities of the following events:

(a) the game terminates at the fourth toss;

(b) the first player wins the game;

(c) the second player wins the game.

Problem 3.79. Range of validity of the Gaussian distribution

How good is the Gaussian distribution as an approximation to the binomial distribution as a function of N? To determine the validity of the Gaussian distribution, consider the next two terms in the power series expansion of $\ln P(n)$:

$$\frac{1}{3!}(n - \tilde{n})^3 C + \frac{1}{4!)}(n - \tilde{n})^4 D, \tag{3.210}$$

with $C = d^3 \ln P(n)/d^3 n$ and $D = d^4 \ln P(n)/d^4 n$ evaluated at $n = \tilde{n}$.

(a) Show that $C = 0$ if $p = q$. Calculate D for $p = q$ and estimate the order of magnitude of the first nonzero correction. Compare this correction to the magnitude of the first nonzero term in $\ln P(n)$ (see (3.116)) and determine the conditions for which the terms beyond $(n - \tilde{n})^2$ can be neglected.

(b) Define the error as

$$E(n) = 1 - \frac{\text{Binomial}(n)}{\text{Gaussian}(n)} \tag{3.211}$$

Plot $E(n)$ versus n and determine the approximate width of $E(n)$.

(c) Show that if N is sufficiently large and neither p nor q is too small, the Gaussian distribution is a good approximation for n near the maximum of $P(n)$. Because $P(n)$ is very small for large $(n - \bar{n})$, the error in the Gaussian approximation for larger n is negligible.

Problem 3.80. Two-dimensional random walk

Consider a random walk on a two-dimensional square lattice where the walker has an equal probability of taking a step to one of four possible directions, north, south, east, or west. Use the central limit theorem to find the probability that the walker is a distance r to $r + dr$ from the origin, where $r^2 = x^2 + y^2$ and r is the distance from the origin after N steps. There is no need to do an explicit calculation.

Problem 3.81. Continuum model of a random walk

One of the first continuum models of a random walk is due to Rayleigh (1919). In the Rayleigh model the length a of each step is a random variable with probability density $p(a)$ and the direction of each step is random. For simplicity consider a walk in two dimensions and choose $p(a)$ so that each step has unit length. Then at each step the walker takes a step of unit length at a random angle. Use the central limit theorem to find the asymptotic form of $p(r, N)\, dr$, the probability that the walker is in the range r to $r + dr$, where r is the distance from the origin after N steps.

Problem 3.82. Suppose there are three boxes each with two balls. The first box has two green balls, the second box has one green and one red ball, and the third box has two red balls. Suppose you choose a box at random and find one green ball. What is the probability that the other ball is green?

Problem 3.83. Open a telephone directory to an random page and make a list corresponding to the last digit n of the first 100 telephone numbers. Find the probability $P(n)$ that the number n appears. Plot $P(n)$ as a function of n and describe its n-dependence. Do you expect that $P(n)$ should be approximately uniform?

*Problem 3.84. Model of a porous rock

A simple model of a porous rock can be imagined by placing a series of overlapping spheres at random into a container of fixed volume V. The spheres represent the rock and the space between the spheres represents the pores. If we write the volume of the sphere as v, it can be shown the fraction of the space between the spheres or the *porosity* ϕ is $\phi = \exp(-Nv/V)$, where N is the number of spheres. For simplicity, consider a two-dimensional system, and write a program to place disks of diameter unity into a square box. The disks can overlap. Divide the box into square cells each of which has an edge length equal to the diameter of the disks. Find the probability of having 0, 1, 2, or 3 disks in a cell for $\phi = 0.03$, 0.1, and 0.5.

*Problem 3.85. Benford's law

Do a search of the Web and find a site that lists the populations of various cities in the world (not necessarily the largest ones) or the cities of your state or region. The quantity of interest is the

first digit of each population. Alternatively, scan the first page of your local newspaper and record the first digit of each of the numbers you find. (The first digit of a number such as 0.00123 is 1.) What is the probability $P(n)$ that the *first* digit is n, where $n = 1, \ldots, 9$? Do you think that $P(n)$ will be the same for all n?

It turns out that the form of the probability $P(n)$ is given by

$$P(n) = \log_{10}\left(1 + \frac{1}{n}\right). \tag{3.212}$$

The distribution (3.212) is known as *Benford's law* and is named after Frank Benford, a physicist. It implies that for certain data sets, the first digit is distributed in a predictable pattern with a higher percentage of the numbers beginning with the digit 1. What are the numerical values of $P(n)$ for the different values of n? Is $P(n)$ normalized? Suggest a hypothesis for the nonuniform nature of the Benford distribution.

Accounting data is one of the many types of data that is expected to follow the Benford distribution. It has been found that artificial data sets do not have first digit patterns that follow the Benford distribution. Hence, the more an observed digit pattern deviates from the expected Benford distribution, the more likely the data set is suspect. Tax returns have been checked in this way.

The frequencies of the first digit of 2000 numerical answers to problems given in the back of four physics and mathematics textbooks have been tabulated and found to be distributed in a way consistent with Benford's law. Benford's Law is also expected to hold for answers to homework problems (see James R. Huddle, "A note on Benford's law," *Math. Comput. Educ.* **31**, 66 (1997)). The nature of Benford's law is discussed by T. P. Hill, "The first digit phenomenon," *Am. Sci.* **86**, 358–363 (1998).

*Problem 3.86.** Ask several of your friends to flip a coin 200 times and record the results or pretend to flip a coin and fake the results. Can you tell which of your friends faked the results? Hint: What is the probability that a sequence of six heads in a row will occur? Can you suggest any other statistical tests?

*Problem 3.87.** Zipf's law

Analyze a text and do a ranking of the word frequencies. The word with rank r is the rth word when the words of the text are listed with decreasing frequency. Make a log-log plot of word frequency f versus word rank r. The relation between word rank and word frequency was first stated by George Kingsley Zipf (1902–1950). This relation states that to a very good approximation for a given text

$$f \sim \frac{1}{r \ln(1.78R)}, \tag{3.213}$$

where R is the number of different words. Note the inverse power law behavior. The relation (3.213) is known as *Zipf's law*. The top 20 words in an analysis of a 1.6 MB collection of 423 short Time magazine articles (245,412 term occurrences) are given in Table 3.8.

*Problem 3.88.** Time of response to emails

If you receive an email, how long does it take for you to respond to it? If you keep a record of your received and sent mail, you can analyze the distribution of your response times – the number of days (or hours) between receiving an email from someone and then replying.

1	the	15861	11	his	1839
2	of	7239	12	is	1810
3	to	6331	13	he	1700
4	a	5878	14	as	1581
5	and	5614	15	on	1551
6	in	5294	16	by	1467
7	that	2507	17	at	1333
8	for	2228	18	it	1290
9	was	2149	19	from	1228
10	with	1839	20	but	1138

Table 3.8: Ranking of the top 20 words.

It turns out that the time it takes people to reply to emails can be described by a power law; that is, $P(\tau) \sim \tau^{-a}$ with $a \approx 1$. Oliveira and Barabási have shown that the response times of Einstein and Darwin to letters can also be described by a power law, but with an exponent $a \approx 3/2$ (see J. G. Oliveira and A.-L. Barabási, "Darwin and Einstein correspondence patterns," Nature **437**, 1251 (2005). Their results suggest that there is an universal pattern for human behavior in response to correspondence. What is the implication of a power law response?

***Problem 3.89.** A doctor has two drugs, A and B, which she can prescribe to patients with a certain illness. The drugs have been rated in terms of their effectiveness on a scale of 1 to 6, with 1 being the least effective and 6 being the most effective. Drug A is uniformly effective with a value of 3. The effectiveness of drug B is variable and 54% of the time it scores a value of 1, and 46% of the time it scores a value of 5. The doctor wishes to provide her patients with the best possible care and asks her statistician friend which drug has the highest probability of being the most effective. The statistician says, "It is clear that drug A is the most effective drug 54% of the time. Thus drug A is your best bet."

Later a new drug C becomes available. Studies show that on the scale of 1 to 6, 22% of the time this drug scores a 6, 22% of the time it scores a 4, and 56% of the time it scores a 2. The doctor, again wishing to provide her patients with the best possible care, goes back to her statistician friend and asks him which drug has the highest probability of being the most effective. The statistician says, "Because there is this new drug C on the market, your best bet is now drug B, and drug A is your worst bet." Show that the statistician is right.

Problem 3.90. Three cards are in a hat. One card is white on both sides, the second is white on one side and red on the other, and the third is red on both sides. The dealer shuffles the cards, takes one out and places it flat on the table. The side showing is red. The dealer now says, "Obviously this card is not the white-white card. It must be either the red-white card or the red-red card. I will bet even money that the other side is red." Is this bet fair?

Problem 3.91. Will an asteroid impact the Earth?

Estimate the probability that an asteroid will impact the Earth and cause major damage. Does it make sense for society to take steps now to guard itself against such an occurrence?

***Problem 3.92.** Response to rare events

The likelihood of the breakdown of the levees near New Orleans was well known before their occurrence on August 30, 2005. Discuss the various reasons why the decision was made not to strengthen the levees. Relevant issues include the ability of people to think about the probability of rare events and the large amount of money needed to strengthen the levees to withstand such an event.

*∗**Problem 3.93.*** Science and society issues

Does capital punishment deter murder? Are vegetarians more likely to have daughters? Does it make sense to talk about a "hot hand" in basketball? Are the digits of π random? See <chance.dartmouth.edu/chancewiki/> and <www.dartmouth.edu/~chance/> and read about interesting issues involving probability and statistics.

Suggestions for further reading

Vinay Ambegaokar, *Reasoning About Luck*, Cambridge University Press (1996). A book developed for a course intended for non-science majors. An excellent introduction to statistical reasoning and its uses in physics.

Peter L. Bernstein, *Against the Gods: The Remarkable Story of Risk*, John Wiley & Sons (1996). The author is a successful investor and an excellent writer. The book includes an excellent summary of the history of probability.

David S. Betts and Roy E. Turner, *Introductory Statistical Mechanics*, Addison-Wesley (1992). Section 3.4 is based in part on Chapter 3 of this text.

Jean-Phillippe Bouchaud and Marc Potters, *Theory of Financial Risks*, Cambridge University Press (2000). This book by two physicists is an example of the application of concepts in probability and statistical mechanics to finance. Although the treatment is at the graduate level and assumes some background in finance, it is recommended for students who might be interested in the overlap of physics, finance, and economics. Also see J. Doyne Farmer, Martin Shubik, and Eric Smith, "Is economics the next physical science?," Phys. Today **58** (9), 37–42 (2005). A related book on the importance of rare events is by Nassim Nicholas Taleb, *The Black Swan: The Impact of the Highly Improbable*, Random House (2007).

The <www.dartmouth.edu/~chance/> encourages its users to apply statistics to everyday events.

Giulio D'Agostini, "Teaching statistics in the physics curriculum: Unifying and clarifying role of subjective probability," Am. J. Phys. **67**, 1260–1268 (1999). The author, whose main research interest is in particle physics, discusses subjective probability and Bayes' theorem. Section 3.4 is based in part on this article.

See <www.math.uah.edu/stat/objects/> for a simulation of the Galton board.

Gene F. Mazenko, *Equilibrium Statistical Mechanics*, John Wiley & Sons (2000). Sections 1.7 and 1.8 of this graduate level text discuss the functional form of the missing information.

Elliott W. Montroll and Michael F. Shlesinger, "On the wonderful world of random walks," in *Studies in Statistical Mechanics*, Vol. XI: Nonequilibrium Phenomena II, J. L. Lebowitz and E. W. Montroll, editors, North-Holland (1984).

Elliott W. Montroll and Wade W. Badger, *Introduction to Quantitative Aspects of Social Phenomena*, Gordon and Breach (1974). The applications of probability that are discussed include traffic flow, income distributions, floods, and the stock market.

Richard Perline, "Zipf's law, the central limit theorem, and the random division of the unit interval," Phys. Rev. E **54**, 220–223 (1996).

S. Redner, "Random multiplicative processes: An elementary tutorial," Am. J. Phys. **58**, 267–273 (1990).

Charles Ruhla, *The Physics of Chance*, Oxford University Press (1992).

B. Schmittmann and R. K. P. Zia, "'Weather' records: Musings on cold days after a long hot Indian summer," Am. J. Phys. **67**, 1269–1276 (1999). A relatively simple introduction to the statistics of extreme values. Suppose that somebody breaks the record for the 100 meter dash. How long do records typically survive before they are broken?

Kyle Siegrist at the University of Alabama in Huntsville has developed many applets to illustrate concepts in probability and statistics. See `<www.math.uah.edu/stat/>` and follow the link to Bernoulli processes.

G. Troll and P. beim Graben, "Zipf's law is not a consequence of the central limit theorem," Phys. Rev. E **57**, 1347–1355 (1998).

Hans Christian von Baeyer, *Information: The New Language of Science*, Harvard University Press (2004). This book raises many profound issues and is not an easy read even though it is well written. Read it in small doses.

Charles A. Whitney, *Random Processes in Physical Systems: An Introduction to Probability-Based Computer Simulations*, John Wiley & Sons (1990).

A discussion by Eliezer Yudkowsky of the intuitive basis of Bayesian reasoning can be found at `<yudkowsky.net/bayes/bayes.html>`.

R. K. P. Zia and B. Schmittmann, "Watching a drunkard for 10 nights: A study of distributions of variances," Am. J. Phys. **71**, 859–865 (2003). See Problem 3.74.

The outcome of tossing a coin is not really random. See Ivars Peterson, "Heads or tails?," Science News Online, `<www.sciencenews.org/articles/20040228/mathtrek.asp>` and Erica Klarreich, "Toss out the toss-up: Bias in heads-or-tails, Science News **165** (9), 131 (2004), `<http://www.sciencenews.org/articles/20040228/fob2.asp>`. Some of the original publications include Joseph Ford, "How random is a coin toss?," Phys. Today **36** (4), 40–47 (1983); Joseph B. Keller, "The probability of heads," Am. Math. Monthly **93**, 191–197 (1986); and Vladimir Z. Vulovic and Richard E. Prange, "Randomness of a true coin toss," Phys. Rev. A **33**, 576–582 (1986).

Chapter 4

The Methodology of Statistical Mechanics

We develop the basic methodology of statistical mechanics and provide a microscopic foundation for the concepts of temperature and entropy.

4.1 Introduction

We first discuss a simple example to make explicit the probabilistic assumptions and nature of calculations in statistical mechanics.

Consider an isolated system of $N = 5$ noninteracting spins with magnetic moment μ and spin $1/2$ in a magnetic field B. If the total energy $E = -\mu B$, what is the mean magnetic moment of a given spin in the system? The essential steps needed to analyze this system can be summarized as follows.

1. Specify the macrostate and accessible microstates of the system. The macroscopic state or *macrostate* of the system corresponds to the information that we know. For this example the observable quantities are the total energy E, the magnetization M, the number of spins N, and the external magnetic field B. (Because the spins are noninteracting, it is redundant to specify both M and E.)

The most complete specification of the system corresponds to the enumeration of the *microstates* or *configurations* of the system. For $N = 5$ there are $2^5 = 32$ total microstates, each specified by the orientation of the N spins. However, not all of the 32 microstates are consistent with the information that $E = -\mu B$. For example, $E = -5\mu B$ for the microstate shown in Figure 4.1(a) is not allowed, that is, such a state is inaccessible. The *accessible* microstates of the system are those that are consistent with the macroscopic conditions. In this example, ten of the thirty-two total microstates are accessible (see Figure 4.1(b)).
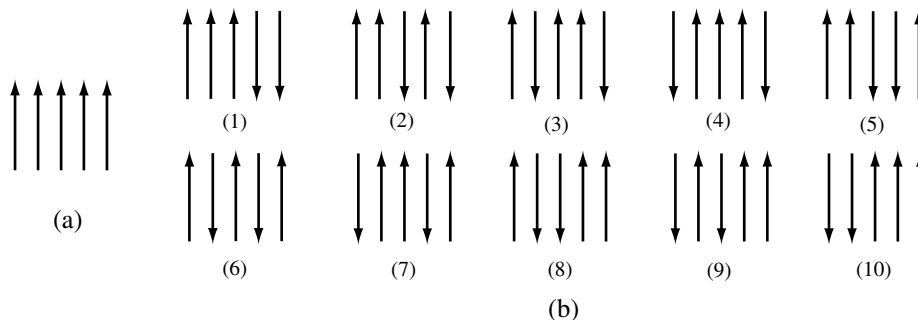
Figure 4.1: (a) Example of an inaccessible macrostate for the ensemble specified by $E = -\mu B, N = 5$. (b) The ten accessible members of the ensemble. Spin 1 is the left most spin.

2. Choose the ensemble. We calculate averages by preparing a collection of identical systems all of which satisfy the macroscopic conditions $E = -\mu B$ and $N = 5$. In this example the ensemble consists of ten systems each of which is in one of the ten accessible microstates.

What can we say about the relative probability of finding the system in one of the ten accessible microstates? Because the system is isolated and each microstate is consistent with the specified macroscopic information, we assume that each microstate in the ensemble is equally likely. This assumption of *equal a priori probabilities* implies that the probability P_n that the system is in microstate n is given by

$$P_n = \frac{1}{\Omega}, \tag{4.1}$$

where Ω represents the number of microstates of energy E. This assumption is equivalent to the principle of least bias or maximum uncertainty that we discussed in Section 3.4.1. For our example, we have $\Omega = 10$, and the probability that the system is in any one of its accessible microstates is $1/10$.

3. Calculate the mean values and other statistical properties. As an example of a probability calculation, we calculate the mean value of the orientation of spin 1 (see Figure 4.1(b)). Because s_1 assumes the value ± 1, we have

$$\langle s_1 \rangle = \sum_{n=1}^{10} P_n s_n \tag{4.2a}$$

$$= \frac{1}{10} \big[(+1) + (+1) + (+1) + (-1) + (+1) + (+1) + (-1) + (+1) + (-1) + (-1) \big] \tag{4.2b}$$

$$= \frac{2}{10} = \frac{1}{5}. \tag{4.2c}$$

The sum is over all the accessible microstates and s_n is the value of spin 1 in the nth member of the ensemble. We see from (4.2c) that the mean value of s_1 is $\langle s_1 \rangle = 1/5$.

Problem 4.1. Simple example

(a) What is the mean value of spin 2 in the above example?

(b) What is the probability p that a given spin points up?

(c) What is the probability that if spin 1 is up, then spin 2 also is up?

There is a more direct way of calculating $\bar{s}_1$ in this case. Because $M = 1$, six out of the ten spins are up. The equivalency of the spins implies that the probability of a spin being up is $6/10$. Hence, $\bar{s} = (3/5)(1) + (2/5)(-1) = 1/5$. What is the implicit assumption that we made in the more direct method?

Problem 4.2. Counting microstates

Consider $N = 4$ noninteracting spins with magnetic moment μ and spin $1/2$ in a magnetic field B.

(a) If the total energy $E = -2\mu B$, what are the accessible microstates and the probabilities that a particular spin has a magnetic moment $\pm\mu$?

(b) Consider $N = 9$ noninteracting spins with total energy $E = -\mu B$. What is the net number of up spins, the number of accessible microstates, and the probabilities that a particular spin has magnetic moment $\pm\mu$?

Problem 4.3. Consider a one-dimensional ideal gas consisting of $N = 5$ particles each of which has the same speed v, but velocity $\pm \mathbf{v}$. The velocity of each particle is independent. What is the probability that all the particles are moving in the same direction?

The model of noninteracting spins that we have considered is an example of an *isolated system*. In this case the system of spins has fixed values of E, B, and N. In general, an isolated system cannot exchange energy or matter with its surroundings nor do work on another system. The macrostate of such a system is specified by E, V, and N (B instead of V for a magnetic system). Our strategy will be to first understand how to treat isolated systems. Conceptually, isolated systems are simpler because all the accessible microstates have the same probability (see Section 4.5).

4.2   A Simple Example of a Thermal Interaction

Now that we have an idea of how we can do probability calculations for an isolated system, we next consider some model systems that can exchange energy with another system. This exchange has the effect of relaxing one of the internal constraints and, as we will see, imposing another. We will see that for nonisolated systems, the probability of each microstate is not the same.

We know what happens when we place two bodies at different temperatures into thermal contact with one another – energy is transferred from the hotter to the colder body until thermal equilibrium is reached and the two bodies have the same temperature. We now consider a simple model that illustrates how statistical concepts can help us understand the transfer of energy and the microscopic nature of thermal equilibrium.

Consider a model system of N noninteracting distinguishable particles such that the energy of each particle is restricted to integer values, that is, $\epsilon_n = 0,\ 1,\ 2,\ 3,\ \ldots$ We can distinguish the particles by their colors, or we can assume that the particles have the same color, but are fixed on

microstate	red	white	blue
1	1	1	1
2	2	0	1
3	2	1	0
4	1	0	2
5	1	2	0
6	0	1	2
7	0	2	1
8	3	0	0
9	0	3	0
10	0	0	3

Table 4.1: The ten accessible microstates of a system of $N = 3$ distinguishable particles with total energy $E = 3$. Each particle may have energy 0, 1, 2, ...

lattice sites. For reasons that we will discuss in Section 6.11, we will refer to this model system as an Einstein solid.[1]

Consider an Einstein solid with $N = 3$ particles (with colors red, white, and blue) in an isolated box and total energy $E = 3$. For these small values of N and E, we can enumerate the accessible microstates by hand. The ten accessible microstates of this system are shown in Table 4.1. Because the energy is specified, the ten accessible microstates are equally probable. What is the probability that if one particle has energy 1, another particle has energy 2?

Problem 4.4. Consider an Einstein solid composed of N particles with total energy E. It can be shown that the general expression for the number of microstates of this system is

$$\Omega = \frac{(E + N - 1)!}{E!\,(N - 1)!}. \tag{4.3}$$

(a) Verify that this expression yields the correct answers for the case $N = 3$ and $E = 3$.

(b) What is the number of microstates for an Einstein solid with $N = 4$ and $E = 6$?

Now that we know how to enumerate the number of microstates for an Einstein solid, consider an isolated system of $N = 4$ particles that is divided into two *subsystems* surrounded by insulating, rigid, impermeable outer walls and separated by a similar partition (see Figure 4.2). Subsystem A consists of two particles, R (red) and G (green), with $E_A = 5$; subsystem B consists of two particles, B (black) and W (white), with energy $E_B = 1$. The total energy E of the composite system consisting of subsystem A plus subsystem B is

$$E = E_A + E_B = 5 + 1 = 6. \tag{4.4}$$

The accessible microstates for the composite system are shown in Table 4.2. We see that subsystem A has $\Omega_A = 6$ accessible microstates and subsystem B has $\Omega_B = 2$ accessible microstates. The total number of microstates Ω accessible to the composite system is

$$\Omega = \Omega_A \times \Omega_B = 6 \times 2 = 12. \tag{4.5}$$

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[1]These particles are equivalent to the quanta of the harmonic oscillator, which have energy $E_n = (n + \frac{1}{2})\hbar\omega$. If we measure the energies from the lowest energy state, $\frac{1}{2}\hbar\omega$, and choose units such that $\hbar\omega = 1$, we have $\epsilon_n = n$.
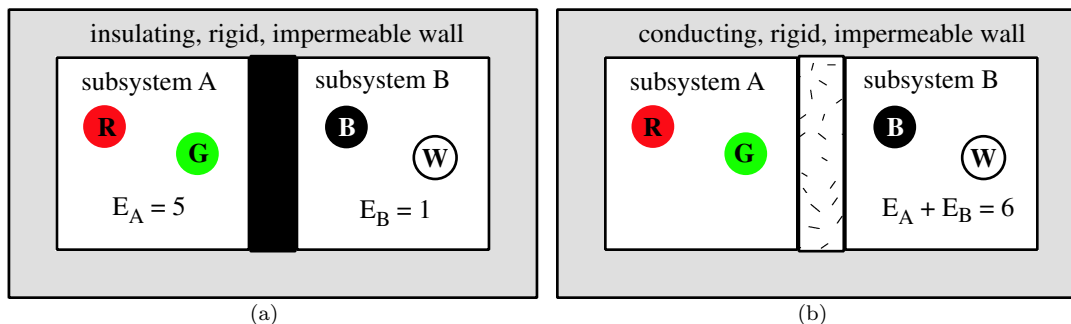
Figure 4.2: Two subsystems, each with two distinguishable particles, surrounded by (a) insulating, rigid, and impermeable outer walls and (b) separated by a conducting, rigid, and impermeable wall. The other walls remain the same.

The partition is an internal constraint that prevents the transfer of energy from one subsystem to another and in this case keeps $E_A = 5$ and $E_B = 1$. (The internal constraint also keeps the volume and number of particles in each subsystem fixed.)

E_A	accessible microstates		E_B	accessible microstates	
	5,0	0,5		1,0	0, 1
5	4,1	1,4	1		
	3,2	2,3			

Table 4.2: The 12 equally probable microstates accessible to subsystems A and B before the removal of the internal constraint. The conditions are $N_A = 2$, $E_A = 5$, $N_B = 2$, and $E_B = 1$.

We now consider a simple example of a thermal interaction. Suppose that the insulating, rigid, impermeable partition separating subsystems A and B is changed to a conducting, rigid, impermeable partition (see Figure 4.2). The partition maintains the volumes V_A and V_B, and hence the single particle energies are not changed. Because the partition is impermeable, the particles cannot penetrate the partition and go from one subsystem to the other. However, energy can be transferred from one subsystem to the other, subject only to the constraint that the total energy of subsystems A and B is constant, that is, $E = E_A + E_B = 6$. The microstates of subsystems A and B are listed in Table 4.3 for all the possible values of E_A and E_B. The total number of microstates $\Omega(E_A, E_B)$ accessible to the composite system whose subsystems have energy E_A and E_B is

$$\Omega(E_A, E_B) = \Omega_A(E_A) \times \Omega_B(E_B). \tag{4.6}$$

For example. if $E_A = 4$ and $E_B = 2$, then subsystem A can be in any one of five microstates and subsystem B can be in any of three microstates. These two sets of microstates of subsystems A and B can be combined to give $5 \times 3 = 15$ microstates of the composite system.

The total number of microstates Ω accessible to the composite system can be found by summing $\Omega_A(E_A)\Omega_B(E_B)$ over the possible values of E_A and E_B consistent with the condition that

E_A	microstates		$\Omega_A(E_A)$	E_B	microstates		$\Omega_B(E_B)$	$\Omega_A\Omega_B$
6	6,0	0,6	7	0	0,0		1	7
	5,1	1,5						
	4,2	2,4						
	3,3							
	5,0	0,5	6		1,0	0,1	2	12
5	4,1	1,4		1				
	3,2	2,3						
	4,0	0,4	5		2,0	0,2	3	15
4	3,1	1,3		2	1,1			
	2,2							
3	3,0	0,3	4	3	3,0	0,3	4	16
	2,1	1,2			2,1	1,2		
2	2,0	0,2	3	4	4,0	0,4	5	15
	1,1				3,1	1,3		
					2,2			
1	1,0	0,1	2	5	5,0	0,5	6	12
					4,1	1,4		
					3,2	2,3		
0		0,0	1	6	6,0	0,6	7	7
					5,1	1,5		
					4,2	2,4		
					3,3			

Table 4.3: The 84 equally probable microstates accessible to the composite system consisting of subsystems A and B after the removal of the internal constraint. The total energy is $E = E_A + E_B = 6$ with $N_A = 2$ and $N_B = 2$.

$E_A + E_B = 6$. Hence, Ω can be expressed as

$$\Omega = \sum_{E_A} \Omega_A(E_A)\Omega_B(E - E_A). \tag{4.7}$$

From Table 4.3 we see that

$$\Omega = (7 \times 1) + (6 \times 2) + (5 \times 3) + (4 \times 4) + (3 \times 5) + (2 \times 6) + (1 \times 7) = 84. \tag{4.8}$$

Because the composite system is isolated, its accessible microstates are equally probable, that is, the composite system is equally likely to be in any one of its 84 accessible microstates. An inspection of Table 4.3 shows that the probability that the energy of the composite system is divided such that $E_A = 2$ and $E_B = 4$ is 15/84. Let $P_A(E_A)$ be the probability that subsystem A has energy E_A. Then $P_A(E_A)$ is given by

$$P_A(E_A) = \frac{\Omega_A(E_A)\Omega_B(E - E_A)}{\Omega}. \tag{4.9}$$

We show in Table 4.4 and Figure 4.3 the various values of $P_A(E_A)$.

E_A	$\Omega_A(E_A)$	$\Omega_B(6 - E_A)$	$\Omega_A\Omega_B$	$P_A(E_A)$
6	7	1	7	7/84
5	6	2	12	12/84
4	5	3	15	15/84
3	4	4	16	16/84
2	3	5	15	15/84
1	2	6	12	12/84
0	1	7	7	7/84

Table 4.4: The probability $P_A(E_A)$ that subsystem A has energy E_A.
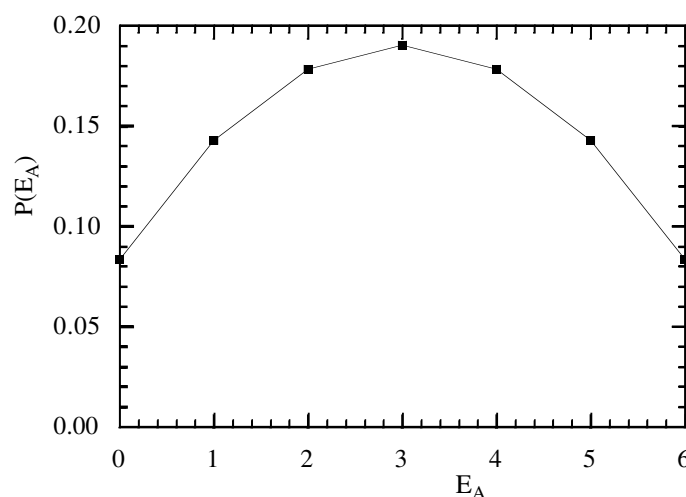
Figure 4.3: The probability $P_A(E_A)$ that subsystem A has energy E_A. The line between the points is only a guide to the eye.

The mean energy of subsystem A is found by doing an ensemble average over the 84 microstates accessible to the composite system. We use the results for $P_A(E_A)$ in Table 4.4 and find that

$$\overline{E}_A = \left(0 \times \frac{7}{84}\right) + \left(1 \times \frac{12}{84}\right) + \left(2 \times \frac{15}{84}\right) + \left(3 \times \frac{16}{84}\right) + \left(4 \times \frac{15}{84}\right) + \left(5 \times \frac{12}{84}\right) + \left(6 \times \frac{7}{84}\right) = 3. \quad (4.10)$$

In this simple case the mean value of E_A is equal to $\tilde{E}_A$, the energy corresponding to the most probable value of $P_A(E_A)$.

Problem 4.5. Use the results of Table 4.4 to find the standard deviation of the energy of subsystem A.

Note that the total number of microstates accessible to the composite system increases from 12 to 84 when the internal constraint is removed. From the microscopic point of view, it is clear that the total number of microstates must either remain the same or increase when an

internal constraint is removed. Because the number of microstates becomes a very large number for macroscopic systems, it is convenient to work with the logarithm of the number of microstates. We are thus led to define the quantity S by the relation

$$S = k \ln \Omega, \tag{4.11}$$

where k is an arbitrary constant. Note the similarity of the definition (4.11) to the expression for the missing information (3.37). We will later identify the quantity S that we have introduced in (4.11) with the thermodynamic entropy we discussed in Chapter 2.

Although our simple model has only four particles, we can ask questions that are relevant to much larger systems. For example, what is the probability that energy is transferred from the "hotter" to the "colder" subsystem? Given that $E_A = 5$ and $E_B = 1$ initially, we see from Table 4.4 that the probability of subsystem A gaining energy when the internal constraint is removed is 7/84. The probability that its energy remains unchanged is 12/84. In the remaining 65/84 cases, subsystem A loses energy and subsystem B gains energy. We expect that if the two subsystems had a larger number of particles, the overwhelming probability would be that that energy goes from the hotter to the colder subsystem.

Problem 4.6. Two Einstein solids in thermal contact

Consider two Einstein solids with $N_A = 3$ and $E_A = 4$ and $N_B = 4$ and $E_B = 2$ initially. The two systems are thermally isolated from one another.

(a) Use the relation (4.3) to determine the initial number of accessible microstates for the composite system.

(b) Then remove the internal constraint so that the two subsystems may exchange energy. Determine the probability $P_A(E_A)$ that system A has energy E_A, the most probable energies $\tilde{E}_A$ and $\tilde{E}_B$, the probability that energy goes from the hotter to the colder system, and the mean and variance of the energy of each subsystem.

(c) Plot P_A versus E_A and discuss its qualitative energy dependence. Make a table similar to the one in Table 4.3, but do not list the microstates explicitly.

Problem 4.7. The applet/application at `<stp.clarku.edu/simulations/EinsteinSolid.html>` determines the number of accessible microstates of an Einstein solid using (4.3) and will help you answer the following questions. Suppose that initially system A has $N_A = 4$ particles with energy $E_A = 10$ and system B has $N_B = 4$ particles with energy $E_B = 2$. Initially, the two systems are thermally isolated from one another. The initial number of states accessible to subsystem A is given by $\Omega_A = 13!/(10!\,3!) = 286$, and the initial number of states accessible to subsystem B is $\Omega_B = 5!/(2!\,3!) = 10$. Then the internal constraint is removed so that the two subsystems may exchange energy.

(a) Determine the probability $P_A(E_A)$ that system A has energy E_A, the most probable energies $\tilde{E}_A$ and $\tilde{E}_B$, the mean and variance of the energy of each subsystem, and the probability that energy goes from the hotter to the colder system.

(b) Discuss the qualitative energy dependence of $P_A(E_A)$.

(c) What is the number of accessible microstates for the (composite) system after the internal constraint has been removed? What is the total entropy (choose units such that $k = 1$)? What is the change in the total entropy of the system?

(d) The entropy of the composite system when each subsystem is in its most probable macrostate is $k \ln \Omega_A(\tilde{E}_A)\Omega_B(E - \tilde{E}_A)$. Compare the value of this contribution to the value of the total entropy, $k \sum_{E_A} \ln \Omega_A(E_A)\Omega_B(E - E_A)$.

(e) Increase N_A, N_B, and the total energy by a factor of ten, and discuss the qualitative changes in the various quantities of interest. Consider successively larger systems until you have satisfied yourself that you understand the qualitative behavior of the various quantities.

Problem 4.8. Suppose that system A is an Einstein solid with $N_A = 8$ particles and system B consists of $N_B = 8$ noninteracting spins that can be either up or down. The external magnetic field is such that $\mu B = 1/2$. The magnitude of μB has been chosen so that the changes in the energy of system B are the same as system A, that is, $\Delta E = \pm 1$. The two systems are initially isolated and the initial energies are $E_A = 4$ and $E_B = 4$. What is the initial entropy of the composite system? Use the fact that $\Omega_B = N_B!/(n!\,(N_B - n)!)$, where n is the number of up spins in system B (see Section 3.5). Remove the internal constraint and allow the two systems to exchange energy. Determine the probability $P_A(E_A)$ that system A has energy E_A, the mean and variance of the energy of each subsystem, the most probable energies $\tilde{E}_A$ and $\tilde{E}_B$, and the probability that energy goes from the hotter to the colder system. What is the change in the total entropy of the system?

From our examples, we conclude that we can identify thermal equilibrium with the most probable macrostate and the entropy with the logarithm of the number of accessible microstates, We also found that the probability $P(E)$ that a system has energy E is approximately a Gaussian if the system is in thermal equilibrium with a much bigger system. What quantity can we identify with the temperature? The results of Problem 4.8 if you were not convinced already, that in general, this quantity is not same as the mean energy per particle of the two systems.

Let's return to the Einstein solid and explore the energy dependence of the entropy. Consider a system with $N_A = 3$, $N_B = 4$, and total energy $E = 10$. The number of microstates for the two systems for the various possible values of E_A are summarized in Table 4.5. We see that that the most probable energies and hence thermal equilibrium corresponds to $\tilde{E}_A = 4$ and $\tilde{E}_B = 6$. In general, what quantity is the same for system A and B at equilibrium? From our understanding of thermal equilibrium, we know that this quantity must be the temperature. In columns 5 and 10 of Table 4.5 we show the inverse slope of the entropy $S_A(E_A)$ and $S_B(E_B)$ of systems A and B calculated from the central difference approximation for the slope at E. For example,

$$\frac{1}{T_A(E_A)} \approx \frac{[S_A(E_A + \Delta E_A) - S(E_A - \Delta E_A)]}{2\Delta E_A}. \tag{4.12}$$

(We have chosen units such that Boltzmann's constant $k = 1$.) We see that the inverse slopes are approximately equal at $E_A = \tilde{E}_A = 4$, corresponding to the value of the most probable energy. (For this small system, the entropy of the composite system is not simply equal to the sum of the entropies of the most probable macrostate, and we do not expect the slopes to be precisely equal.

To obtain more insight into how temperature is related to the slope of the entropy, we look at an energy away from equilibrium, say $E_A = 2$ in Table 4.5. Note that the slope of $S_A(E_A = 2)$,

E_A	$\Omega_A(E_A)$	$\ln\Omega_A(E_A)$	T_A^{-1}	T_A	E_B	$\Omega_B(E_B)$	$\ln\Omega_B(E_B)$	T_B^{-1}	T_B	$\Omega_A\Omega_B$
10	66	4.19	na	na	0	1	0	na	na	66
9	55	4.01	0.19	5.22	1	4	1.39	1.15	0.87	220
8	45	3.81	0.21	4.72	2	10	2.30	0.80	1.24	450
7	36	3.58	0.24	4.20	3	20	3.00	0.63	1.60	720
6	28	3.33	0.27	3.71	4	35	3.56	0.51	1.94	980
5	21	3.05	0.31	3.20	5	56	4.03	0.44	2.28	1176
4	15	2.71	0.37	**2.70**	6	84	4.43	0.38	**2.60**	1260
3	10	2.30	0.46	2.18	7	120	4.79	0.34	2.96	1200
2	6	1.79	0.60	1.66	8	165	5.11	0.30	3.30	990
1	3	1.10	0.90	1.11	9	220	5.39	0.28	3.64	660
0	1	0	na	na	10	286	5.66	na	na	286

Table 4.5: The number of states for subsystems A and B for total energy $E = E_A + E_B = 10$ with $N_A = 3$ and $N_B = 4$. The number of states was determined using (4.3). There are a total of 8008 microstates. The most probable energy of subsystem A is $\tilde{E}_S = 4$ and the fraction of microstates associated with the most probable macrostate is $1260/8008 \approx 0.157$. This fraction will approach unity as the number of particles in the systems become larger.

0.60, is steeper than the slope, 0.30, of $S_B(E_B = 8)$, which means that if energy is passed from A to B, the entropy gained by A will be greater than the entropy lost by B, and the total entropy would increase. Because we know that the entropy is a maximum in equilibrium and energy is transferred spontaneously from "hot" to "cold," a steeper slope must correspond to a lower temperature. This reasoning suggests that the temperature is associated with the inverse slope of the energy dependence of the entropy.

Problem 4.9. The applet/application at `<stp.clarku.edu/simulations/entropy.html>` computes the entropies of two Einstein solids in thermal contact. Explore the effect of increasing the values of N_A, N_B, and the total energy E. Discuss the qualitative dependence of S_A, S_B, and S_{total} on the energy E_A. In particular, explain why S_A is an increasing function of E_A and S_B is a decreasing function of E_A. Given this dependence of S_A and S_B on E_A, why does S_{total} have a maximum at a particular value of E_A?

You might wish to skip to Section 4.5 where we will formally develop the relations between the number of accessible microstates of an isolated system to various quantities including the entropy and the temperature.

Boltzmann probability distribution. We next consider the Einstein solid in another physical context. Consider an isolated Einstein solid of six particles with total energy $E = 12$. We focus our attention on one of the particles and consider it to be a subsystem able to exchange energy with the other five particles. This example is similar to the ones we have considered, but in this case the subsystem consists of only one particle. The quantity of interest is the mean energy of the subsystem and the probability P_n that the subsystem is in state n with energy ϵ_n. The number of ways that the subsystem can be in state n is unity because the subsystem consists of only one particle. So for this special subsystem of one particle, there is a one-to-one correspondence between the microstate of the system and the energy of the system.

microstate n	ϵ_n	$E - \epsilon_n$	Ω_B		P_n
12	12	0	$4!/(0!\,4!) =$	1	0.00016
11	11	1	$5!/(1!\,4!) =$	5	0.00081
10	10	2	$6!/(2!\,4!) =$	15	0.00242
9	9	3	$7!/(3!\,4!) =$	35	0.00566
8	8	4	$8!/(4!\,4!) =$	70	0.01131
7	7	5	$9!/(5!\,4!) =$	126	0.02036
6	6	6	$10!/(6!\,4!) =$	210	0.03394
5	5	7	$11!/(7!\,4!) =$	330	0.05333
4	4	8	$12!/(8!\,4!) =$	495	0.07999
3	3	9	$13!/(9!\,4!) =$	715	0.11555
2	2	10	$14!/(10!\,4!) =$	1001	0.16176
1	1	11	$15!/(11!\,4!) =$	1365	0.22059
0	0	12	$16!/(12!\,4!) =$	1820	0.29412

Table 4.6: The number of microstates accessible to a subsystem of one particle that can exchange energy with a system of five particles. The subsystem is in microstate n with energy $\epsilon_n = n$. The third column is the energy of the system of $N = 5$ particles. The total energy of the composite system is $E = 12$. The total number of microstates is 6188.

The number of accessible microstates of the composite system is shown in Table 4.6 using the relation (4.3). From Table 4.6 we can determine the mean energy of the subsystem of one particle:

$$\bar{\epsilon} = \sum_{n=0}^{12} \epsilon_n P_n = \frac{1}{6188}\big[(0 \times 1820) + (1 \times 1365) + (2 \times 1001) + (3 \times 715) + (4 \times 495) + (5 \times 330)$$
$$+ (6 \times 210) + (7 \times 126) + (8 \times 70) + (9 \times 35) + (10 \times 15) + (11 \times 5) + (12 \times 1)\big]$$
$$= 2. \tag{4.13}$$

The probability P_n that the subsystem is in microstate n is plotted in Figure 4.4. Note that P_n decreases monotonically with increasing energy. A visual inspection of the energy dependence of P_n in Figure 4.4 indicates that P_n can be approximated by an exponential of the form

$$P_n = \frac{1}{Z} e^{-\beta \epsilon_n}, \tag{4.14}$$

where $\epsilon_n = n$ in this example and Z is a normalization constant. Given the form (4.14), we can estimate the parameter β from the slope of $\ln P_n$ versus ϵ_n. The result is that $\beta \approx 0.57$. You might wish to skip to Section 4.6 to read about the generalization of these results.

Problem 4.10. Another Einstein solid

Consider an Einstein solid with $N_A = 1$ and $N_B = 3$ with a total energy $E = 6$.

(a) Calculate the probability P_n that system A is in microstate n. Is this probability the same as the probability that the system A has energy ϵ_n?
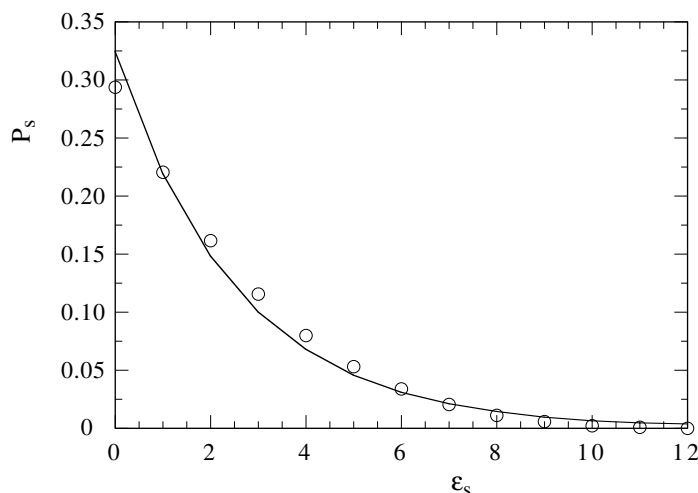
Figure 4.4: The probability P_n for the subsystem to be in state n with energy $\epsilon_n = n$. The subsystem can exchange energy with a system of $N = 5$ particles. The total energy of the composite system of six particles is $E = 12$. The circles are the values of P_n given in Table 4.6. The continuous line corresponds to P_n calculated from (4.14) with $\beta = 0.57$.

(b) In Table 4.3 we considered a similar composite system of four particles, except that $N_A = 2$, in contrast to part a for which $N_A = 1$. Why does the probability calculated in part a differ from that calculated in part prob:4/pn.b?

Problem 4.11. From Table 4.3 determine the probability P_n that system A is in microstate n with energy E_n for the different possible energies of A. (The microstate n corresponds to the state of system A.) What is the qualitative dependence of P_n on E_n, the energy of the microstate?

Problem 4.12. Use the applet/application at <stp.clarku.edu/simulations/EinsteinSolid.html> to compute the probability P_n that a subsystem of one particle is in microstate n, assuming that it can exchange energy with an Einstein solid of $N = 11$ particles. The total energy of the two systems is $E = 36$.

(a) Compare your result for P_n to the form (4.14) and compute the parameter β from a semilog plot. Also determine the mean energy of the subsystem of one particle and show that it is given by $\epsilon \approx 1/\beta$.

(b) Calculate the constant Z by normalizing the probability and show that Z is given approximately by $Z = (1 - e^{-\beta})^{-1}$.

We will generalize the results we have found here in Example 4.4.

Problem 4.13. Qualitative behavior of the probabilities

(a) Explain why the probability $P_n(E_n)$ that system A is in microstate n with energy E_n is a monotonically decreasing function of E_n, given that the system is in thermal contact with a

much larger system. (We could equally well write $P_n(E_n)$ as $P_n(E_A)$, but we choose the former notation to emphasize that the system is in a particular microstate. The specification of E_A alone specifies the macrostate of the system.)

(b) Explain why the probability $P_A(E_A)$ that system A has energy E_A has a Gaussian-like form.

Problem 4.14. Rapid increase in the number of states

(a) Consider an Einstein solid of $N = 10$ distinguishable oscillators. What is the total number of accessible microstates $\Omega(E)$ for $E = 10, 10^2, 10^3, \ldots$? Is $\Omega(E)$ a rapidly increasing function of E for fixed N?

(b) Is Ω a rapidly increasing function of N for fixed E?

(c) Use Stirling's approximation (3.103) to find the large E behavior of Ω for fixed $N \gg 1$.

4.3 Counting Microstates

In the examples we have considered so far, we have seen that the most time consuming task is enumerating (counting) the number of accessible microstates for a system of fixed energy and number of particles. We now discuss how to count the number of accessible microstates for several other systems of interest.

4.3.1 Noninteracting spins

We first reconsider an isolated system of N noninteracting spins with spin $1/2$ and magnetic moment μ in an external magnetic field B. Because we can distinguish spins at different lattice sites, a particular state or configuration of the system is specified by giving the orientation (up or down) of each of the N spins. We want to find the total number of accessible microstates $\Omega(E, B, N)$ for particular values of E, B, and N.

We know that if n spins are parallel to B and $N - n$ spins are antiparallel to B, the energy of the system is

$$E = n(-\mu B) + (N - n)(\mu B) = -(2n - N)\mu B. \tag{4.15}$$

For a given N and B, n specifies the energy and vice versa. If we solve (4.15) for n, we find

$$n = \frac{N}{2} - \frac{E}{2\mu B}. \tag{4.16}$$

As we found in (3.88), the total number of microstates with energy E is given by the number of ways n spins out of N can be up. This number is given by

$$\Omega(n, N) = \frac{N!}{n!\,(N - n)!}, \tag{4.17}$$

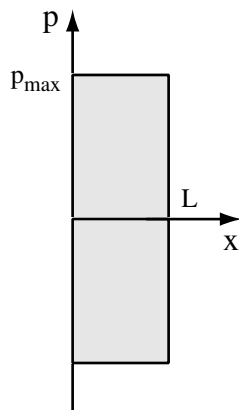where n is related to E by (4.16). We will apply this result in Example 4.2 on page 191.

Figure 4.5: The phase space for a single particle of mass m and energy E in a one-dimensional box of length L. The maximum value of the momentum is $p_{\max} = \sqrt{2mE}$. Any point within the shaded rectangle corresponds to a microstate with energy less than or equal to E.

4.3.2   *One-dimensional Ising model

It is instructive to discuss the number of states for the one-dimensional Ising model. For small N we can determine $\Omega(E, N)$ by counting on our fingers. For example, it is easy to verify that $\Omega(-2, 2) = 2$ and $\Omega(0, 2) = 2$ and $\Omega(-3, 3) = 2$ and $\Omega(1, 3) = 6$ using periodic boundary conditions. The general expression for $\Omega(E, N)$ for the one-dimensional Ising model for even N in the absence of an external magnetic field is

$$\Omega(E, N) = 2\binom{N}{i} = 2\frac{N!}{i!\,(N-i)!}, \qquad (i = 0, 2, 4, \ldots, N) \tag{4.18}$$

where $i = (E + N)/2$. The energy E is measured in units of J so E is an integer. We will discuss the Ising model in more detail in Chapter 5.

Problem 4.15. Verify that (4.18) gives the correct answers for $N = 2$ and 4.

4.3.3   A particle in a one-dimensional box

Classical calculation. Consider the microstates of a single classical particle of mass m confined to a one-dimensional box of length L. We know that the microstate of a particle is specified by its position x and momentum p.[2] We say that the microstate (x, p) is a point in *phase space* (see Figure 4.5).

As in Section 4.3.1, we would like to calculate the number of microstates of the system with energy E. Because the values of the position and momenta of a particle are continuous variables, this question is not meaningful and instead we will determine the quantity $g(E)\Delta E$, the number of microstates between E and $E + \Delta E$; the quantity $g(E)$ is the *density of states*. However, it is

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[2]We could equally well specify the velocity v rather than p, but the momentum p is the appropriate conjugate variable to x in the formal treatment of classical mechanics.

easier to first calculate $\Gamma(E)$, the number of microstates of the system with energy less than or equal to E. Then the number of microstates between E and $E + \Delta E$, $g(E)\Delta E$, is related to $\Gamma(E)$ by

$$g(E)\Delta E = \Gamma(E + \Delta E) - \Gamma(E) \approx \frac{d\Gamma(E)}{dE} \Delta E. \tag{4.19}$$

If the energy of the particle is E and the dimension of the box is L, then the microstates of the particle with energy less than or equal to E are restricted to the rectangle shown in Figure 4.5, where $p_{\max} = \sqrt{2mE}$. Because the possible values of x and p are continuous, there are an infinite number of microstates within the rectangle. As we discussed in Section 3.6, we have to group or bin the microstates so that we can count them, and hence we divide the rectangle in Figure 4.5 into bins or cells of area $\Delta x \Delta p$.

The area of phase space occupied by the trajectory of a particle whose position x is less than or equal to L and whose energy is less than or equal to E is equal to $2p_{\max}L$. Hence, the number of cells or microstates equals

$$\Gamma_{\mathrm{cl}}(E) = \frac{2p_{\max}L}{\Delta x \Delta p} = 2\frac{L}{\Delta x \Delta p}(2mE)^{1/2}, \tag{4.20}$$

where the values of Δx and Δp are arbitrary. What is the corresponding density of states?

Quantum calculation. The most fundamental description of matter at the microscopic level is given by quantum mechanics. Although the quantum mechanical description is more abstract, we will find that it makes counting microstates more straightforward.

As before, we consider a single particle of mass m in a one-dimensional box of length L. According to de Broglie, a particle has wave properties associated with it, and the corresponding standing wave has a node at the boundaries of the box. The wave function of the wave with one antinode can be represented as in Figure 4.6; the corresponding wavelength is given by

$$\lambda = 2L. \tag{4.21}$$

In general, the greater the number of antinodes of the wave, the greater the energy associated with the particle. The possible wavelengths that are consistent with the boundary conditions at $x = 0$ and $x = L$ satisfy

$$\lambda_n = \frac{2L}{n}, \qquad (n = 1, 2, 3, \ldots) \tag{4.22}$$

where the index n labels the quantum state of the particle and can be any nonzero, positive integer. From the de Broglie relation,

$$p = \frac{h}{\lambda}, \tag{4.23}$$

and the nonrelativistic relation between the energy E and the momentum p, $E = p^2/2m$, we find that the eigenvalues of a particle in a one-dimensional box are given by

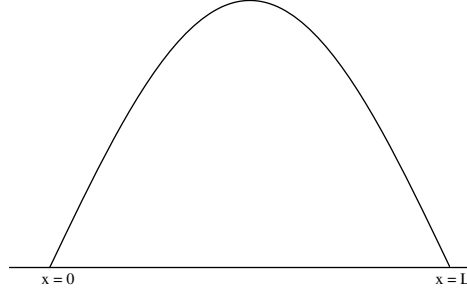$$E_n = \frac{p_n^2}{2m} = \frac{h^2}{2m\,\lambda_n^2} = \frac{n^2 h^2}{8mL^2}. \tag{4.24}$$

Figure 4.6: Representation of the ground state wave function of a particle in a one-dimensional box. Note that the wave function equals zero at $x = 0$ and $x = L$.

It is now straightforward to count the number of microstates with energy less than or equal to E. The value of n for a given E is (see (4.24))

$$n = \frac{2L}{h}(2mE)^{1/2}. \tag{4.25}$$

Because successive microstates correspond to values of n that differ by unity, the number of states with energy less than or equal to E is given by

$$\Gamma_{\text{qm}}(E) = n = \frac{2L}{h}(2mE)^{1/2}. \tag{4.26}$$

Unlike the classical case, the number of states $\Gamma_{\text{qm}}(E)$ for a quantum particle in a one-dimensional box has no arbitrary parameters such as Δx and Δp. If we require that the classical and quantum enumeration of microstates agree in the semiclassical limit,[3] we see that the number of microstates, $\Gamma_{\text{cl}}(E)$ and $\Gamma_{\text{qm}}(E)$, agrees for all E if we let $2/(\Delta x \Delta p) = 1/(\pi\hbar)$. This requirement implies that the area $\Delta x \Delta p$ of a cell in phase space is given by

$$\Delta x \, \Delta p = h. \tag{4.27}$$

We see that Planck's constant h can be interpreted as the volume (area for a two-dimensional phase space) of the fundamental cell in phase space. That is, in order for the counting of microstates in the classical system to be consistent with the more fundamental counting of microstates in a quantum system, we cannot specify a microstate of the classical system more precisely than to assign it to a cell of area h in phase space. This fundamental limitation implies that the subdivision of phase space into cells of volume less than h is physically meaningless, a result consistent with the Heisenberg uncertainty principle.

It will be convenient to introduce the wave vector k by the relation $k = 2\pi/\lambda$. Then we can rewrite the deBroglie relation (4.23) as

$$p = \hbar k. \tag{4.28}$$

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[3]Note that the semiclassical limit is not equivalent to simply letting $\hbar \to 0$.

For a particle in a one-dimensional box, we can express the condition (4.22) for a standing wave as

$$k = \frac{\pi}{L} n. \qquad (n = 1,\, 2,\, 3,\, \ldots) \tag{4.29}$$

Problem 4.16. Suppose that the energy of an electron in a one-dimensional box of length L is $E = 144\,(h^2/8mL^2)$. How many microstates are there with energy less than or equal to this value of E?

4.3.4 One-dimensional harmonic oscillator

The one-dimensional harmonic oscillator provides another example for which we can straightforwardly count the number of microstates in both the classical and quantum cases. The total energy of the harmonic oscillator is given by

$$E = \frac{p^2}{2m} + \frac{1}{2}kx^2, \tag{4.30}$$

where k is the spring constant and m is the mass of the particle.

Classical calculation. The shape of the phase space area traversed by the trajectory $x(t), p(t)$ can be determined from (4.30) by dividing both sides by E and substituting $\omega^2 = k/m$:

$$\frac{x(t)^2}{2E/m\omega^2} + \frac{p(t)^2}{2mE} = 1. \tag{4.31}$$

where the total energy E is a constant of the motion. From the form of (4.31) we see that the shape of phase space of a one-dimensional harmonic oscillator is an ellipse,

$$\frac{x^2}{a^2} + \frac{p^2}{b^2} = 1, \tag{4.32}$$

with $a^2 = 2E/(m\omega^2)$ and $b^2 = 2mE$. Hence, the area of phase space is $\pi ab = 2\pi E/\omega$, and the number of states with energy less than or equal to E is given by

$$\Gamma_{\text{cl}}(E) = \frac{\pi ab}{\Delta x\,\Delta p} = \frac{2\pi E}{\omega\,\Delta x\,\Delta p}. \tag{4.33}$$

Quantum mechanical calculation. The energy eigenvalues of the harmonic oscillator are given by

$$E_n = (n + \frac{1}{2})\,\hbar\omega. \qquad (n = 0,\, 1,\, 2,\, \ldots) \tag{4.34}$$

Hence the number of microstates is given by

$$\Gamma_{\text{qm}}(E) = n = \frac{E}{\hbar\omega} - \frac{1}{2} \rightarrow \frac{E}{\hbar\omega}. \tag{4.35}$$

We see that $\Gamma_{\text{qm}}(E) = \Gamma_{\text{cl}}(E)$ for all E, if $2\pi/(\Delta x\,\Delta p) = \hbar$ or $\Delta x\,\Delta p = h$ as before.
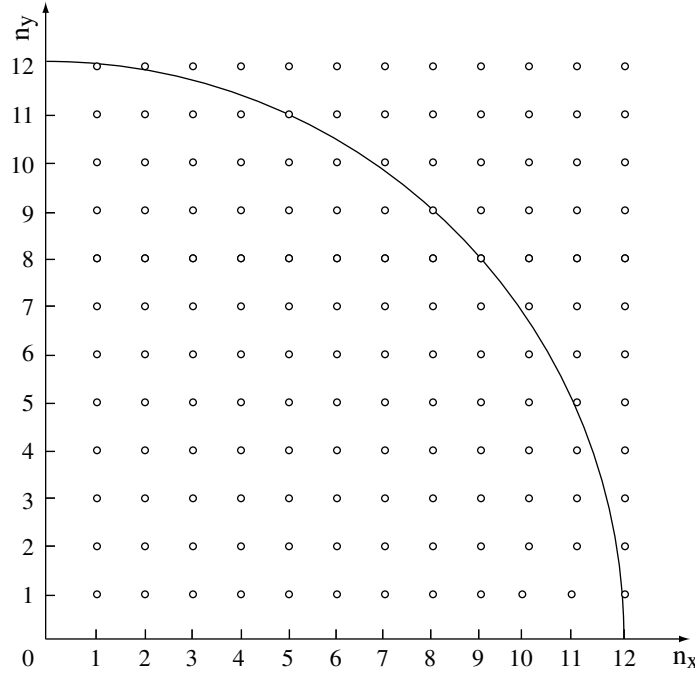
Figure 4.7: The points represent possible values of n_x and n_y such that $R^2 = n_x^2 + n_y^2 = 12^2$. Note that n_x and n_y are integers such that $n_x, n_y \geq 1$. Each point represents a single particle microstate. What is the total number of states for $R = 12$? The corresponding number from the asymptotic relation is $\Gamma(E) = \pi \, 12^2/4 \approx 113$.

4.3.5 One particle in a two-dimensional box

Consider a single particle of mass m in a rectangular box of sides L_x and L_y. The energy of the particle is given by

$$E = \frac{\mathbf{p}^2}{2m} = \frac{1}{2m}(p_x{}^2 + p_y{}^2). \tag{4.36}$$

Because the wave function takes the form of a standing wave in two dimensions, The wave vector $\mathbf{k}$ satisfies the conditions (see (4.29))

$$k_x = \frac{\pi}{L_x}n_x, \qquad k_y = \frac{\pi}{L_y}n_y. \qquad (n_x, n_y = 1, 2, 3, \ldots) \tag{4.37}$$

The corresponding eigenvalues are given by

$$E_{n_x, n_y} = \frac{h^2}{8m}\left[\frac{n_x{}^2}{L_x{}^2} + \frac{n_y{}^2}{L_y{}^2}\right]. \tag{4.38}$$

The states of the particle are labeled by the two integers n_x and n_y with $n_x, n_y > 0$. The possible values of n_x, n_y lie at the centers of squares of unit area as shown in Figure 4.7. For

simplicity, we assume that the box is square so that $L_x = L_y$. The values of (n_x, n_y) for a given E satisfy the condition

$$R^2 = {n_x}^2 + {n_y}^2 = \left(\frac{2L}{h}\right)^2 (2mE). \tag{4.39}$$

For large values of n_x and n_y, the values of n_x and n_y that correspond to states with energy less than or equal to E lie inside the positive quadrant of a circle of radius R, where

$$R = \frac{2L}{h}(2mE)^{1/2}. \tag{4.40}$$

Recall that n_x and n_y are both positive. Hence, the number of states with energy less than or equal to E is given by

$$\Gamma(E) = \frac{1}{4}\pi R^2 = \pi\frac{L^2}{h^2}(2mE). \tag{4.41}$$

Note that $V = L^2$ in this case.

Problem 4.17. Finite size effects in two dimensions

The expression (4.41) for $\Gamma(E)$ is valid only for large E because the area of a quadrant of a circle overestimates the number of lattice points n_x, n_y inside a circle of radius R. Use the applet/application at <stp.clarku.edu/simulations/numberofstates> and explore how the relation $\Gamma = \pi R^2/4$ approximates the actual number of microstates. The program computes the number of nonzero, positive integers that satisfy the condition $n_x^2 + n_y^2 \leq R^2$. What is the minimum value of R for which the difference between the asymptotic relation and the exact count is less than 1%?

4.3.6 One particle in a three-dimensional box

The generalization to three dimensions is straightforward. If we assume that the box is a cube with linear dimension L, we have

$$E = \frac{h^2}{8mL^2}[n_x^2 + n_y^2 + n_z^2]. \tag{4.42}$$

The values of n_x, n_y, and n_z that correspond to microstates with energy less than or equal to E lie inside the positive octant of a sphere of radius R given by

$$R^2 = n_x^2 + n_y^2 + n_z^2 = \left(\frac{2L}{h}\right)^2 (2mE). \tag{4.43}$$

Hence

$$\Gamma(E) = \frac{1}{8}\left(\frac{4}{3}\pi R^3\right) = \frac{\pi}{6}\left(\frac{2L}{h}\right)^3 (2mE)^{3/2} = \frac{4\pi}{3}\frac{V}{h^3}(2mE)^{3/2}, \tag{4.44}$$

where we have let $V = L^3$.

Problem 4.18. Finite size effects in three dimensions

The expression (4.44) for $\Gamma(E)$ is valid only for large E because the area of an octant of a sphere overestimates the number of lattice points n_x, n_y, n_z. Use the applet/application at <stp.clarku.edu/simulations/numberofstates> to determine how the relation $\Gamma = \pi R^3/6$ approximates the total number of microstate.

Problem 4.19. Estimation of the number of states

Estimate the number of microstates accessible to a gas molecule at typical room temperatures and pressures. We can estimate the mean energy E of a gas molecule such as nitrogen at room temperature by using the relation $E = 3NkT/2$. Calculate the number of microstates $\Gamma(E)$ with energy less than E accessible to such a molecule enclosed in a box having a volume of one liter ($10^3\,\mathrm{cm}^3$). Consider a small energy interval $\Delta E = 10^{-27}\,\mathrm{J}$ that is much smaller than E, and calculate the number of microstates $g(E)\Delta E$ accessible to the molecule in the range between E and $E + \Delta E$.

4.3.7 Two noninteracting identical particles and the semiclassical limit

Consider two noninteracting particles of mass m of the same species in a one-dimensional box of length L. The total energy is given by

$$E_{n_1,n_2} = \frac{h^2}{8mL^2}[n_1^2 + n_2^2], \tag{4.45}$$

where the quantum numbers n_1 and n_2 are positive nonzero integers. To count the microstates correctly, we need to take into account that particles of the same species are *indistinguishable*, one of the fundamental principles of quantum mechanics.

As an example of how we would count the microstates of this two particle system, suppose that the total energy is such that $n_1^2 + n_2^2 \le 25$. The values of n_1 and n_2 that satisfy this constraint are given in Table 4.7. However, the indistinguishability of the particles means that we cannot simply assign the quantum numbers n_1 and n_2 subject only to the constraint that $n_1^2 + n_2^2 \le 25$. For example, because the state $(n_1 = 1, n_2 = 2)$ is indistinguishable from the state $(n_1 = 2, n_2 = 1)$, we can count only one of these states.

The assignment of quantum numbers is further complicated by the fact that the particles must obey quantum statistics. We will discuss the nature of quantum statistics in Section 6.5. In brief, the particles must obey either Bose or Fermi statistics. If the particles obey Bose statistics, then any number of particles can be in the same single particle quantum state. However, if the particles obey Fermi statistics, then two particles cannot be in the same single particle quantum state, and hence the states $(n_1, n_2) = (1, 1)$, $(2, 2)$, $(3,3)$ are excluded.

Because the particles are indistinguishable, there are fewer microstates than if the particles were distinguishable, and we might think that counting the microstates is easier. However, the counting problem (enumerating the accessible microstates) is much more difficult because we cannot enumerate the states for each particle individually. For example, if $n_1 = 1$, then $n_2 \neq 1$. However, the counting of states can be simplified in the semiclassical limit. Because the indistinguishability of particles of the same species is intrinsic, the particles remain indistinguishable even as we let $h \to 0$. Because the classical limit corresponds to very large quantum numbers and the total number of states is huge, we can ignore the possibility that two particles will be in the same single particle quantum state and assume that the particles occupy single particle states that are all different. That is, in the semiclassical limit, there are many more microstates than particles and including a few extra microstates won't make any difference.

For the simple example summarized in Table 4.7, the assumption that every particle is in a different microstate implies that we can ignore the microstates $(1, 1)$, $(2, 2)$, and $(3, 3)$. Hence, in

distinguishable particles		Bose statistics		Fermi statistics		semiclassical	
n_1	n_2	n_1	n_2	n_1	n_2	n_1	n_2
1	1	1	1				
2	1	2	1	2	1	2	1
1	2					1	2
2	2	2	2				
3	1	3	1	3	1	3	1
1	3					1	3
3	2	3	2	3	2	3	2
2	3					2	3
3	3	3	3				
4	1	4	1	4	1	4	1
1	4					1	4
4	2	4	2	4	2	4	2
2	4					2	4
4	3	4	3	4	3	4	3
3	4					3	4

Table 4.7: The quantum numbers of two noninteracting identical particles of mass m in a one-dimensional box of length L with energies such that $n_1^2 + n_2^2 \leq 25$. If the two particles obey Fermi statistics, they cannot be in the same microstate, so $n_1 = 1$ and $n_2 = 1$ is not allowed for example. There is no such restriction for Bose statistics. Because the particles are identical and hence indistinguishable quantum mechanically, $n_1 = 1$, $n_2 = 2$ is indistinguishable from $n_1 = 2$, $n_2 = 1$. In the semiclassical limit, there are many many states and the possibility of both particles being in the same state is ignored. However, the particles remain indistinguishable. The number of microstates of this two particle system is $12/2! = 6$ in the semiclassical limit.

the semiclassical limit, we are left with six states $(2,1)$, $(3,1)$, $(3,2)$, $(4,1)$, $(4,2)$, and $(4,3)$ that satisfy the criterion $n_1^2 + n_2^2 \leq 25$.

This example illustrates how we can simplify the counting of the microstates in the semiclassical limit. We first count the total number of microstates of the N identical particles assuming that the particles are distinguishable. For $N = 2$ and the constraint that $n_1^2 + n_2^2 \leq 25$, we would find 12 microstates, assuming that the two particles are in different single particle states (see the last column of Table 4.7). We then correct for the overcounting of the microstates due to the indistinguishability of the particles by dividing by $N!$, the number of permutations of the different single particle states. For our example we would correct for the overcounting by dividing by the 2! ways of permuting two particles, and we obtain a total of $12/2! = 6$ states.

4.4 The Number Of States of N Noninteracting Particles: Semiclassical Limit

We now apply these considerations to count the number of microstates of N noninteracting particles in a three-dimensional box in the semiclassical limit. A simpler way to do so that yields the correct E and V dependence is given in Problem 4.20, but the numerical factors will not be identical to the result of the more accurate calculation that we discuss here.

The idea is to first count the microstates assuming that the N particles are distinguishable and then divide by $N!$ to correct for the overcounting. We know that for one particle in a three-dimensional box, the number of microstates with energy less than or equal to E is given by the volume of the positive part of the three-dimensional sphere of radius R (see (4.40)). For N distinguishable particles in a three-dimensional box, the number of microstates with energy less than or equal to E is given by the volume of the positive part of a $3N$-dimensional hypersphere of radius $R = (2mE)^{1/2}(2L/h)$. To simplify the notation, we consider the calculation of $V_n(R)$, the volume of a n-dimensional hypersphere of radius R, and write $V_n(R)$ as

$$V_n(R) = \int_{r_1^2+r_2^2+\cdots+r_n^2<R^2} d\mathbf{r}_1 \, d\mathbf{r}_2 \cdots d\mathbf{r}_n. \tag{4.46}$$

It is shown in Section 4.14.1 that $V_n(R)$ is given by (for integer n)

$$V_n(R) = \frac{2\pi^{n/2}}{n\Gamma(n/2)}R^n, \tag{4.47}$$

where the Gamma function $\Gamma(n) = (n-1)!$, $\Gamma(n+1) = n\Gamma(n)$ if n is an integer, and $\Gamma(1/2) = \sqrt{\pi}/2$. The cases $n = 2$ and $n = 3$ yield the expected results, $V_2 = 2\pi R^2/(2\Gamma(1)) = \pi R^2$ because $\Gamma(1) = 1$, and $V_3 = 2\pi^{3/2}R^3/(3\Gamma(3/2)) = \frac{4}{3}\pi R^3$ because $\Gamma(3/2) = \Gamma(1/2) = \pi^{1/2}/2$. The volume of the positive part of a n-dimensional sphere of radius R is given by

$$\Gamma_n(R) = \left(\frac{1}{2}\right)^n V_n(R). \tag{4.48}$$

(The volume $\Gamma_n(R)$ should not be confused with the Gamma function $\Gamma(n)$.)

We are interested in the case $n = 3N$ and $R = (2mE)^{1/2}(2L/h)$. In this case the volume $\Gamma(E,V,N)$ is given by

$$\Gamma(E,V,N) = \left(\frac{1}{2}\right)^{3N} \frac{2\pi^{3N/2}}{3N(3N/2-1)!}R^{3N/2} \tag{4.49a}$$

$$= \left(\frac{1}{2}\right)^{3N} \frac{\pi^{3N/2}}{(3N/2)!}R^{3N/2} \tag{4.49b}$$

$$= \left(\frac{1}{2}\right)^{3N} \left(\frac{2L}{h}\right)^{3N/2} \frac{\pi^{3N/2}}{(3N/2)!}(2mE)^{3N/2} \tag{4.49c}$$

$$= \left(\frac{V}{h^3}\right)^N \frac{(2\pi mE)^{3N/2}}{(3N/2)!}. \tag{4.49d}$$

If we include the factor of $1/N!$ to correct for the overcounting of microstates in the semiclassical limit, we obtain the desired result:

$$\Gamma(E, V, N) = \frac{1}{N!} \left(\frac{V}{h^3} \right)^N \frac{(2\pi mE)^{3N/2}}{(3N/2)!}. \qquad \text{(semiclassical limit)} \qquad (4.50)$$

A more convenient expression for Γ can be found by using Stirling's approximation for $N \gg 1$. We have

$$\ln \Gamma = -\ln N! + N \ln \frac{V}{h^3} + \frac{3}{2} N \ln(2\pi mE) - \ln \left(\frac{3N}{2} \right)! \qquad (4.51a)$$

$$= -N \ln N + N + N \ln V - \frac{3N}{2} \ln h^2 + \frac{3}{2} N \ln(2\pi mE) - \frac{3}{2} N \ln \frac{3N}{2} + \frac{3N}{2} \qquad (4.51b)$$

$$= N \ln \frac{V}{N} + \frac{3}{2} N \ln \frac{4\pi mE}{3Nh^2} + \frac{5}{2} N \qquad (4.51c)$$

$$= N \ln \frac{V}{N} + \frac{3}{2} N \ln \frac{mE}{3N\pi\hbar^2} + \frac{5}{2} N, \qquad (4.51d)$$

where we have let $h = 2\pi\hbar$ to obtain (4.51d) from (4.51c).

Problem 4.20. We can obtain an equivalent expression for $\Gamma(E, V, N)$ using simpler physical considerations. We write

$$\Gamma(E, V, N) \approx \frac{1}{N!} \Gamma_1(\frac{E}{N}, V) \Gamma_1(\frac{E}{N}, V) \dots \Gamma_1(\frac{E}{N}, V), \qquad (4.52)$$

where $\Gamma_1(E, V)$ is the number of states of a single particle with energy less than E in a three-dimensional box of volume V. We have assumed that on the average each particle has an energy E/N. Find the form of $\Gamma(E, V, N)$ using the relation (4.44) for Γ_1. Compare the V and E-dependencies of $\Gamma(E, V, N)$ obtained from this simple argument to (4.50). What about the N-dependence?

Problem 4.21. Calculate $g(E, V, N)$ and verify that $\Gamma(E, V, N)$ and $g(E, V, N)$ are rapidly increasing functions of $E, V,$ and N.

4.5 The Microcanonical Ensemble (Fixed E, V, and N)

So far, we have learned how to count the number of microstates of an isolated system. Such a system of particles is specified by the energy E, volume V, and number of particles N. All microstates that are consistent with these conditions are assumed to be equally probable. The collection of systems in different microstates and specified values of E, V, and N is called the *microcanonical ensemble*. In general, the energy E is a continuous variable, and the energy is specified to be in the range E to $E + \Delta E$.[4]

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[4]For a quantum system, the energy E must always be specified in some range. The reason is that if the energy were specified exactly, the system would have to be in an eigenstate of the system. If it were, the system would remain in this eigenstate indefinitely, and a statistical treatment would be meaningless.

In the following we show how the quantities that correspond to the usual thermodynamic quantities, for example, the entropy, temperature, and pressure, are related to the number of microstates. We will then use these relations to derive the ideal gas equation of state and other well known results using (4.51d) for the number of microstates of an ideal gas of N particles in a volume V with energy E.

We first establish the connection between the number of accessible microstates to various thermodynamic quantities by using arguments that are similar to our treatment of the simple models that we considered in Section 4.2. Consider two isolated systems A and B that are separated by an insulating, rigid, and impermeable wall. The macrostate of each system is specified by E_A, V_A, N_A and E_B, V_B, N_B, respectively, and the corresponding number of microstates is $\Omega_A(E_A, V_A, N_A)$ and $\Omega_B(E_B, V_B, N_B)$. Equilibrium in this context means that each accessible microstate is equally represented in our ensemble. The number of microstates of the composite system consisting of the two isolated subsystems A and B is

$$\Omega = \Omega_A(E_A, V_A, N_A) \, \Omega_B(E_B, V_B, N_B). \tag{4.53}$$

We want a definition of the entropy that is a measure of the number of microstates and that is additive. It was assumed by Boltzmann that S is related to Ω by the well known formula, first proposed by Planck:

$$\boxed{S = k \ln \Omega.} \tag{4.54}$$

Note that if we substitute (4.53) in (4.54), we find that $S = S_A + S_B$, and S is an additive function as it must be.

Next we modify the wall between A and B so that it becomes conducting, rigid, and impermeable. We say that we have relaxed the internal constraint of the composite system. The two subsystems are now in thermal contact so that the energies E_A and E_B can vary, subject to the condition that the total energy $E = E_A + E_B$ is fixed; the volumes V_A and V_B and particle numbers N_A and N_B remain unchanged. What happens to the number of accessible microstates after we relax the internal constraint? If subsystem A has energy E_A, it can be in any one of its $\Omega(E_A)$ microstates. Similarly, subsystem B can be in any one of its $\Omega_B(E - E_A)$ microstates. Because every possible state of A can be combined with every possible state of B to give a different state of the composite system, it follows that the number of microstates accessible to the composite system when A has energy E_A is the product $\Omega_A(E_A)\Omega_B(E - E_A)$. Hence, the total number of accessible microstates after the subsystems are in thermal equilibrium is

$$\Omega(E) = \sum_{E_A} \Omega_A(E_A)\Omega_B(E - E_A). \tag{4.55}$$

The probability that system A has energy E_A is given by

$$P(E_A) = \frac{\Omega_A(E_A)\Omega_B(E - E_A)}{\Omega(E)}. \tag{4.56}$$

Note that the logarithm of (4.55) does not yield a sum of two functions. However, the dominant contribution to the right-hand side of (4.55) comes from the term with $E_A = \tilde{E}_A$, where $\tilde{E}_A$ is the most probable value of E_A. With this approximation we can write

$$\Omega \approx \Omega_A(\tilde{E}_A)\Omega_B(E - \tilde{E}_A). \tag{4.57}$$

The approximation (4.57) becomes more and more accurate as the thermodynamic limit ($N, V \to \infty, \rho = N/V = $ constant) is approached and allows us to write

$$S = k \ln \Omega = S_A + S_B \tag{4.58}$$

before and after the constraint is removed. We see immediately that one consequence of the proposed relation between S and Ω is that the entropy increases or remains unchanged after an internal constraint is relaxed.

The relation $S = k \ln \Omega$ is not mysterious. It is a matter of counting the number of accessible microstates and assuming that they are all equally probable. The connection between the entropy and the probability distribution of the system's microstates was one of the great achievements of Ludwig Boltzmann, and the equation $S = k \ln W$ appears on his tombstone.[5]

Given the definition (4.54) of S as a function of E, V, and N, it is natural to adopt the thermodynamic definitions of temperature, pressure, and chemical potential:

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_{V,N} \tag{4.59}$$

$$\frac{P}{T} = \left(\frac{\partial S}{\partial V}\right)_{E,N} \tag{4.60}$$

$$\frac{\mu}{T} = -\left(\frac{\partial S}{\partial N}\right)_{E,V}. \tag{4.61}$$

We have made the connection between statistical mechanics and thermodynamics.

How should we generalize the relation of S to the number of microstates for a system in which the energy is a continuous variable? Three possibilities are

$$S = k \ln g(E)\Delta E \tag{4.62a}$$

$$S = k \ln \Gamma \tag{4.62b}$$

$$S = k \ln g(E). \tag{4.62c}$$

It is easy to show that in the limit $N \to \infty$, the three definitions yield the same result (see Problem 4.23). The reason is that $\Gamma(E)$ and $g(E)$ are such rapidly increasing functions of E that it makes no difference whether we include the microstates with energy less than or equal to E or just the states between E and $E + \Delta E$.

Example 4.1. Find the pressure and thermal equations of state of an ideal classical gas.

Solution. If we use any of the definitions of S given in (4.62), we find that the entropy of an ideal gas in the semiclassical limit for $N \to \infty$ is given by

$$S(E, V, N) = Nk\left[\ln \frac{V}{N} + \frac{3}{2} \ln \frac{mE}{3N\pi\hbar^2} + \frac{5}{2}\right]. \tag{4.63}$$

---

[5]See `<en.wikipedia.org/wiki/Ludwig_Boltzmann>` for a summary of Boltzmann's life and accomplishments and a photograph of his tombstone. Boltzmann never wrote down the relation $S = k \ln \Omega$ and referred only to S and the logarithm of the probability of a state being proportional. And the constant k was introduced by Planck, not by Boltzmann.

Problem 4.22. Compare the form of S given in (4.63) with the form of S determined from thermodynamic considerations in Section 2.19.

Problem 4.23. Equivalent definitions of the entropy

Verify the result (4.63) for the entropy S of an ideal gas using any of the definitions of S given in (4.62).

We now use the result (4.63) for S to obtain the thermal equation of state of an ideal classical gas. From (4.63) we see that

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_{V,N} = \frac{3}{2}\frac{Nk}{E}, \tag{4.64}$$

and hence we obtain the familiar result

$$E = \frac{3}{2}NkT. \tag{4.65}$$

The pressure equation of state follows from (4.60) and (4.63) and is given by

$$\frac{P}{T} = \left(\frac{\partial S}{\partial V}\right)_{E,N} = \frac{Nk}{V},$$

and hence

$$PV = NkT. \tag{4.66}$$

We have finally derived the equations of state of an ideal classical gas from first principles! We see that we can calculate the thermodynamic information for an isolated system by counting all the accessible microstates as a function of the total energy E, volume V, and number of particles N. Do the equations of state depend on $\hbar$ and the various constants in (4.50)?

Note that we originally defined the ideal gas temperature scale in Section 2.4 by assuming that $T \propto P$. We then showed that the ideal gas temperature scale is consistent with the thermodynamic temperature defined by the relation $1/T = (\partial S/\partial E)_{V,N}$. Finally, we have shown that the association of S with the logarithm of the number of accessible microstates is consistent with the relation $P \propto T$ for an ideal classical gas.

Problem 4.24. Use the relations (4.63) and (4.65) to obtain S as a function of T, V, and N instead of E, V, and N. This relation is known as the *Sackur-Tetrode* equation.

Problem 4.25. Use (4.61) and (4.63) to derive the dependence of the chemical potential μ on E, V, and N for a ideal classical gas. Then use (4.65) to determine $\mu(T, V, N)$. We will derive $\mu(T, V, N)$ for the ideal classical gas more simply in Section 6.8.

Example 4.2. Consider a system of N noninteracting spins and find the dependence of its temperature T on the total energy E. What is the probability that a given spin is up?

Solution. First we have to find the dependence of the entropy S on the energy E of the system. As discussed in Sec. 4.3.1, the energy E for a system with n spins up out of N in a magnetic field B is given by

$$E = -(n-n')\mu B = -[n-(N-n)]\mu B = -(2n-N)\mu B, \tag{4.15}$$

where $n' = N - n$ is the number of down spins and μ is the magnetic moment of the spins. The corresponding number of microstates is given by (4.17):

$$\Omega(n) = \frac{N!}{n!(N-n)!}. \qquad (4.17)$$

From (4.15), we find that the value of n corresponding to a given E is given by

$$n = \frac{1}{2}\Big(N - \frac{E}{\mu B}\Big). \qquad (4.67)$$

The thermodynamic temperature T is given by

$$\frac{1}{T} = \Big(\frac{\partial S}{\partial E}\Big)_{B,N} = \frac{dS(n)}{dn}\frac{dn}{dE} = -\frac{1}{2\mu B}\frac{dS}{dn}. \qquad (4.68)$$

To calculate dS/dn, we use the approximation (3.106) for large n:

$$\frac{d}{dn}\ln n! = \ln n, \qquad (4.69)$$

and find

$$\frac{dS(n)}{dn} = k[-\ln n + \ln(N-n)], \qquad (4.70)$$

where $S(n) = k\ln\Omega(n)$ from (4.17). Hence

$$\frac{1}{T} = -k\frac{1}{2\mu B}\ln\frac{N-n}{n}. \qquad (4.71)$$

Equation (4.71) yields T as a function of E by eliminating n using (4.67).

The natural variables in the microcanonical ensemble are E, V, and N. Hence, T is a derived quantity and is found as a function of E. As shown in Problem 4.26, we can rewrite this relation to express E as a function T. The result is

$$E = -N\mu B\tanh\frac{\mu B}{kT} = -N\mu B\tanh\beta\mu B, \qquad (4.72)$$

where $\beta = 1/kT$.

The probability p that a given spin is up is equal to the ratio n/N. We can solve (4.71) for n/N and obtain (see Problem 4.26)

$$p = \frac{n}{N} = \frac{1}{1 + e^{-2\mu B/kT}}, \qquad (4.73a)$$

$$= \frac{e^{\mu B/kT}}{e^{\mu B/kT} + e^{-\mu B/kT}} = \frac{e^{\beta\mu B}}{e^{\beta\mu B} + e^{-\beta\mu B}}, \qquad (4.73b)$$

We have obtained the result for p that we promised in Section 3.5.

ensemble	macrostate	probability distribution	thermodynamics
microcanonical	E, V, N	$P_n = 1/\Omega$	$S(E, V, N) = k \ln \Omega$
canonical	T, V, N	$P_n = e^{-\beta E_n}/Z$	$F(T, V, N) = -kT \ln Z$
grand canonical	T, V, μ	$P_n = e^{-\beta(E_n - \mu N_n)}/\mathcal{Z}$	$\Omega(T, V, \mu) = -kT \ln \mathcal{Z}$

Table 4.8: Summary of the three most common ensembles. Note that Ω is the number of accessible microstates in the microcanonical ensemble and the thermodynamic potential in the grand canonical ensemble.

Note we have had to consider all N spins even though the spins do not interact with each another. The reason is that the N spins have a definite energy and hence we cannot assign the orientation of the spins independently. We will obtain the result (4.73) by a more straightforward method in Section 4.6.

Problem 4.26. Solve (4.71) for n/N and verify (4.73). Then use (4.15) to solve for E as a function of T for a system of N noninteracting spins.

Although the microcanonical ensemble is conceptually simple, it is not the most practical ensemble. The major problem is that because we must satisfy the constraint that E is specified, we cannot assign energies to each particle individually, even if the particles do not interact. Another problem is that because each microstate is as important as any other, there are no obvious approximation methods that retain only the most important microstates. Moreover, isolated systems are very difficult to realize experimentally, and the temperature rather than the energy is a more natural independent variable.

Before we discuss the other common ensembles, we summarize their general features in Table 4.8. The internal energy E is fixed in the microcanonical ensemble and hence only the mean temperature is specified and the temperature fluctuates. In the canonical ensemble the temperature T and hence the mean energy is fixed, but the energy fluctuates. Similarly, the chemical potential and hence the mean number of particles is fixed in the grand canonical ensemble, and the number of particles fluctuates. In all of these ensembles, the volume V is fixed which implies that the pressure fluctuates. We also can choose an ensemble in which the pressure is fixed and the volume fluctuates.

*Problem 4.27. Consider a collection of N distinguishable, harmonic oscillators with total energy E. The oscillators are distinguishable because they are localized on different lattice sites. In one dimension the energy of each particle is given by $\epsilon_n = (n + \frac{1}{2})\hbar\omega$, where ω is the angular frequency. Hence, the total energy can be written as $E = (Q + \frac{1}{2}N)\hbar\omega$, where Q is the number of quanta. Calculate the dependence of the temperature T on the total energy E in the microcanonical ensemble using the result that the number of accessible microstates in which N distinguishable oscillators can share Q indistinguishable quanta is given by $\Omega = (Q + N - 1)!/Q!(N - 1)!$ (see (4.3)). Use this relation to find $E(T)$. The thermodynamics of this system is calculated much more simply in the canonical ensemble as shown in Example 4.56.

4.6 Systems in Contact with a Heat Bath: The Canonical Ensemble (Fixed T, V, and N)

We now assume that the system of interest can exchange energy with a much larger system known as a *heat bath*. The heat bath is sufficiently large that it is not significantly affected by the smaller system. For example, if we place a glass of cold water into a room, the temperature of the water will eventually reach the temperature of the air in the room. Because the volume of the glass is small compared to the volume of the room, the cold water does not cool the air appreciably and the air is an example of a heat bath.

The composite system, the system of interest plus the heat bath, is an isolated system. We can characterize the macrostate of the composite system by E, V, N. The accessible microstates of the composite system are equally probable. If the system of interest is in a microstate with energy E_n, then the energy of the heat bath is $E_b = E - E_n$. Because the system of interest is much smaller than the heat bath, we know that $E_n \ll E$.[6]

For a given microstate of the system, the heat bath can be in any one of a large number of microstates such that the total energy of the composite system is E. The probability P_n that the system is in microstate n with energy E_n is given by (see (4.53))

$$P_n = \frac{1 \times \Omega_b(E - E_n)}{\sum_n \Omega_b(E - E_n)}, \tag{4.74}$$

where $\Omega_b(E - E_n)$ is the number of microstates of the heat bath for a given microstate n of the system of interest. As E_n increases, $\Omega_b(E - E_n)$, the number of accessible microstates available to the heat bath, decreases. We conclude that P_n is a decreasing function of E_n, because the larger the value of E_n, the less energy is available to the heat bath.

We can simplify the form of P_n by using the fact that $E_n \ll E$. As we have seen before, we cannot approximate $\Omega_b(E - E_n)$ directly because Ω_b is a rapidly varying function of its argument. For this reason we take the logarithm of (4.74) and write

$$\ln P_n = C + \ln \Omega_b(E_b = E - E_n), \tag{4.75}$$

where C is related to the denominator of (4.74) and does not depend on E_n. We now expand $\ln \Omega_b(E - E_n)$ and write

$$\ln P_n \approx C + \ln \Omega_b(E) - E_n \Big(\frac{\partial \ln \Omega_b(E_b)}{\partial E_b} \Big)_{E_b = E} \tag{4.76a}$$

$$= C + \ln \Omega_b(E) - \frac{E_n}{kT}. \tag{4.76b}$$

We have used the relation

$$\beta \equiv \frac{1}{kT} = \Big(\frac{\partial \ln \Omega_b(E_b)}{\partial E_b} \Big)_{N,V}, \tag{4.77}$$

---

[6]Note that it is not clear how we should assign the potential energy of interaction of particles at the interface of the system and the heat bath. If the number of particles in the system of interest is large, the number of particles near the interface between the two systems is small in comparison to the number of particles in the bulk so that the potential energy of interaction of particles near the surface can be ignored. Nevertheless, these interactions are essential in order for the system to come into thermal equilibrium with the heat bath.
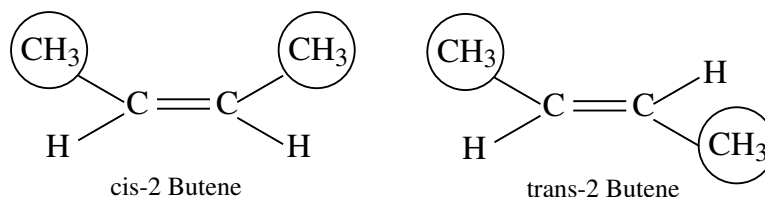
Figure 4.8: In general, different structure implies different chemical properties.

where T is the temperature of the heat bath. As can be seen from (4.77), β is proportional to the inverse temperature of the heat bath. From (4.76b) we obtain

$$\boxed{P_n = \frac{1}{Z}\, e^{-\beta E_n}}. \qquad \text{(Boltzmann distribution)} \qquad (4.78)$$

The function Z is found from the normalization condition $\sum_n P_n = 1$ and is given by

$$\boxed{Z = \sum_n e^{-\beta E_n}}. \qquad \text{(partition function)} \qquad (4.79)$$

The "sum over states" $Z(T, V, N)$ is known as the *partition function*. (In German Z is known as the *Zustandsumme*, a more descriptive term.) Note that P_n applies to a system in equilibrium with a heat bath at temperature T. The nature of the system has changed from Section 4.5.

Problem 4.28. Discuss the relation between the qualitative results that we obtained in Table 4.6 and the Boltzmann distribution in (4.78).

Problem 4.29. The hydrocarbon 2-butene, $CH_3\text{-}CH = CH\text{-}CH_3$ occurs in two conformations (geometrical structures) called cis- and trans. The cis (on this side) conformation of 2-butene has both CH_3 groups on the same side of the $C = C$ double bond. In the trans (across) conformation the CH_3 groups are on opposite sides of the double bond (see Figure 4.8). The energy difference ΔE between the two conformations is approximately $\Delta E/k = 4180\,\text{K}$, with the trans conformation lower than the cis conformation. Determine the relative abundance of the two conformations at $T = 300\,\text{K}$ and $T = 1000\,\text{K}$.

In the canonical ensemble the temperature T is fixed by the heat bath, and a macrostate is specified by the temperature T, volume V, and the number of particles N. The mean energy of the system is given by

$$\overline{E} = \sum_n P_n E_n = \frac{1}{Z} \sum_n E_n\, e^{-\beta E_n}, \qquad (4.80)$$

where we have substituted the Boltzmann form (4.78) for the probability distribution. We use a trick similar to that used in Section 3.5 to obtain a simpler form for $\overline{E}$. First we write

$$\overline{E} = -\frac{1}{Z}\frac{\partial}{\partial \beta} \sum_n e^{-\beta E_n}, \qquad (4.81)$$

where we have used the fact that $\frac{\partial}{\partial\beta}(e^{-\beta E_n}) = -E_n e^{-\beta E_n}$. Because

$$\frac{\partial Z}{\partial \beta} = -\sum_n E_n e^{-\beta E_n}, \tag{4.82}$$

we can write

$$\boxed{\overline{E} = -\frac{1}{Z}\frac{\partial Z}{\partial \beta} = -\frac{\partial}{\partial \beta}\ln Z}. \tag{4.83}$$

We see that $\overline{E}$ is a function of T for fixed V and N and can be expressed as a derivative of Z.

In the same spirit, we can express C_V, the heat capacity at constant volume, in terms of Z. We have

$$C_V = \frac{\partial \overline{E}}{\partial T} = \frac{d\beta}{dT}\frac{\partial \overline{E}}{\partial \beta}, \tag{4.84}$$

$$= \frac{1}{kT^2}\Big[\frac{1}{Z}\frac{\partial^2 Z}{\partial \beta^2} - \frac{1}{Z^2}\Big(\frac{\partial Z}{\partial \beta}\Big)^2\Big], \tag{4.85}$$

where $\partial \overline{E}/\partial \beta$ has been calculated from (4.83). Because

$$\overline{E^2} = \frac{1}{Z}\sum_n E_n^2\, e^{-\beta E_n} = \frac{1}{Z}\frac{\partial^2 Z}{\partial \beta^2}, \tag{4.86}$$

we obtain the relation

$$\boxed{C_V = \frac{1}{kT^2}\big[\overline{E^2} - \overline{E}^2\big]}. \tag{4.87}$$

Equation (4.87) relates the response of the system to a change in energy to the equilibrium energy fluctuations. Note that we can calculate the variance of the energy, a measure of the magnitude of the energy fluctuations, from the heat capacity. We will later find other examples of the relation of the linear response of an equilibrium system to the equilibrium fluctuations of an associated quantity.[7]

Problem 4.30. The isothermal compressibility of a system is defined as $\kappa = -(1/V)\big(\partial V/\partial P\big)_T$. Explain why κ is a linear response. In analogy to the relation of C_V to fluctuations in the energy, what type of fluctuations do you think are related to κ (at fixed T, P, and N)?

Because the energy is restricted to a very narrow range in the microcanonical ensemble and can range anywhere between zero and infinity in the canonical ensemble, it is not obvious that the two ensembles give the same results for the thermodynamic properties of a system. One way to understand why the thermodynamic properties are independent of the choice of ensemble is to use the relation (4.87) to estimate the range of energies in the canonical ensemble that have a significant probability. Because both E and C_V are extensive quantities, they are proportional to N. Hence, the relative fluctuations of the energy in the canonical ensemble is given by

$$\frac{\sqrt{\overline{E^2} - \overline{E}^2}}{\overline{E}} = \frac{\sqrt{kT^2 C_V}}{\overline{E}} \sim \frac{N^{1/2}}{N} \sim N^{-1/2}. \tag{4.88}$$

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[7] The relation (4.87) is important conceptually and is useful for simulations at a given temperature (see Section 4.11). However, it is almost always more convenient to *calculate* C_V from its definition in (4.84).

From (4.88) we see that in the limit of large N, the relative fluctuations in the values of E that would be observed in the canonical ensemble are vanishingly small. For this reason the mean energy in the canonical ensemble is a well defined quantity just like it is in the microcanonical ensemble. However, the fluctuations in the energy are qualitatively different in the two ensembles.

Problem 4.31. The Boltzmann probability given by (4.78) is the probability that the system is in a particular microstate with energy E_n. On the basis of what you have learned so far, what do you think is the form of the probability $p(E)\Delta E$ that the system has energy between E and $E + \Delta E$?

In addition to the relation of the mean energy to $\partial \ln Z/\partial \beta$, we can express the mean pressure $\overline{P}$ in terms of $\partial \ln Z/\partial V$. If the system is in microstate n, then a quasistatic change dV in the volume produces the energy change

$$dE_n = \frac{dE_n}{dV}dV = -\pi_n\, dV. \tag{4.89}$$

The quantity dE_n in (4.89) is the work done on the system in state n to produce the volume change dV. The relation (4.89) defines the pressure $\pi_n = -dE_n/dV$ of the system in microstate n.[8] Hence, the mean pressure of the system is given by

$$\overline{P} = \sum_n \pi_n P_n. \tag{4.90}$$

From (4.78), (4.79), and (4.90) we can express the mean pressure as

$$\overline{P} = kT\Big(\frac{\partial \ln Z}{\partial V}\Big)_{T,N}. \tag{4.91}$$

Note that in defining the pressure, we assumed that a small change in the volume does not change the probability distribution P_n of the microstates, but changes only the energy E_n of the microstates. In general, a perturbation of the system will induce transitions between the different microstates of the system and hence change the probabilities P_n as well as the energy of the microstates. That is, if the system is initially in microstate n, it will not stay in this state as the volume is changed. However, if the change occurs sufficiently slowly so that the system can adjust to the change, then the system will remain in state n. As discussed in Chapter 2, such a change is called quasistatic.

We can use the relation $\overline{E} = \sum_n P_n E_n$ to write the total change in the energy as

$$d\overline{E} = \sum_n E_n dP_n + \sum_n P_n dE_n. \tag{4.92}$$

The second term in (4.92) can be written as

$$\sum_n P_n\, dE_n = \sum_n P_n\, \frac{dE_n}{dV}dV. \tag{4.93}$$

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[8]We have written the pressure in microstate n as π_n rather than P_n or p_n to avoid confusion with the probability.
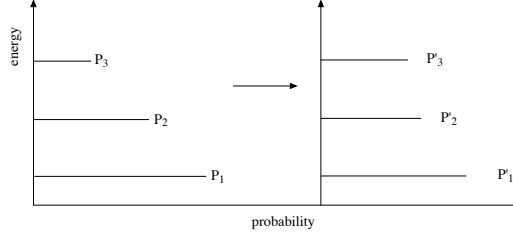
Figure 4.9: The The probability distribution changes when energy is transferred to the system incoherently, that is, by heating. The energy levels remain fixed if no work is done on the system.

The identification of the second term in (4.92) with the work done on the system allows us to rewrite (4.92) as

$$d\overline{E} = \sum_n E_n\, dP_n - \overline{P}\, dV. \tag{4.94}$$

If we use the fundamental thermodynamic relation (2.132), $dE = TdS - PdV$ (for fixed N), we can identify the first term in (4.94) with the change in entropy of the system. Hence, we have

$$TdS = \sum_n E_n\, dP_n. \tag{4.95}$$

From (4.95) we see that a change in entropy of the system is related to a change in the probability distribution (see Figure 4.9).

We can use (4.95) to obtain an important conceptual expression for the entropy. We rewrite $P_n = e^{-\beta E_n}/Z$ as $E_n = -kT(\ln Z + \ln P_n)$, and substitute this relation for E_n into (4.95):

$$TdS = \sum_n E_n\, dP_n = -kT \sum_n \ln Z\, dP_n - kT \sum_n \ln P_n\, dP_n. \tag{4.96}$$

The first term in (4.96) is zero because the total change in the probability must sum to zero. From (4.96) we write

$$dS = -k \sum_n \ln P_n\, dP_n, \tag{4.97a}$$

$$= -k \sum_n d(P_n \ln P_n). \tag{4.97b}$$

We integrate both sides of (4.97b) to obtain the desired result:

$$\boxed{S = -k \sum_n P_n \ln P_n}. \tag{4.98}$$

We have assumed that the constant of integration is zero (see the following). The quantity defined by (4.11) and (4.98) is known as the *statistical entropy* in contrast to the *thermodynamic entropy* introduced in Chapter 2. Note the similarity of (4.98) to the uncertainty function defined in (3.38).

The relation (4.98) for S is also applicable to the microcanonical ensemble. If there are Ω accessible microstates, then $P_n = 1/\Omega$ for each state because each state is equally likely. Hence,

$$S = -k \sum_{n=1}^{\Omega} \frac{1}{\Omega} \ln \frac{1}{\Omega} = -k\Omega \frac{1}{\Omega} \ln \frac{1}{\Omega} = k \ln \Omega. \tag{4.99}$$

The constant of integration in going from (4.97b) to (4.98) must be set to zero so that S reduces to its form in the microcanonical ensemble. We see that we can interpret (4.98) as the generalization of its microcanonical form with the appropriate weight for each state.

It is remarkable that the statistical entropy defined by (4.11) and (4.98) is equivalent to its thermodynamic definition which can be expressed as

$$dS = \frac{dQ}{T}. \tag{4.100}$$

The relation (4.98) is of fundamental importance and shows that the entropy is uniquely determined by the probability distribution P_n of the different microstates. Note that complete predictability (only one accessible microstate) implies the vanishing of the entropy. Also as the number of accessible microstates increases, the greater the value of S and hence the higher the degree of unpredictability of the system.

The idea of entropy has come a long way. It was first introduced into thermodynamics as a state function to account for the irreversible behavior of macroscopic systems under certain conditions. The discovery of the connection between this quantity and the probability distribution of the system's microstates was one of the great achievements of Ludwig Boltzmann. Since then, our understanding of entropy has been extended by Shannon and Jaynes and others to establish a link between thermodynamics and information theory (see Section 3.4.1). In this context we can say that S is a measure of the lack of information, because the greater the number of microstates that are available to a system in a given macrostate, the less we know about which microstate the system is in.

Although the relation (4.11) is of fundamental importance, we will not use it to calculate the entropy in any of the applications that we consider. The calculation of the entropy will be discussed in Section 4.7.

The third law of thermodynamics. The third law was first formulated by Nernst in 1906 based on experimental observations. We can easily see that the law follows from the statistical definition of the entropy. At $T = 0$, the system is in the ground state which we will label by 0. From (4.98) we see that if $P_n = 1$ for state 0 and is zero for all other microstates, then $S = 0$. We conclude that $S \to 0$ as $T \to 0$ if the system has an unique ground state. This behavior is what is expected for simple systems. However, as will discuss in the following, the statement that $S(T = 0) = 0$ at $T = 0$ is in general not correct. So we will state Nernst's theorem or the third law of thermodynamics as

The entropy of a system at $T = 0$ is a well-defined constant. For any processes that bring a system at $T = 0$ from one equilibrium state to another, $\Delta S = 0$.

If there are $g(0)$ microstates with the same ground state energy, then the corresponding (residual) entropy is $S(T = 0) = k \ln g(0)$. In this case the ground state is degenerate.[9] As an example, because an electron has spin $1/2$, it has two quantum states for each value of its momentum. In practice, there is always a very small, but nonzero magnetic field due to the Earth's magnetic field for example. So if we could measure the residual entropy directly, we would find that $S(T = 0) = 0$. However, there are some complex systems for which $g(0) \propto e^N$.[10] In either case, we conclude that the heat capacities must go to zero as $T \rightarrow 0$ (see Problem 4.49).

Problem 4.32. Explain why the entropy associated with the ground state of a system of N electrons is $kN \ln 2$.

4.7 Connection Between Statistical Mechanics and Thermo-dynamics

We have seen that the statistical quantity that enters into the calculation of the mean energy and the mean pressure is not Z, but $\ln Z$ (see (4.83) and (4.91)). We also learned in Section 2.21 that the Helmholtz free energy $F = E - TS$ is the thermodynamic potential for the variables T, V, and N. Because this set of variables corresponds to the variables specified by the canonical ensemble, it is natural to look for a connection between $\ln Z$ and F, and we define the latter as

$$\boxed{F = -kT \ln Z}. \quad \text{(statistical mechanics definition of the free energy)} \quad (4.101)$$

At this stage the quantity defined in (4.101) has no obvious relation to the thermodynamic potential $F = E - TS$ that we defined in (2.151).

We now show that F as defined by (4.101) is equivalent to the thermodynamic definition $F = E - TS$. This equivalence and the relation (4.101) gives the fundamental relation between statistical mechanics and thermodynamics for given values of T, V, and N, just as $S = k \ln \Omega$ gives the fundamental relation between statistical mechanics and thermodynamics for given values of E, V, and N (see Table 4.8).

We write the total change in the quantity $\beta F = -\ln Z$ as

$$d(\beta F) = -\frac{1}{Z}\frac{\partial Z}{\partial \beta}d\beta - \frac{1}{Z}\frac{\partial Z}{\partial V}\,dV$$
$$= \overline{E}\,d\beta - \beta\overline{P}\,dV, \quad (4.102)$$

where we have used (4.83) and (4.90). We add and subtract $\beta d\overline{E}$ to the right-hand side of (4.102) to find

$$d(\beta F) = \overline{E}d\beta + \beta d\overline{E} - \beta d\overline{E} - \beta\overline{P}dV \quad (4.103\text{a})$$
$$= d(\beta\overline{E}) - \beta(d\overline{E} + \overline{P}dV). \quad (4.103\text{b})$$

---

[9]An energy level is said to be degenerate if there are two or more microstates with the same energy.

[10]A simple example of a system with a nontrivial number of ground states is the Ising antiferromagnet on the triangular lattice. We will discuss this system in Problem 5.16. In this case the system has a nonzero entropy at zero temperature.

Hence, we can write

$$d(\beta F - \beta \overline{E}) = -\beta(d\overline{E} + \overline{P}dV). \tag{4.104}$$

From the thermodynamic relation $dE = TdS - PdV$ (for fixed N), we can rewrite (4.104) as

$$d(\beta F - \beta \overline{E}) = -\beta(d\overline{E} + \overline{P}dV) = -\beta TdS = -dS/k. \tag{4.105}$$

If we integrate (4.105), we find

$$S/k = \beta(\overline{E} - F) + \text{constant}, \tag{4.106}$$

or

$$F = \overline{E} - TS + \text{constant}. \tag{4.107}$$

If we make the additional assumption that the free energy should equal the internal energy of the system at $T = 0$, we can set the constant in (4.107) equal to zero, and we obtain

$$F = \overline{E} - TS. \tag{4.108}$$

Equation (4.108) is equivalent to the thermodynamic definition of the Helmholtz free energy with E replaced by $\overline{E}$. In the following, we will write E instead of $\overline{E}$ because the distinction will be clear from the context.

In Section 2.21 we showed that the Helmholtz free energy F is the natural thermodynamic potential for given values of T, V, and N and that

$$S = -\Big(\frac{\partial F}{\partial T}\Big)_{V,N}. \tag{4.109}$$

$$P = -\Big(\frac{\partial F}{\partial V}\Big)_{T,N} \tag{4.110}$$

$$\mu = \Big(\frac{\partial F}{\partial N}\Big)_{T,V}. \tag{4.111}$$

These relations still hold with $F = -kT \ln Z$.

We have found that if we start with the statistical mechanical relation $F = -kT \ln Z$ (see (4.101)), we obtain the thermodynamic relation $F = E - TS$ (see (4.108)). It is instructive to start with the latter and show that it implies that $F = -kT \ln Z$. We substitute $E = -\partial \ln Z/\partial \beta$ and the relation $S = k\beta^2(\partial F/\partial \beta)$ (see (4.109)) and find

$$F = E - TS = -\frac{\partial \ln Z}{\partial \beta} - \beta \Big(\frac{\partial F}{\partial \beta}\Big)_{V,N}. \tag{4.112}$$

We rewrite (4.112) as

$$F + \beta \Big(\frac{\partial F}{\partial \beta}\Big)_{V,N} = -\frac{\partial \ln Z}{\partial \beta} = \Big(\frac{\partial \beta F}{\partial \beta}\Big)_{V,N}. \tag{4.113}$$

If we integrate both sides of (4.113), we find (up to a constant) that

$$F = -kT \ln Z. \tag{4.114}$$

4.8 Simple Applications of the Canonical Ensemble

To gain experience with the canonical ensemble, we consider some relatively simple examples. In all of these examples, the goal is to calculate the partition function. Then we calculate the free energy using (4.101), the entropy from (4.109), and the mean energy from (4.83). (In these simple examples, the volume of the system will not be relevant, so we will not calculate the pressure.) In principle, we can follow this "recipe" for any physical system. We will later find that summing over the microstates to evaluate the partition function is usually a formidable task and can be done exactly in only a few cases.

Example 4.3. Consider a system consisting of two distinguishable particles. Each particle has two states with single particle energies 0 and Δ. The quantity Δ is called the energy gap. The system is in equilibrium with a heat bath at temperature T. What are the thermodynamic properties of the system?

Solution. The states of this two-particle system are $(0,0)$, $(0,\Delta)$, $(\Delta,0)$, and (Δ,Δ). The partition function Z_2 is given by

$$Z_2 = \sum_{n=1}^{4} e^{-\beta E_n} \tag{4.115a}$$

$$= 1 + 2e^{-\beta\Delta} + e^{-2\beta\Delta} \tag{4.115b}$$

$$= (1 + e^{-\beta\Delta})^2. \tag{4.115c}$$

We see that we can express Z_2 in terms of Z_1, the partition function for one particle:

$$Z_1 = \sum_{n=1}^{2} e^{-\beta\epsilon_n} = 1 + e^{-\beta\Delta}. \tag{4.116}$$

By comparing the forms of (4.115c) and (4.116), we find that

$$Z_2 = Z_1^2. \tag{4.117}$$

What do you expect the relation is between Z_N, the partition function for N noninteracting distinguishable particles, and Z_1?

Note that if the two particles were indistinguishable, there would be three microstates if the particles were bosons and one microstate if the particles are fermions, and the relation (4.117) would not hold.

Because Z_2 is simply related to Z_1, we can consider the statistical properties of a system consisting of one particle with Z_1 given by (4.116). From (4.78) we find the probability that the system is in each of its two possible states is given by:

$$p_1 = \frac{1}{Z_1} = \frac{1}{1 + e^{-\beta\Delta}} \tag{4.118a}$$

$$p_2 = \frac{e^{-\beta\Delta}}{Z_1} = \frac{e^{-\beta\Delta}}{1 + e^{-\beta\Delta}}. \tag{4.118b}$$

The average energy is given by

$$\bar{e} = \sum_{n=1}^{2} P_n \epsilon_n = \frac{\Delta\, e^{-\beta\Delta}}{1 + e^{-\beta\Delta}}. \tag{4.119}$$

We will use a lower case symbol to denote the results for one particle.

Of course, $\bar{e}$ could also be found from the relation $\bar{e} = -\partial \ln Z_1/\partial\beta$. For our example, we have

$$Z_1 = 1 + e^{-\beta\Delta} \tag{4.120}$$

and

$$\frac{\partial Z}{\partial\beta} = -\Delta e^{-\beta\Delta}. \tag{4.121}$$

Hence

$$\bar{e} = -\frac{\partial}{\partial\beta} \ln Z_1 = -\frac{1}{Z}\frac{\partial Z}{\partial\beta} = \frac{\Delta e^{-\beta\Delta}}{1 + e^{-\beta\Delta}}, \tag{4.122}$$

in agreement with (4.119). The energy of N noninteracting, distinguishable particles of the same type is given by $\overline{E} = N\bar{e}$.

It is easy to calculate the various thermodynamic quantities directly from the partition function in (4.115c). The free energy per particle, f, is given by

$$f = -kT \ln Z_1 = -kT \ln[1 + e^{-\beta\Delta}], \tag{4.123}$$

and s, the entropy per particle, is given by

$$s = -\left(\frac{\partial f}{\partial T}\right)_V = k \ln[1 + e^{-\beta\Delta}] + k\frac{\beta\Delta}{1 + e^{\beta\Delta}}. \tag{4.124}$$

If we had not already calculated the average energy $\bar{e}$, we could also obtain it from the relation $\bar{e} = f - Ts$. Confirm that the various ways of determining $\bar{e}$ yield the same results as found in (4.119). The behavior of the various thermodynamic properties of this system are explored in Problem 4.53.

Example 4.4. Determine the thermodynamic properties of a one-dimensional harmonic oscillator in equilibrium with a heat bath at temperature T.

Solution. The energy levels of a single harmonic oscillator are given by

$$\epsilon_n = (n + \frac{1}{2})\hbar\omega. \qquad (n = 0, 1, 2, \ldots) \tag{4.125}$$

The corresponding partition function is

$$Z = \sum_{n=0}^{\infty} e^{-\beta\hbar\omega(n+1/2)} = e^{-\beta\hbar\omega/2} \sum_{n=0}^{\infty} e^{-n\beta\hbar\omega} \tag{4.126a}$$

$$= e^{-\beta\hbar\omega/2}(1 + e^{-\beta\hbar\omega} + e^{-2\beta\hbar\omega} + \cdots) = e^{-\beta\hbar\omega/2}(1 + x + x^2 + \cdots), \tag{4.126b}$$

where $x = e^{-\beta\hbar\omega}$. The infinite sum in (4.126b) is a geometrical series in x and can be summed using the result that $1 + x + x^2 + \ldots = 1/(1-x)$ (see Appendix A). The result is

$$Z = \frac{e^{-\beta\hbar\omega/2}}{1 - e^{-\beta\hbar\omega}},$$

(4.127)

and

$$\ln Z = -\frac{1}{2}\beta\hbar\omega - \ln(1 - e^{-\beta\hbar\omega}).$$

(4.128)

Problem 4.33. Thermodynamics of a system of harmonic oscillators in the canonical ensemble

(a) Show that

$$f = \frac{1}{2}\hbar\omega + kT\ln(1 - e^{-\beta\hbar\omega})$$

(4.129)

$$s = k\Big[\frac{\beta\hbar\omega}{e^{\beta\hbar\omega} - 1} - \ln(1 - e^{-\beta\hbar\omega})\Big]$$

(4.130)

$$e = \hbar\omega\Big[\frac{1}{2} + \frac{1}{e^{\beta\hbar\omega} - 1}\Big].$$

(4.131)

Equation (4.131) is Planck's formula for the mean energy of an oscillator at temperature T. The heat capacity is discussed in Problem 4.56.

(b) Given the result (4.131) what is the mean energy of a system of N harmonic oscillators in equilibrium with a heat bath at temperature T?

(c) Compare your answer with the result for the energy of N harmonic oscillators calculated in the microcanonical ensemble in Problem 4.27. Do the two ensembles give identical results?

Equation (4.79) for Z is a sum over all the microstates of the system. Because the energies of the different microstates may be the same, we can group together microstates with the same energy and write (4.79) as

$$Z = \sum_{\text{levels}} g(E_l)\, e^{-\beta E_l},$$

(4.132)

where $g(E_l)$ is the number of microstates with energy E_l. The sum in (4.132) is over all the energy levels of the system, rather than over all the microstates of the system.

Example 4.5. Consider a three level single particle system with five microstates with energies 0, ϵ, ϵ, ϵ, and 2ϵ. What is $g(\epsilon_l)$ for this system? What is the mean energy of the system if it is equilibrium with a heat bath at temperature T?

Solution. The partition function is given by (see (4.132))

$$Z_1 = 1 + 3e^{-\beta\epsilon} + e^{-2\beta\epsilon}.$$

(4.133)

Hence, the mean energy of a single particle is given by

$$\bar{e} = \epsilon\frac{3e^{-\beta\epsilon} + 2e^{-2\beta\epsilon}}{1 + 3e^{-\beta\epsilon} + e^{-2\beta\epsilon}}.$$

(4.134)

What is the energy of N such particles?

Problem 4.34. In Section 4.3.2 we were given the number of states with energy E for the one-dimensional Ising model. Use the result (4.18) to calculate the free energy of the one-dimensional Ising model for $N = 2$ and 4.

4.9 Example of a Simple Thermometer

Consider a system of one particle which we will call a *demon* that can exchange energy with another system (see page 17). The demon obeys the following rules or algorithm:

1. Set up an initial microstate of the system with the desired total energy and assign an initial energy to the demon. (The initial demon energy is usually set to zero.)

2. Make a trial change in the microstate. For the Einstein solid, choose a particle at random and randomly increase or decrease its energy by unity. For a system of particles, change the position of a particle by a small random amount. For the Ising model, flip a spin chosen at random. Compute the change in energy of the system, ΔE. If $\Delta E \leq 0$, accept the change, and increase the energy of the demon by $|\Delta E|$. If $\Delta E > 0$, accept the change if the demon has enough energy to give to the system, and reduce the demon's energy by ΔE. If a trial change is not accepted, the existing microstate is counted in the averages. In either case the total energy of the system plus the demon remains constant.

3. Repeat step 2 many times choosing particles (or spins) at random.

4. Compute the averages of the quantities of interest once the system and the demon have reached equilibrium.

The demon can trade energy with the system as long as its energy remains greater than its lower bound, which we have chosen to be zero. The demon is a facilitator that allows the particles in the system to indirectly trade energy with one another.

In Problems 4.35 and 4.37 we use the demon algorithm to determine the probability that the demon is in a particular microstate.

Problem 4.35. The demon and the ideal gas

Consider a demon that exchanges energy with an ideal classical gas of N identical particles of mass m in one dimension. Because the energy of a particle depends only on its speed, the positions of the particles are irrelevant in this case. The demon chooses a particle at random and change its velocity by an amount, δ, chosen at random between $-\Delta$ and Δ. The change in energy of the system is the difference $\Delta E = \frac{1}{2}[(v + \delta)^2 - v^2]$, where we have chosen units so that $m = 1$. The parameter Δ is chosen so that the percentage of accepted changes is between 30% to 50%. The applet/application at `<stp.clarku.edu/simulations/demon/idealgas.html>` implements this algorithm. The applet chooses the special microstate for which all the velocities of the particles in the system are identical so that the system has the desired initial energy. The initial demon energy is set to zero for simplicity.

(a) The demon can be considered to be a small system in equilibrium with a much larger system. Before you do the simulation, sketch the energy-dependence of the probability $p(E_d)dE_d$ that the demon has an energy between E_d and $E_d + dE_d$.

(b) Consider a small number of particles, say $N = 10$. After the demon and the system have reached equilibrium, what is $\overline{E}_d$, the mean energy of the demon, and $\overline{E}/N$, the mean energy per particle of the system? Fix $N = 20$ and increase the total energy of the system. How does the ratio of $\overline{E}_d/(\overline{E}/N)$ depend on the total energy?

(c) Compare the initial mean velocity of the particles in the system to the mean value after equilibrium has been established. Would your results be different if the demon had a nonzero initial energy if the total energy of the demon plus the system was the same as before?

(d) Run for a sufficient number of trials so that the form of $p(E_d)$ is well defined. Use the Enable log scale button in the Views menu to verify the exponential form of $p(E_d)$. Fit your results to the form $p(E_d) \propto \exp(-\beta E_d)$, where β is a parameter. Given the form of $p(E_d)$, determine analytically the dependence of the mean demon energy on β (see Problem 4.36) and compare your prediction with your numerical results. Estimate T from the inverse slope of $\ln p(E_d)$ versus E_d. (The units are such that the Boltzmann constant $k = 1$.)

(e) What is the relation of the mean energy per particle in the system to the temperature? Use the results that you found in parts (b) and (d) to explain the relation between $\overline{E}_d$ and $\overline{E}/N$.

(f) How do your results change for an ideal gas in two and three dimensions?

Problem 4.36. Temperature dependence of the mean demon energy I

A demon exchanges energy with an ideal classical gas of N particles in one dimension (see Problem 4.35). What is the mean energy of the demon?

In this case the demon energy is a continuous variable. Hence,

$$\overline{E}_d = \frac{\int_0^\infty E_d \, e^{-\beta E_d}}{\int_0^\infty e^{-\beta E_d}}. \tag{4.135}$$

(a) Explain why the relation (4.135) for the demon energy is reasonable and determine the temperature dependence of $\overline{E}_d$.

(b) Would this temperature dependence be different if the gas were two- or three-dimensional? Would the temperature dependence change if the particles in the gas interacted with one another?

Problem 4.37. The demon and the Einstein solid

Consider a demon that exchanges energy with an Einstein solid of N particles. The demon chooses a particle at random and randomly increases or decreases its energy by one unit consistent with the constraint that $E_d \geq 0$. In this case the energy of the particle chosen also must remain nonnegative. If a trial change is not accepted, the existing microstate is counted in all averages. Use the applet/application at <stp.clarku.edu/simulations/demon/einsteinsolid.html>.

a) Choose $N = 20$ and $E = 40$. Does E_d eventually reach a well defined average value? If so, what is the mean energy of the demon after equilibrium between the demon and the system has been established? Compare the values of $\overline{E}_d$ and $\overline{E}/N$, the mean energy per particle of the system.

b) Compute the probability $P(E_{\rm d})$ that the demon has the energy $E_{\rm d}$. Fit your results to the form $P(E_{\rm d}) \propto \exp(-\beta E_{\rm d})$, where β is a parameter. Then increase E to $E = 80$. How do the various averages change? If time permits, increase E and N and determine any changes in $P(E_{\rm d}$ and the ratio $\overline{E}_{\rm d}/\overline{E}/N$.

c) Is there a simple relation between $\overline{E}_{\rm d}$ and $\overline{E}/N$?

Problem 4.38. Temperature dependence of the mean demon energy II

A demon exchanges energy with a system of an Einstein solid of N particles (see Problem 4.37). What is the mean energy of the demon?

(a) Explain why the energy of the demon is restricted to integer values.

(b) Explain why the demon's mean energy is given by

$$\overline{E}_{\rm d} = \frac{\sum_{n=0}^{\infty} n e^{-\beta n}}{\sum_{n=0}^{\infty} e^{-\beta n}}. \tag{4.136}$$

(c) Do the sums in (4.136) to determine the temperature dependence of $\overline{E}_{\rm d}$. (It is necessary to only do the sum in the denominator of (4.136).)

(d) Why is the temperature dependence of $\overline{E}_{\rm d}$ different if the demon exchanges energy with an ideal gas rather than an Einstein solid?

(e) In what limit does the temperature dependence become the same?

4.10 Simulations of the Microcanonical Ensemble

How can we implement the microcanonical ensemble on a computer? One way to do so for a classical system of particles is to use the method of molecular dynamics (see Section 1.5). In this method we choose initial conditions for the positions and velocities of each particle that are consistent with the desired values of E, V, and N. The numerical solution of Newton's equations generates a trajectory in $3N$-dimensional phase space. Each point on the trajectory represents a microstate of the microcanonical ensemble with the additional condition that the momentum of the center of mass is fixed. The averages over the phase space trajectory represent a time average.

To do such a simulation we need to be careful to choose a representative initial condition. For example, suppose that we started with the particles in one corner of the box. Even though a microstate with all the particles in one corner is as likely to occur as other microstates with the same energy, there are many more microstates for which the particles are spread throughout the box than there are those with particles in one corner.

As we will justify further in Section 6.3, we can identify the temperature of a system of interacting particles with the kinetic energy per particle using the relation (4.65). (For the ideal gas the total energy is simply the kinetic energy.) If we were to do a molecular dynamics simulation, we would find that the total energy is (approximately) constant, but the kinetic energy and hence the temperature fluctuates. The mean temperature of the system becomes well defined if the system

is in equilibrium, the number of particles in the system is sufficiently large, and the simulation is done for a sufficiently long time.

Our assumption that a molecular dynamics simulation generates microstates consistent with the microcanonical ensemble is valid as long as a representative sample of the accessible microstates can be reached during the duration of the simulation. Such a system is said to be *quasi-ergodic*.

What if we have a system of fixed total energy for which Newton's equations of motion is not applicable? For example, there is no dynamics for Einstein solid in which the particles have only integer values of the energy. Another general way of generating representative microstates is to use a *Monte Carlo* method. As an example, consider a system of N noninteracting distinguishable particles whose single particle energies are $0, 1, 2, \ldots$ For this model the relevant variables are the quantum numbers of each particle such that their sum equals the desired total energy E. Given a set of quantum numbers, how do we generate another set of quantum numbers with the same energy? Because we want to generate a representative sample of the accessible states, we need to make all changes at random. One possibility is to choose a particle at random and make a trial change in its energy by ± 1. However, such a trial change would change the total energy of the system and hence not be acceptable. (For this simple example of noninteracting particles, we could choose two particles at random and make trial changes, some of which would leave the total energy unchanged.)

A more interesting example is the Ising model in which the spins interact with their nearest neighbors with an energy $+J$ if the spins are parallel and energy $-J$ if the spins are antiparallel (see Section 1.10.3). We will discuss the Ising model in some detail in Chapter 5. Here it is sufficient to understand that the individual spins interact with one another.

The condition that the total energy be fixed makes sampling the accessible microstates of the Ising model difficult. If we choose a spin at random and flip it, the change will change the energy of the system in general. This difficulty is analogous to the difficulty that we have already found doing calculations in the microcanonical ensemble. We can circumvent this difficulty by relaxing the condition that the total energy be fixed by adding to the system of N particles an extra degree of freedom called the demon, as we discussed in Section 4.9. The total energy of the demon plus the original system is fixed. Because the demon is one particle out of $N + 1$, the fluctuations in the energy of the original system are order $1/N$, which goes to zero as $N \to \infty$.

4.11 Simulations of the Canonical Ensemble

Suppose that we wish to simulate a system that is in equilibrium with a heat bath at temperature T. One way to do so is to start with an arbitrary microstate of energy E and weight it by its relative probability $e^{-\beta E}$. For example, for the Einstein solid considered in Section 4.10, we could generate another microstate by choosing a particle at random and changing its energy by ± 1 at random. A new microstate would be generated and the mean energy of the system would be estimated by

$$\overline{E}(T) = \frac{\sum_{n=1}^{M} E_n e^{-\beta E_n}}{\sum_{n=1}^{M} e^{-\beta E_n}}, \tag{4.137}$$

where E_n is the energy of microstate n and the sum is over the M states that have been generated in this way. However, this procedure would be very inefficient because the M states would include

many states whose weight in averages such as (4.137) would be very small.

To make the sampling procedure effective, we need to generate microstates with probabilities proportional to their weight, that is, proportional to $e^{-\beta E_n}$. In this way we would generate states with the highest probability. Such a sampling procedure is known as *importance sampling*. The simplest and most common method of importance sampling in statistical mechanics is known as the *Metropolis algorithm*. The method is based on the fact that the ratio of the probability that the system is in state j with energy E_j to the probability of being in state i with energy E_i is $p_j/p_i = e^{-\beta(E_j - E_i)} = e^{-\beta \Delta E}$, where $\Delta E = E_j - E_i$. We interpret this ratio as the probability of making a transition from state i to state j. If $\Delta E < 0$, the quantity $e^{-\beta \Delta E}$ is greater than unity, and the probability is unity. The Metropolis algorithm can be summarized as follows:

1. Choose an initial microstate, for example, choose random initial energies for each particle in an Einstein solid or random positions in a system of particles interacting via the Lennard-Jones potential.

2. Make a trial change in the microstate. For the Einstein solid, choose a particle at random and increase or decrease its energy by unity. For a system of particles, change the position of a particle by a small random amount. Compute the change in energy of the system, ΔE, corresponding to this change. If $\Delta E < 0$, then accept the change. If $\Delta E > 0$, accept the change with probability $w = e^{-\beta \Delta E}$. To do so, generate a random number r uniformly distributed in the unit interval. If $r \leq w$, accept the new microstate; otherwise, retain the previous microstate.

3. Repeat step 2 many times.

4. Compute the averages of the quantities of interest once the system has reached equilibrium.

Problem 4.39. Simulation of the Einstein solid in equilibrium with a heat bath

Use the Metropolis algorithm to simulate an Einstein solid of N particles at a temperature T. The applet/application at `<stp.clarku.edu/simulations/EinsteinSolidHeatBath.html>` implements the Metropolis algorithm by choosing a particle at random and randomly increasing or decreasing its energy by one unit. If the energy is decreased, the change is accepted. If the energy is increased, the program generates a number r at random in the unit interval and accepts the change if $r \leq e^{-\beta}$, where $\beta = 1/T$. (As usual, we choose units such that Boltzmann's constant $k = 1$.) If a trial change is not accepted, the existing microstate is counted in all averages.

(a) Choose $N = 20$ and $\beta = 1$. Does the energy of the system eventually reach a well defined average? If so, vary β and determine $\overline{E}(T)$.

(b) Compare your results to the analytical results you found in Example 4.4.

4.12 Grand Canonical Ensemble (Fixed T, V, and μ)

In Section 4.6 we derived the Boltzmann probability distribution for a system in equilibrium with a heat bath at temperature T. The role of the heat bath is to fix the temperature and hence the mean energy of the system. We now find the probability distribution for a system in equilibrium

with a heat bath at temperature T and a particle reservoir with chemical potential μ. In this case the role of the particle reservoir is to fix the chemical potential and hence the mean number of particles. This ensemble is known as the *grand canonical ensemble*.

As before, the composite system is isolated with total energy E, total volume V, and total number of particles N. The probability that the (sub)system is in microstate n with energy E_n and N_n particles is given by (see (4.74))

$$P_n = \frac{1 \times \Omega_{\rm b}(E - E_n, N - N_n)}{\sum_n \Omega_{\rm b}(E - E_n, N - N_n)}. \tag{4.138}$$

The difference between (4.74) and (4.138) is that we have allowed both the energy and the number of particles of the system of interest to vary. As before, we take the logarithm of both sides of (4.138) and exploit the fact that $E_n \ll E$ and $N_n \ll N$. We have

$$\ln P_n \approx \text{constant} - E_n \frac{\partial \ln \Omega_{\rm b}(E)}{\partial E} - N_n \frac{\partial \ln \Omega_{\rm b}(N)}{\partial N}. \tag{4.139}$$

The derivatives in (4.139) are evaluated at $E_{\rm bath} = E$ and $N_{\rm reservoir} = N$, respectively. If we substitute $\beta = \partial \ln \Omega_{\rm b}/\partial E$ (see (4.77)) and $\beta\mu = -\partial \ln \Omega_{\rm b}/\partial N$ (see (2.125)), we obtain

$$\ln P_n = \text{constant} - \frac{E_n}{kT} + \frac{\mu N_n}{kT}, \tag{4.140}$$

or

$$\boxed{P_n = \frac{1}{\mathcal{Z}} e^{-\beta(E_n - \mu N_n)}}. \qquad \text{(Gibbs distribution)} \tag{4.141}$$

Equation (4.141) is the Gibbs probability distribution for a variable number of particles. This distribution gives the probability that the system is in state n with energy E_n and N_n particles. The *grand partition function* $\mathcal{Z}$ in (4.141) is found from the normalization condition

$$\sum_n P_n = 1. \tag{4.142}$$

Hence, we obtain

$$\boxed{\mathcal{Z} = \sum_n e^{-\beta(E_n - \mu N_n)}}. \tag{4.143}$$

In analogy to the relations we found in the canonical ensemble, we expect that there is a simple relation between the Landau potential defined in (2.167) and the grand partition function. Because the derivation of this relation proceeds as in Sec. 4.6, we simply give the relation:

$$\boxed{\Omega = -kT \ln \mathcal{Z}}. \tag{4.144}$$

Example 4.6. Many impurity atoms in a semiconductor exchange energy and electrons with the electrons in the conduction band. Consider the impurity atoms to be in thermal and chemical equilibrium with the conduction band, which can be considered to be an energy and particle reservoir. Assume that Δ is the ionization energy of the impurity atom. Find the probability that an impurity atom is ionized.

Solution. Suppose that one and only one electron can be bound to an impurity atom. Because an electron has a spin, both spin orientations ↑ and ↓ are possible. An impurity atom has three allowed states: state 1 without an electron (atom ionized), state 2 with an electron attached with spin ↑, and state 3 with an electron attached with spin ↓. We take the zero of energy to correspond to the two bound states. The microstates of the system are summarized below.

state n	description	N	ϵ_n
1	electron detached	0	$-\Delta$
2	electron attached, spin ↑	1	0
3	electron attached, spin ↓	1	0

The grand partition function of the impurity atom is given by

$$\mathcal{Z} = e^{\beta\Delta} + 2e^{\beta\mu}. \tag{4.145}$$

Hence, the probability that an atom is ionized (state 1) is given by

$$P(\text{ionized}) = \frac{e^{\beta\Delta}}{e^{\beta\Delta} + 2e^{\beta\mu}} = \frac{1}{1 + e^{-\beta(\Delta-\mu)}}. \tag{4.146}$$

4.13   *Entropy and Disorder

Many texts and articles for the scientifically literate refer to entropy as a measure of "disorder" or "randomness." This interpretation is justified by the relation, $S = k \ln \Omega$. The argument is that an increase in the disorder in a system corresponds to an increase in Ω. Usually a reference is made to a situation such as the tendency of students' rooms to become messy. There are two problems with this interpretation – it adds nothing to our understanding of entropy and is inconsistent with our naive understanding of structural disorder.

We have already discussed the interpretation of the entropy as a measure of the uncertainty or lack of information. Thus, we already have a precise definition of entropy and can describe a student's messy room as having a high entropy because of our lack of information about the location of a particular paper or article of clothing. We could define disorder as lack of information, but such a definition does not help us to understand entropy any better because it would not provide an independent understanding of disorder.

The other problem with introducing the term disorder to describe entropy is that it can lead to incorrect conclusions. In the following we will describe two examples where the crystalline phase of a given material has a higher entropy than the liquid phase. Yet you would probably agree that a crystal is more ordered than a liquid. So how can a crystal have a higher entropy?

Suppose that you are going on a short trip and need to pack your suitcase with only a few articles.[11] In this case the volume of the suitcase is much greater than the total volume of the articles you wish to pack, and you would probably just randomly throw the articles into the suitcase. Placing the articles in an ordered arrangement would require extra time and the ordered arrangement would probably be destroyed during transport. In statistical mechanics terms we say

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[11]This example is due to Laird (see the references).

that there are many more ways in which the suitcase can be packed in a disordered arrangement than the ordered one. Hence, we could include that the disordered state has a higher entropy than the ordered state. This low density case is consistent with the usual association of entropy and disorder.

Now suppose that you are going on a long trip and need to pack many articles in the same suitcase, that is, the total volume of the articles to be packed is comparable to the volume of the suitcase. In this high density case you probably know from experience that randomly throwing the articles into the suitcase won't allow you to shut the suitcase. Such a configuration is incompatible with the volume constraints of the suitcase. If you randomly throw the articles in the suitcase many times, you might find a few configurations that would allow you to close the suitcase. In contrast, if you pack the articles in a neat and ordered arrangement, the suitcase can be closed. Also there are many such configurations that would satisfy the constraints. We conclude that the number of ordered arrangements (of the articles in the suitcase) is greater than the number of corresponding disordered arrangements. Therefore an ordered arrangement in the high density suitcase has a higher entropy than a structurally disordered state. The association of disorder with entropy is not helpful here.

The suitcase example is an example of an *entropy-driven transition* because energy did not enter into our considerations at all. Another example of an entropy-driven transition is a system of hard spheres or hard disks. In this seemingly simple model the interaction between two particles is given by

$$u(r) = \begin{cases} \infty & r < \sigma \\ 0 & r \geq \sigma. \end{cases} \tag{4.147}$$

For this model only non-overlapping configurations are allowed and so the potential energy is zero. Hence, the internal energy is solely kinetic and the associated contribution of the energy to the free energy is the ideal gas part which depends only on the temperature and the density. Hence, the difference in the free energy $\Delta F = \Delta E - T\Delta S$ between a hard sphere crystal and a hard sphere fluid at the same density and temperature must equal $-T\Delta S$.

In the following problem we will do an exploratory simulation of a system of hard disks that suggests that there is a transition from a fluid at low density to a crystal at high density (at fixed temperature). Thus at some density ΔF must become negative, which can occur only if $\Delta S = S_{\text{crystal}} - S_{\text{fluid}}$ is positive. We conclude that at high density the entropy of the crystal must be greater than that of a fluid at equal temperature and density for a fluid-solid (freezing) transition to exist.

Problem 4.40. Simulation of hard disks

The dynamics of a system of hard disks are straightforward in principle because the particles move in straight lines in between collisions. The applet/application at <stp.clarku.edu/simulations/hardDisks> finds when the next two particles are going to collide and moves the particles accordingly.

(a) Run the simulation for the default parameters and record the density and the results for PA/NkT and the temperature. Is the temperature a useful quantity for hard disks? Does it fluctuate during the simulation. If not why not? Does the pressure P fluctuate?

(b) Compute PA/NkT as a function of density for a fixed number of particles. Is there any evidence of a phase transition where the slope of the pressure with respect to density changes abruptly?

Vocabulary

composite system, subsystem

equal a priori probabilities

microcanonical ensemble, canonical ensemble, grand canonical ensemble

Boltzmann distribution, Gibbs distribution

entropy S, Helmholtz free energy F, Gibbs free energy G, Landau potential Ω

demon algorithm, Metropolis algorithm

4.14 Supplementary Notes

4.14.1 The volume of a hypersphere

We derive the volume of a hypersphere of n dimensions given in (4.47). As in (4.46), the volume is given by

$$V_n(R) = \int_{x_1^2 + x_2^2 + \cdots + x_n^2 < R^2} dx_1\, dx_2 \cdots dx_n. \tag{4.148}$$

Because $V_n(R) \propto R^n$ for $n = 2$ and 3, we expect that V_n is proportional to R^n. Hence, we write

$$V_n = C_n R^n, \tag{4.149}$$

where C_n is the (unknown) constant of proportionality that depends only on n. We rewrite the volume element $dV_n = dx_1\, dx_2 \cdots dx_n$ as

$$dV_n = dx_1\, dx_2 \cdots dx_n = S_n(R)\, dR = nC_n R^{n-1} dR, \tag{4.150}$$

where $S_n = nC_n R^{n-1}$ is the surface area of the hypersphere. As an example, for $n = 3$ we have $dV_3 = 4\pi R^2\, dR$ and $S_3 = 4\pi R^2$. To find C_n for general n, consider the identity (see Appendix A)

$$I_n = \int_{-\infty}^{\infty} dx_1 \cdots \int_{-\infty}^{\infty} dx_n\, e^{-(x_1^2 + \cdots + x_n^2)} = \Big[\int_{-\infty}^{\infty} dx\, e^{-x^2}\Big]^n = \pi^{n/2}. \tag{4.151}$$

The left-hand side of (4.151) can be written as

$$I_n = \int_{-\infty}^{\infty} dx_1 \cdots \int_{-\infty}^{\infty} dx_n\, e^{-(x_1^2 + \cdots + x_n^2)} = \int_0^{\infty} dR\, S_n(R)\, e^{-R^2}$$
$$= nC_n \int_0^{\infty} dR\, R^{n-1}\, e^{-R^2}. \tag{4.152}$$

We can relate the integral in (4.152) to the Gamma function $\Gamma(n)$ defined by the relation

$$\Gamma(n) = \int_0^\infty dx\, x^{n-1}\, e^{-x}. \tag{4.153}$$

The relation (4.153) holds for $n > -1$ and whether or not n is an integer. We make the change of variables $x = R^2$ so that

$$I_n = \frac{1}{2} n C_n \int_0^\infty dx\, x^{n/2-1}\, e^{-x} = \frac{1}{2} n C_n\, \Gamma(n/2). \tag{4.154}$$

A comparison of (4.154) with (4.151) yields the relation

$$C_n = \frac{2\pi^{n/2}}{n\Gamma(n/2)} = \frac{\pi^{n/2}}{(n/2)\Gamma(n/2)}. \tag{4.155}$$

It follows that

$$V_n(R) = \frac{2\pi^{n/2}}{n\Gamma(n/2)} R^n. \tag{4.156}$$

4.14.2 Fluctuations in the canonical ensemble

To gain more insight into the spread of energies that are actually observed in the canonical ensemble, we determine the probability $P(E)\Delta E$ that a system in equilibrium with a heat bath at temperature T has energy E in the range ΔE. In most macroscopic systems, the number of microstates with the same energy is large. In such a case the probability that the system is in any of the microstates with energy E_l can be written as

$$P_l = \frac{g(E_l)e^{-\beta E_l}}{\sum_l g(E_l)e^{-\beta E_l}}, \tag{4.157}$$

where $g(E_l)$ is the number of microstates with energy E_l. As in (4.132)) the sum in the denominator in (4.157) is over the different energy levels of the system. In the thermodynamic limit $N, V \to \infty$, the spacing between consecutive energy levels becomes very small and we can regard E as a continuous variable. We write $P(E)dE$ for the probability that the system in the range E and $E + dE$ and let $g(E)\, dE$ be the number of microstates between E and $E + dE$. (The function $g(E)$ is the density of states and is the same function discussed in Section 4.3.) Hence, we can rewrite (4.157) as

$$P(E)\, dE = \frac{g(E)e^{-\beta E} dE}{\int_0^\infty g(E)e^{-\beta E} dE}. \tag{4.158}$$

As we did in Section 3.7, we can find an approximate form of $P(E)$ by expanding $P(E)$ about $E = \tilde{E}$, the most probable value of E. To do so, we evaluate the derivatives $\partial \ln P/\partial E$ and $\partial^2 \ln P/\partial E^2$ using (4.158):

$$\left(\frac{\partial \ln P}{\partial E}\right)_{E=\tilde{E}} = \left(\frac{\partial \ln g}{\partial E}\right)_{E=\tilde{E}} - \beta = 0. \tag{4.159}$$

and

$$\left(\frac{\partial^2 \ln P}{\partial E^2}\right)_{E=\tilde{E}} = \left(\frac{\partial^2 \ln g}{\partial E^2}\right)_{E=\tilde{E}}. \tag{4.160}$$

We have

$$\left(\frac{\partial^2 \ln g}{\partial E^2}\right)_{E=\tilde{E}} = \frac{\partial}{\partial E}\left(\frac{\partial \ln g}{\partial E}\right)_{E=\tilde{E}} = \frac{\partial \beta}{\partial E}. \tag{4.161}$$

Finally, we obtain

$$\frac{\partial \beta}{\partial E} = -\frac{1}{kT^2}\frac{\partial T}{\partial E} = -\frac{1}{kT^2 C_V}. \tag{4.162}$$

We can use the above results to expand $\ln P(E)$ about $E = \tilde{E}$ through second order in $(E-\tilde{E})^2$. The result is

$$\ln P(E) = \ln P(\tilde{E}) - \frac{(E-\tilde{E})^2}{2kT^2 C_V} + \dots \tag{4.163}$$

or

$$P(E) = P(\tilde{E})e^{-(E-\tilde{E})^2/2kT^2 C_V}. \tag{4.164}$$

If we compare (4.164) to the standard form of a Gaussian distribution (3.129), we see that $\overline{E} = \tilde{E}$ and $\sigma_E^2 = kT^2 C_V$ as expected.

Additional Problems

Problem 4.41. Discuss the statistical nature of the Clausius statement of the second law that energy cannot go spontaneously from a colder to a hotter body. Under what conditions is the statement applicable? In what sense is this statement incorrect?

Problem 4.42. Given our discussion of the second law of thermodynamics from both the macroscopic and microscopic points of view, discuss the following quote due to Arthur Stanley Eddington:

> The law that entropy always increases, the Second Law of Thermodynamics, holds ... the supreme position among the laws of Nature. If someone points out to you that your pet theory of the universe is in disagreement with Maxwell's equations, then so much the worse for Maxwell's equations... But if your theory is found to be against the second law of thermodynamics, I can give you no hope; there is nothing for it but to collapse in deepest humiliation.

Problem 4.43. Consider an isolated composite system consisting of subsystems 1 and 2 that can exchange energy with each other. Subsystem 1 consists of three noninteracting spins, each having magnetic moment μ. Subsystem 2 consists of two noninteracting spins each with a magnetic moment 2μ. A magnetic field B is applied to both systems.

(a) Suppose that the total energy is $E = -3\mu B$. What are the accessible microstates of the composite system? What is the probability $P(M)$ that system 1 has magnetization M?

Table 4.9: Listing of inline problems.

(b) Suppose that systems 1 and 2 are initially separated from each other and that the net magnetic moment of 1 is -3μ and the net magnetic moment of 2 is $+4\mu$. The systems are then placed in thermal contact with one another and are allowed to exchange energy. What is the probability $P(M)$ that the net magnetic moment of system 1 has one of its possible values M? What is the mean value of the net magnetic moment of system 1?

Problem 4.44. Consider two isolated systems of noninteracting spins with $N_A = 4$ and $N_B = 16$. If their initial energies are $E_A = -2\mu B$ and $E_B = -2\mu B$, what is the total number of microstates available to the composite system? If the two systems are now allowed to exchange energy with one another, what is the probability that system 1 has energy E_A? What is the mean value of E_A and its relative fluctuations of E_A? Calculate the analogous quantities for system B. What is the most probable macrostate for the composite system?

Problem 4.45. Show that the relations (4.59)–(4.61) follow from the thermodynamic relation $dE = TdS - PdV + \mu dN$ (see (2.132)).

Problem 4.46. Suppose that the number of states between energy E and $E + \Delta E$ of an isolated system of N particles in a volume V is given by

$$g(E)\Delta E = c(V - bN)^N (E + \frac{N^2 a}{V})^{3N/2}\Delta E, \tag{4.165}$$

where a, b, and c are constants. What is the entropy of the system? Determine the temperature T as a function of E. What is the energy in terms of T, the density $\rho = N/V$, and the parameters

a and *b*? What is the pressure as a function of T and ρ? What are the units of the parameters *a* and *b*?

Problem 4.47. Discuss the assumptions that are needed to derive the classical ideal gas equations of state, (4.65) and (4.66).

Problem 4.48. Assume that $g(E) = E^{3N/2}$ for a classical ideal gas. Plot $g(E), e^{-\beta E}$, and the product $g(E) e^{-\beta E}$ versus E for $N = 6$ and $\beta = 1$. What is the qualitative behavior of the three functions? Show that the product $g(E)e^{-\beta E}$ has a maximum at $\tilde{E} = 3N/(2\beta)$. Compare this value to the mean value of E given by

$$\overline{E} = \frac{\int_0^\infty E g(E) e^{-\beta E} dE}{\int_0^\infty g(E) e^{-\beta E} dE}. \tag{4.166}$$

Problem 4.49. Explain why the various heat capacities must go to zero as $T \to 0$.

Problem 4.50. The partition function of a hypothetical system is given by

$$\ln Z = aT^4 V, \tag{4.167}$$

where a is a constant. Evaluate the mean energy E, the pressure P, and the entropy S.

Problem 4.51. An analogy for the heat capacity

The following analogy might be useful for understanding the temperature dependence of the heat capacity of a two level system.

(a) Suppose that you walk into a store with little money in your pocket (and no credit card). Would you care about the prices of the articles you wished to purchase? Would you care about the prices if you had just won the lottery?

(b) Suppose that you wish to purchase a car that costs $20,000 but have no money. You then find a dollar bill on the street. Has your "capacity" for purchasing the car increased? Suppose that your uncle gives you $8000. Has your capacity for purchasing the car increased substantially? How much money would you need before you might think about buying the car?

Problem 4.52. Show that the partition function Z_{12} of two independent distinguishable systems 1 and 2 both in equilibrium with a heat bath at temperature T equals the product of the partition functions of the separate systems:

$$Z_{12} = Z_1 Z_2. \tag{4.168}$$

Problem 4.53. Qualitative temperature dependence of two level system

(a) Consider a system of N noninteracting, distinguishable particles each of which can be in single particle states with energy 0 and Δ (see Example 4.3). The system is in equilibrium with a beat bath at temperature T. Sketch the probabilities that a given particle is in the ground state and the excited state with energy Δ, and discuss the limiting behavior of the probabilities for low and high temperatures. What does high and low temperature mean in this case? Sketch the T-dependence of the mean energy $E(T)$ and give a simple argument for its behavior. From your sketch of $E(T)$ sketch the T-dependence of the heat capacity $C(T)$ and describe its qualitative behavior. Give a simple physical argument why C has a maximum and estimate the temperature at which the maximum occurs.

(b) Calculate $C(T)$ explicitly and verify that its behavior is consistent with the qualitative features illustrated in your sketch. The maximum in the heat capacity of a two state system is called the Schottky anomaly, but the characterization of this behavior as anomaly is a misnomer because many systems behave as two level systems at low temperatures.

Problem 4.54. Consider a system of N noninteracting, distinguishable particles. Each particle can be in one of three states with energies 0, Δ, and 10Δ. Without doing an explicit calculation, sketch the temperature dependence of the heat capacity at low temperatures.

Problem 4.55. Consider a system of one particle in equilibrium with a heat bath. The particle has two microstates of energy $\epsilon_1 = 0$ and $\epsilon_2 = \Delta$. Find the probabilities p_1 and p_2 when the mean energy of the system is 0.2Δ, 0.4Δ, 0.5Δ, 0.6Δ, and Δ, respectively. What are the corresponding temperatures? (Hint: Write the mean energy as $x\Delta$ and express your answers in terms of x.)

Problem 4.56. Harmonic oscillators in equilibrium with a heat bath

(a) Calculate the heat capacity C_V of a system of N one-dimensional harmonic oscillators (see Example 4.4).

(b) Plot the T-dependence of the mean energy E and the heat capacity $C = dE/dT$. Show that $E \to kT$ at high temperatures for which $kT \gg \hbar\omega$. This result corresponds to the classical limit and will be shown in Section 6.3 to be a consequence of the equipartition theorem. In this limit the thermal energy kT is large in comparison to $\hbar\omega$, the separation between energy levels. Hint: expand the exponential function in (4.131).

(c) Show that at low temperatures for which $\hbar\omega \gg kT$, $E = \hbar\omega(\frac{1}{2} + e^{-\beta\hbar\omega})$. What is the value of the heat capacity? Why is the latter so much smaller than it is in the high temperature limit?

(d) Verify that $S \to 0$ as $T \to 0$ in agreement with the third law of thermodynamics, and that at high T, $S \to kN \ln(kT/\hbar\omega)$. The latter result implies that the effective number of microstates over which the probability is nonzero is $ekT/\hbar\omega$. This result is reasonable because the width of the Boltzmann probability distribution is kT, and hence the number of microstates that are occupied at high temperature is $kT/\hbar\omega$.

Problem 4.57. In the canonical ensemble the temperature is fixed and the constant volume heat capacity is related to the variance of the energy fluctuations (see (4.87)). As discussed on page 207, the temperature fluctuates in the microcanonical ensemble. Guess how the constant volume heat capacity might be expressed in the microcanonical ensemble.

Problem 4.58. Consider the system illustrated in Figure 4.10. The system consists of two distinguishable particles, each of which can be in either of two boxes. Assume that the energy of a particle is zero if it is in the left box and r if it is in the right box. There is also a correlation energy term that lowers the energy by Δ if the two particles are in the same box.

(a) Enumerate the $2^2 = 4$ microstates and their corresponding energy.

(b) Suppose that $r = 1$ and $\Delta = 15$. Sketch the qualitative behavior of the heat capacity C as a function of T.
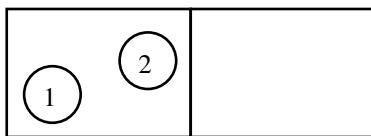
Figure 4.10: The two particles considered in Problem 4.58. The two distinguishable particles can each be in one of the two boxes. The energy of the system depends on which box the particles occupy.

(c) Calculate the partition function Z for arbitrary values of r and Δ and use your result to find the mean energy and the heat capacity. Explain your result for C in simple terms.

(d) What is the probability that the system is in a particular microstate?

Problem 4.59. Consider a system in equilibrium with a heat bath at temperature T and a particle reservoir at chemical potential μ. The reservoir has a maximum of four distinguishable particles. Assume that the particles in the system do not interact and can be in one of two states with energies zero or Δ. Determine the (grand) partition function of the system.

Problem 4.60. Constant pressure ensemble

In the text we derived the form of the probability distribution for a system with fixed T, V, and N (the canonical ensemble) and fixed T, V, and μ (the grand canonical ensemble). What is the form of the probability distribution for an equilibrium system with fixed T, P, and N? This ensemble has no generally accepted name and is not particularly useful for calculations. However, it is useful for doing simulations at a given pressure rather than for a given volume.

Problem 4.61. Demonstration of an entropy-driven transition

The following demonstration illustrates an entropy-driven transition. Get a bag of M & M's or similar disk-shaped candy. Ball bearings work better, but they are not as tasty. You will also need a flat bottom glass dish (preferably square) that fits on an overhead projector.

Place the glass dish on the overhead projector and add a few of the candies. Shake the dish gently from side to side to simulate the effects of temperature. You should observe a two-dimensional model of a gas. Gradually add more candies while continuing to shake the dish. As the density is increased further, you will begin to notice clusters of hexagonal crystals. Do these clusters disappear if you shake the dish faster? At what density do large clusters of hexagonal crystals begin to appear? Is this density less than the maximum packing density?

Suggestions for Further Reading

Joan Adler, "A walk in phase space: Solidification into crystalline and amorphous states," Am. J. Phys. **67**, 1145–1148 (1999). Adler and Laird discuss the demonstration in Problem 4.61.

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Brian B. Laird, "Entropy, disorder and freezing," J. Chem. Educ. **76**, 1388–1390 (1999).

Thomas A. Moore and Daniel V. Schroeder, "A different approach to introducing statistical mechanics," Am. J. Phys. **65**, 26–36 (1997).

F. Reif, *Statistical Physics*, Volume 5 of the Berkeley Physics Series, McGraw-Hill (1965).

W. G. V. Rosser, *An Introduction to Statistical Physics*, Ellis Horwood Limited (1982). As far as we know, this book was the first to introduce the Einstein solid in the context of the counting of states and the thermal interaction of simple systems.

Daniel V. Schroeder, *An Introduction to Thermal Physics*, Addison-Wesley (1999).

Ruth Chabay and Bruce Sherwood, *Matter & Interactions*, John Wiley & Sons (2002), Vol. 1, Modern Mechanics.

Chapter 5

Magnetic Systems

We apply the general formalism of statistical mechanics developed in Chapter 4 to the Ising model, a model magnetic system for which the interactions between the magnetic moments are important. We will discover that these interactions lead to a wide range of phenomena, including the existence of phase transitions and other cooperative phenomena. Computer simulation methods will be used extensively and a simple approximation method known as mean-field theory will be introduced.

5.1   Paramagnetism

We first review the behavior of a system of noninteracting magnetic moments with spin $1/2$ in equilibrium with a heat bath at temperature T. We discussed this system in Section 4.3.1 and in Example 4.2 using the microcanonical ensemble. We will find that this system is much easier to treat in the canonical ensemble.

Because we have assumed that the magnetic moments or spins are noninteracting, the only interaction is that of the spins with an external magnetic field B in the z direction. The magnetic field due to the spins themselves is assumed to be negligible. The energy of interaction of a spin with the external magnetic field B is given by

$$E = -\boldsymbol{\mu} \cdot \mathbf{B} = -\mu_z B = -\mu B s, \tag{5.1}$$

where μ_z is the component of the magnetic moment in the direction of the magnetic field B. We write $\mu_z = s\mu$, where $s = \pm 1$. (The association of the magnetic moment of the electron with its spin is an intrinsic quantum mechanical effect (see Section 5.9.1). We assume that the spins are fixed on a lattice so that they are *distinguishable* even though the spins are intrinsically quantum mechanical.

What would we like to know about the properties of a system of noninteracting spins? In the absence of an external magnetic field, there are not many physical quantities of interest. The spins

point randomly up or down because there is no preferred direction, and the mean internal energy is zero. In contrast, in the presence of an external magnetic field, the net magnetic moment and the energy of the system are nonzero. In the following we will calculate their mean values as a function of the temperature T and external magnetic field B.

As will learn from experience, the easiest ensemble to use is usually the canonical ensemble. Because each spin is independent of the others and distinguishable, we can find the partition function for one spin, Z_1, and use the relation $Z_N = Z_1^N$ to obtain Z_N, the partition function for N spins. (We reached a similar conclusion in Example 4.3.) We can derive the relation between Z_1 and Z_N by writing the energy of the N spins as $E = -\mu B \sum_{i=1}^{N} s_i$ and expressing the partition function Z_N for the N-spin system as

$$Z_N = \sum_{s_1=\pm1} \sum_{s_2=\pm1} \cdots \sum_{s_N=\pm1} e^{\beta\mu B \Sigma_{i=1}^{N} s_i} \tag{5.2}$$

$$= \sum_{s_1=\pm1} \sum_{s_2=\pm1} \cdots \sum_{s_N=\pm1} e^{\beta\mu B s_1} e^{\beta\mu B s_2} \cdots e^{\beta\mu B s_N}$$

$$= \sum_{s_1=\pm1} e^{\beta\mu B s_1} \sum_{s_2=\pm1} e^{\beta\mu B s_2} \cdots \sum_{s_N=\pm1} e^{\beta\mu B s_N}$$

$$= \Big[\sum_{s_1=\pm1} e^{\beta\mu B s_1} \Big]^N = Z_1^N. \tag{5.3}$$

To find Z_1 we write

$$Z_1 = \sum_{s=\pm1} e^{-\beta\mu B s} = e^{\beta\mu B(-1)} + e^{\beta\mu B(+1)} = 2\cosh\beta\mu B, \tag{5.4}$$

where we have performed the sum over $s = \pm1$. Hence, the partition function for N spins is simply

$$Z_N = (2\cosh\beta\mu B)^N . \tag{5.5}$$

We now use the canonical ensemble formalism that we developed in Section 4.6 to find the thermodynamic properties of the system for a given T and B. The free energy is given by

$$F = -kT \ln Z_N = -NkT \ln Z_1 = -NkT \ln(2\cosh\beta\mu B). \tag{5.6}$$

The mean energy $\overline{E}$ is

$$\overline{E} = -\frac{\partial \ln Z_N}{\partial \beta} = \frac{\partial(\beta F)}{\partial \beta} = -N\mu B \tanh\beta\mu B. \tag{5.7}$$

In the following we will frequently omit the mean value notation because it will be clear from the context that an average is implied. From (5.7) we see that $E \to 0$ as $T \to \infty$ ($\beta \to 0$).

Problem 5.1. Comparison of results of two ensembles

(a) Compare the result (5.7) for the mean energy of a system of noninteracting spins in the canonical ensemble to the corresponding result that you found in Problem 4.26 for the microcanonical ensemble.

(b) Compare the results for the thermodynamics of system of noninteracting spins with the corresponding results found in Example 4.3.

The heat capacity C is a measure of the change of the temperature due to the addition of energy at constant magnetic field. The heat capacity at constant magnetic field can be expressed as

$$C = \left(\frac{\partial \overline{E}}{\partial T}\right)_B = -k\beta^2 \frac{\partial \overline{E}}{\partial \beta}. \tag{5.8}$$

(We will write C rather than C_B because no confusion will result.) From (5.7) and (5.8), we find that the heat capacity of a system of N noninteracting spins is given by

$$C = N(\beta\mu B)^2 \operatorname{sech}^2 \beta\mu B. \tag{5.9}$$

Note that the heat capacity is always positive, goes to zero as $T \to 0$ consistent with the third law of thermodynamics, and goes to zero at high T.

Magnetization and Susceptibility. Two additional macroscopic quantities of interest are the mean magnetic moment or magnetization (in the z direction)

$$\overline{M} = \mu \sum_{i=1}^{N} \overline{s}_i, \tag{5.10}$$

and the isothermal susceptibility χ_T:

$$\boxed{\chi_T = \left(\frac{\partial M}{\partial B}\right)_T}. \tag{5.11}$$

Often it is more convenient to work with the mean magnetization per spin $\overline{m}$, an intensive variable, which is defined as

$$\overline{m} = \frac{1}{N}\overline{M}. \tag{5.12}$$

We also will sometime drop the factor of μ in (5.10) so that M becomes the net of number of spins pointing in a given direction. The distinction between M and m and their various meanings will be clear from the context.

The susceptibility χ_T is a measure of the change of the magnetization due to a change in the external magnetic field and is another example of a linear response function. We can express M and χ_T in terms of derivatives of $\ln Z$ by noting that the total energy can be written in the general form as

$$E = E_0 - MB, \tag{5.13}$$

where E_0 is the energy of interaction of the spins with themselves and $-MB$ is the energy of interaction of the spins with the magnetic field. (For noninteracting spins $E_0 = 0$.) The form of E in (5.13) implies that we can write Z in the form

$$Z = \sum_s e^{-\beta(E_{0,s} - M_s B)}, \tag{5.14}$$

where M_s and $E_{0,s}$ are the values of M and E_0 in microstate s. From (5.14) we have

$$\frac{\partial Z}{\partial B} = \sum_s \beta M_s \, e^{-\beta(E_{0,s} - M_s B)}, \tag{5.15}$$

and hence the mean magnetization is given by

$$\overline{M} = \frac{1}{Z} \sum_s M_s e^{-\beta(E_{0,s} - M_s B)} \tag{5.16a}$$

$$= \frac{1}{\beta Z} \frac{\partial Z}{\partial B} = kT \frac{\partial \ln Z_N}{\partial B}. \tag{5.16b}$$

If we substitute the relation $F = -kT \ln Z$, we obtain

$$\boxed{\overline{M} = -\frac{\partial F}{\partial B}}. \tag{5.17}$$

Problem 5.2. Relation of the zero field susceptibility to the magnetization fluctuations

Use considerations similar to that used to derive (5.16b) to show that in the limit $B \to 0$ the susceptibility in zero magnetic field can be written as

$$\boxed{\chi_{\mathrm{T}} = \frac{1}{kT}[\overline{M^2} - \overline{M}^2]}. \tag{5.18}$$

The quantity χ_{T} in (5.18) is the *zero-field susceptibility*.[1] Note the similarity of the form (5.18) with the form (4.87) for the heat capacity C_V.

The quantities C_V and χ_{T} are examples of *linear response functions*. For example, χ_{T} is a measure of the reponse of the magnetization to a very weak magnetic field. The relations of the response functions C_V and χ_{T} to the equilibrium fluctuations of the energy and magnetization, respectively, are special cases of a general result known as the fluctuation-dissipation theorem.

From (5.6) and (5.17) we find that the mean magnetization of a system of noninteracting spins is

$$M = N\mu \, \tanh(\beta\mu B). \tag{5.19}$$

The susceptibility can be calculated using (5.11) and (5.19) and is given by

$$\chi_{\mathrm{T}} = N\mu^2 \beta \, \mathrm{sech}^2(\beta\mu B). \tag{5.20}$$

For high temperatures ($kT \gg \mu B$) or small β ($\beta \ll \mu B$), $\mathrm{sech}(\beta\mu B) \to 1$, and the leading behavior of χ_{T} is given by

$$\chi_{\mathrm{T}} \to N\mu^2\beta = \frac{N\mu^2}{kT}. \qquad (kT \gg \mu B) \tag{5.21}$$

The result (5.21) is known as the Curie form for the isothermal susceptibility and is commonly observed for magnetic materials at high temperatures.

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[1] We will use the same notation for the zero-field isothermal susceptibility and the isothermal susceptibility in a nonzero field because the distinction will be clear from the context.

We see that M is zero at $B = 0$ for all $T > 0$ implying that the system is paramagnetic. For $B \neq 0$, we note that $M \to 0$ as $\beta \to 0$ (high T), which implies that $\chi_T \to 0$ as $T \to \infty$. Because a system of noninteracting spins is paramagnetic, such a model is not applicable to materials such as iron that can have a nonzero magnetization even when the magnetic field is zero. Ferromagnetism is due to the interactions between the spins.

Problem 5.3. Thermodynamics of noninteracting spins

(a) Plot the magnetization per spin as given by (5.19) and the heat capacity C as given by (5.9) as a function of T. Give a simple argument why C must have a broad maximum somewhere between $T = 0$ and $T = \infty$. What is the relation of a system of noninteracting spins to the system considered in Example 4.3?

(b) Plot the isothermal susceptibility χ_T versus T for fixed B and describe its limiting behavior for low and high T.

(c) Calculate the entropy of a system of N noninteracting spins and discuss its limiting behavior at low and high temperatures.

Problem 5.4. Adiabatic demagnetization

Consider a solid containing N noninteracting paramagnetic atoms whose magnetic moments can be aligned either parallel or antiparallel to the magnetic field B. The system is in equilibrium with a heat bath at temperature T. The magnetic moment is $\mu = 9.274 \times 10^{-24}$ J/tesla.

(a) If $B = 4$ tesla, at what temperature are 75% of the spins oriented in the $+z$ direction?

(b) Assume that $N = 10^{23}$, $T = 1$ K, and that B is increased quasistatically from 1 tesla to 10 tesla. What is the magnitude of the energy transfer from the heat bath?

(c) If the system is now thermally isolated at $T = 1$ K and B is quasistatically decreased from 10 tesla to 1 tesla, what is the final temperature of the system? This process is known as *adiabatic demagnetization*.

5.2 Thermodynamics of Magnetism

Note that in Section 5.1 we chose the canonical ensemble specified by T, B, and N. In this ensemble the free energy F defined by the relation $F = -kT \ln Z$ implies that F is a function of T, B, and N. Because B is specified, the magnetization M fluctuates. It can be shown (see Section 5.9.2) that the magnetic work done on a magnetic system with magnetization M in an external magnetic field B is given by $dW = -M dB$. For fixed N, we have the thermodynamic relation

$$dF(T, B) = -S dT - M dB. \tag{5.22}$$

From (5.22) we obtain (5.17) for the magnetization in terms of the free energy. We note that if M is specified and B is allowed to fluctuate, we can define $G = F + MH$ so that

$$dG(T, M) = -S dT + B dM. \tag{5.23}$$

5.3 The Ising Model

As we saw in Section 5.1, the absence of interactions between the spins implies that the system can only be paramagnetic. The most important model of a system that exhibits a phase transition is the *Ising model*, the harmonic oscillator of statistical mechanics.[2] The model was proposed by Wilhelm Lenz (1888–1957) in 1920 and was solved exactly for the one-dimensional case by his student Ernst Ising in 1925.[3] Ising was very disappointed because the one-dimensional case does not have a phase transition. Lars Onsager (1903–1976))[4] solved the Ising model exactly in 1944 for two dimensions in the absence of an external magnetic field and showed that there was a phase transition in two dimensions.[5] The two-dimensional Ising model is the simplest model of a phase transition.

In the Ising model the spin at every site is either up (+1) or down (−1). Unless otherwise stated, the interaction is between nearest neighbors only and is given by −J if the spin are parallel and +J if the spins are antiparallel. The total energy can be expressed in the form[6]

$$E = -J \sum_{i,j=\text{nn}(i)}^{N} s_i s_j - H \sum_{i=1}^{N} s_i, \qquad \text{(Ising model)} \qquad (5.24)$$

where $s_i = \pm 1$ and J is known as the exchange constant. In the following, we will refer to s itself as the spin.[7] The first sum in (5.24) is over all pairs of spins that are nearest neighbors. The interaction between two nearest neighbor spins is counted only once. We have implicitly assumed that the external magnetic field is in the up or positive z direction. The factors of μ_0 and g have been incorporated into the quantity H which we will refer to as the magnetic field. In the same spirit the magnetization becomes the net number of positive spins rather than the net magnetic moment. A discussion of how magnetism occurs in matter in given in Section 5.9.1.

In addition to the conceptual difficulties of statistical mechanics, there is no standard procedure for calculating the partition function. In spite of the apparent simplicity of the Ising model, we can find exact solutions only in one dimension and in two dimensions in the absence of a magnetic field.[8] In other cases we need to use approximation methods and computer simulations.

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[2] Each year hundreds of papers are published that apply the Ising model to problems in such diverse fields as neural networks, protein folding, biological membranes, and social behavior. For this reason the Ising model is sometimes known as the fruit fly of statistical mechanics.

[3] A biographical note about Ising's life is at <www.bradley.edu/las/phy/personnel/ising.html>.

[4] See <en.wikipedia.org/wiki/Lars_Onsager> for a summary of Onsager's life.

[5] The model is sometimes known as the Lenz-Ising model. The history of the Ising model is discussed by Stephen Brush.

[6] If we interpret the spin as a operator, then the energy is really a Hamiltonian. The distinction is unimportant here.

[7] Because the spin **S** is a quantum mechanical object, we expect that the commutator of the spin operator with the Hamiltonian is nonzero. However, because the Ising model retains only the component of the spin along the direction of the magnetic field, the commutator of the spin **S** with the Hamiltonian is zero, and we can treat the spins in the Ising model as if they were classical.

[8] In three dimensions it has been shown that the Ising model is *NP-complete*, that is, it is computationally intractable. The three-dimensional Ising model (and the two-dimensional Ising model with nearest neighbor and next nearest neighbor interactions falls into the same class as other hard problems such as the traveling salesman problem. See <www.sandia.gov/LabNews/LN04-21-00/sorin_story.html> and <www.siam.org/siamnews/07-00/ising.pdf>. The Ising model is also of interest to computer scientists in part for this reason.

In Section 5.4 we will discuss the one-dimensional Ising model for which we can find an exact solution. In Section 5.5 we will briefly discuss the nature of the exact solutions for the two-dimensional Ising model. We will find that the two-dimensional Ising model exhibits a continuous phase transition. We will also consider simulations of the Ising model to gain more insight into the behavior of the Ising model. In Section 5.6 we will discuss a relatively simple approximation known as mean-field theory that is applicable to a wide variety of systems. A more advanced discussion of the Ising model is given in Chapter 9. In Sections 5.9.3 and 5.9.4 we discuss two common types of perturbation expansions.

5.4 The Ising chain

In the following we describe several methods for obtaining exact solutions of the one-dimensional Ising model and introduce an additional physical quantity of interest.

5.4.1 Exact enumeration

The canonical ensemble is the natural choice for calculating the thermodynamic properties of the Ising model. Because the spins are interacting, we no longer have the relation $Z_N = Z_1^N$, and we have to calculate Z_N directly. The calculation of the partition function Z_N is straightforward in principle. The goal is to enumerate all the microstates of the system and the corresponding energies, calculate Z_N for finite N, and then take the limit $N \to \infty$. The difficulty is that the total number of states, 2^N, is too many for $N \gg 1$. However, for the one-dimensional Ising model (Ising chain) we can calculate Z_N for small N and quickly see how to generalize to arbitrary N.

For a finite chain we need to specify the boundary condition for the spin at each end. One possibility is to choose free ends so that the spin at each end has only one interaction (see Figure 5.1(a)). Another choice is toroidal boundary conditions as shown in Figure 5.1(b). This choice implies that the Nth spin is connected to the first spin so that the chain forms a ring. The choice of boundary conditions does not matter in the thermodynamic limit, $N \to \infty$.

In the absence of an external magnetic field, we will find that it is more convenient to choose free boundary conditions when calculating Z directly. The energy of the Ising chain in the absence of an external magnetic field is given explicitly by

$$E = -J \sum_{i=1}^{N-1} s_i s_{i+1}. \qquad \text{(free boundary conditions)} \qquad (5.25)$$

We begin by calculating the partition function for two spins. There are four possible states: both spins up with energy $-J$, both spins down with energy $-J$, and two states with one spin up and one spin down with energy $+J$ (see Figure 5.2). Thus Z_2 is given by

$$Z_2 = 2e^{\beta J} + 2e^{-\beta J} = 4 \cosh \beta J. \qquad (5.26)$$

In the same way we can enumerate the eight microstates for $N = 3$ (see Problem 5.5). We

(a)

(b)
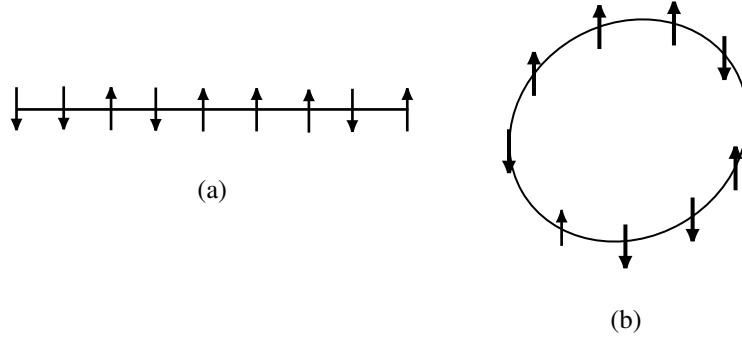
Figure 5.1: (a) Example of free boundary conditions for $N = 9$ spins. The spins at each end interact with only one spin. In contrast, all the other spins interact with two spins. (b) Example of toroidal boundary conditions. The Nth spin interacts with the first spin so that the chain forms a ring. As a result, all the spins have the same number of neighbors and the chain does not have a surface.

Figure 5.2: The four possible configurations of the $N = 2$ Ising chain.

find that

$$Z_3 = 2\,e^{2\beta J} + 4 + 2\,e^{-2\beta J} \tag{5.27a}$$

$$= 2(e^{\beta J} + e^{-\beta J})^2 = 8(\cosh \beta J)^2 \tag{5.27b}$$

$$= (e^{\beta J} + e^{-\beta J})Z_2 = (2\cosh \beta J)Z_2. \tag{5.27c}$$

The relation (5.27c) between Z_3 and Z_2 suggests a general relation between Z_N and Z_{N-1}:

$$Z_N = (2\cosh \beta J)Z_{N-1} = 2\big(2\cosh \beta J\big)^{N-1}. \tag{5.28}$$

We can derive the recursion relation (5.28) directly by writing Z_N for the Ising chain in the form

$$Z_N = \sum_{s_1 = \pm 1} \cdots \sum_{s_N = \pm 1} e^{\beta J \sum_{i=1}^{N-1} s_i s_{i+1}}. \tag{5.29}$$

The sum over the two possible states for each spin yields 2^N microstates. To understand the meaning of the sums in (5.29), we write (5.29) for $N = 3$:

$$Z_3 = \sum_{s_1 = \pm 1} \sum_{s_2 = \pm 1} \sum_{s_3 = \pm 1} e^{\beta J s_1 s_2 + \beta J s_2 s_3}. \tag{5.30}$$

The sum over s_3 can be done independently of s_1 and s_2, and we have

$$Z_3 = \sum_{s_1=\pm 1} \sum_{s_2=\pm 1} e^{\beta J s_1 s_2} \big[e^{\beta J s_2} + e^{-\beta J s_2} \big] \tag{5.31a}$$

$$= \sum_{s_1=\pm 1} \sum_{s_2=\pm 1} e^{\beta J s_1 s_2} 2 \cosh \beta J s_2 = 2 \sum_{s_1=\pm 1} \sum_{s_2=\pm 1} e^{\beta J s_1 s_2} \cosh \beta J. \tag{5.31b}$$

We have used the fact that the cosh function is even and hence $\cosh \beta J s_2 = \cosh \beta J$, independently of the sign of s_2. The sum over s_1 and s_2 in (5.31b) is straightforward, and we find,

$$Z_3 = (2 \cosh \beta J) Z_2, \tag{5.32}$$

in agreement with (5.27c).

The analysis of (5.29) proceeds similarly. Note that spin N occurs only once in the exponential and we have, independently of the value of s_{N-1},

$$\sum_{s_N=\pm 1} e^{\beta J s_{N-1} s_N} = 2 \cosh \beta J. \tag{5.33}$$

Hence we can write Z_N as

$$Z_N = (2 \cosh \beta J) Z_{N-1}. \tag{5.34}$$

We can use the general result (5.28) for Z_N to find the Helmholtz free energy:

$$F = -kT \ln Z_N = -kT \big[\ln 2 + (N-1) \ln(2 \cosh \beta J) \big]. \tag{5.35}$$

In the thermodynamic limit $N \to \infty$, the term proportional to N in (5.35) dominates, and we have the desired result:

$$F = -NkT \ln \big(2 \cosh \beta J \big). \tag{5.36}$$

Problem 5.5. Exact enumeration

Enumerate the 2^N microstates for the $N = 3$ and $N = 4$ Ising chain and find the corresponding contributions to Z_3 and Z_4 for free boundary conditions. Then show that Z_3 and Z_4 satisfy the recursion relation (5.34) for free boundary conditions.

Problem 5.6. Thermodynamics of the Ising chain

(a) What is the ground state of the Ising chain?

(b) What is the behavior of S in the limits $T \to 0$ and $T \to \infty$? The answers can be found without doing an explicit calculation.

(c) Use (5.36) for F to verify the following results for the entropy S, the mean energy E, and the heat capacity C of the Ising chain:

$$S = Nk \Big[\ln(e^{2\beta J} + 1) - \frac{2\beta J}{1 + e^{-2\beta J}} \Big]. \tag{5.37}$$

$$E = -NJ \tanh \beta J. \tag{5.38}$$

$$C = Nk(\beta J)^2 (\operatorname{sech} \beta J)^2. \tag{5.39}$$

Verify your answers for the limiting behavior of S given in part (b). A plot of the T-dependence of the heat capacity in the absence of a magnetic field is given in Figure 5.3.
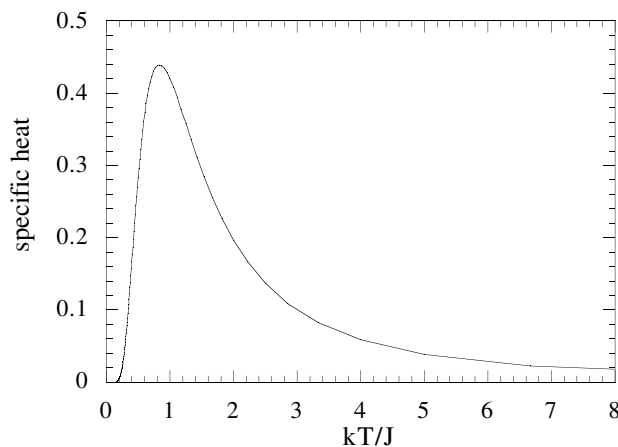
Figure 5.3: The temperature dependence of the heat capacity C of an Ising chain in the absence of an external magnetic field. At what value of kT/J does C exhibit a maximum? Explain.

*Problem 5.7. Density of states

In Problem 4.18 the density of states was given without proof for the one-dimensional Ising model for even N and toroidal boundary conditions:

$$\Omega(E, N) = 2\binom{N}{i} = 2\frac{N!}{i!\,(N-i)!}, \qquad (i = 0, 2, 4, \ldots, N)$$

with $E = 2\,i - N$.

(a) Use this form of Ω and the relation

$$Z_N = \sum_E \Omega(E, N)e^{-\beta E} \tag{5.40}$$

to find the free energy for small values of (even) N.

(b) Use the results for Z_N that you found by exact enumeration to find $\Omega(E, N)$ for small values of N.

5.4.2   *Spin-spin correlation function

We can gain further insight into the properties of the Ising model by calculating the spin-spin correlation function $G(r)$ defined as

$$G(r) = \overline{s_k s_{k+r}} - \overline{s_k}\,\overline{s_{k+r}}. \tag{5.41}$$

Because the average of s_k is independent of the choice of the site k and equals $m = M/N$, the magnetization per spin, and $G(r)$ can be written as

$$G(r) = \overline{s_k s_{k+r}} - m^2. \tag{5.42}$$
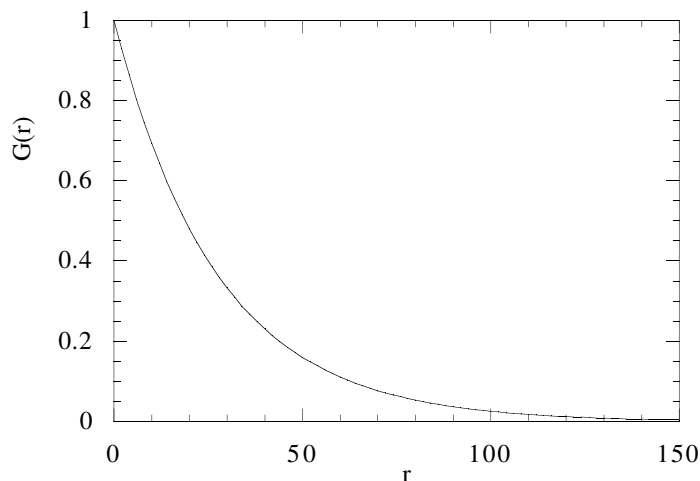
Figure 5.4: Plot of the spin-spin correlation function $G(r)$ as given by (5.43) for the Ising chain for $\beta J = 2$.

The average is over all spin configurations. Because all lattice sites are equivalent, $G(r)$ is independent of the choice of k and depends only on the separation r (for a given T and H), where r is the separation between the two spins in units of the lattice constant. Note that $G(r = 0) = \overline{m^2} - \overline{m}^2 \propto \chi_{\mathrm{T}}$ (see (5.18)).

The spin-spin correlation function tells us the degree to which a spin at one site is correlated with a spin at another site. If the spins are not correlated, then $G(r) = 0$. At high temperatures the interaction between spins is unimportant, and hence the spins are randomly oriented in the absence of an external magnetic field. Thus in the limit $kT \gg J$, we expect that $G(r) \to 0$ for fixed r. For fixed T and H, we expect that if spin k is up, then the two adjacent spins will have a greater probability of being up than down. Why? As we move away from spin k, we expect that the probability that spin $k + r$ is up will decrease. Hence, we expect that $G(r) \to 0$ as $r \to \infty$.

We will show in the following that $G(r)$ can be calculated exactly for the Ising chain. The result is

$$G(r) = \big(\tanh \beta J \big)^r. \tag{5.43}$$

A plot of $G(r)$ for $\beta J = 2$ is shown in Figure 5.4. Note that $G(r) \to 0$ for $r \gg 1$ as expected.

We also see from Figure 5.4 that we can associate a length with the decrease of $G(r)$. We will define the *correlation length* ξ by writing $G(r)$ in the form

$$G(r) = e^{-r/\xi}. \tag{5.44}$$

For the one-dimensional Ising model

$$\xi = -\frac{1}{\ln(\tanh \beta J)}. \tag{5.45}$$

At low temperatures, $\tanh \beta J \approx 1 - 2e^{-2\beta J}$, and

$$\ln\left(\tanh \beta J\right) \approx -2e^{-2\beta J}. \tag{5.46}$$

Hence

$$\xi = \frac{1}{2}e^{2\beta J}. \qquad (\beta J \gg 1) \tag{5.47}$$

From (5.47) we see that the correlation length becomes very large for low temperatures ($\beta J \gg 1$). The correlation length gives the length scale for the decay of correlations between the spins.

Problem 5.8. What is the maximum value of $\tanh \beta J$? Show that for finite values of βJ, $G(r)$ given by (5.43) decays with increasing r.

To calculate $G(r)$ we assume free boundary conditions and consider only the zero-field case. It is convenient to generalize the Ising model and assume that the magnitude of each of the nearest neighbor interactions is arbitrary so that the total energy E is given by

$$E = -\sum_{i=1}^{N-1} J_i s_i s_{i+1}, \tag{5.48}$$

where J_i is the interaction energy between spin i and spin $i+1$. At the end of the calculation we will set $J_i = J$. We will find in Section 5.4.4, that $m = 0$ for $T > 0$ for the one-dimensional Ising model. Hence, we can write $G(r) = \overline{s_k s_{k+r}}$. For the form (5.48) of the energy, $\overline{s_k s_{k+r}}$ is given by

$$\overline{s_k s_{k+r}} = \frac{1}{Z_N} \sum_{s_1=\pm 1} \cdots \sum_{s_N=\pm 1} s_k s_{k+r} \, \exp\Big[\sum_{i=1}^{N-1} \beta J_i s_i s_{i+1}\Big], \tag{5.49}$$

where

$$Z_N = 2 \prod_{i=1}^{N-1} 2\cosh \beta J_i. \tag{5.50}$$

The right-hand side of (5.49) is the value of the product of two spins separated by a distance r in a particular configuration times the probability of that configuration.

We now use a trick similar to that used in Appendix A to calculate various integrals. If we take the derivative of the exponential with respect to J_k, we bring down a factor of $s_k s_{k+1}$. Hence, the nearest neighbor spin-spin correlation function $G(r=1) = \overline{s_k s_{k+1}}$ for the Ising model with $J_i = J$ can be expressed as

$$\overline{s_k s_{k+1}} = \frac{1}{Z_N} \sum_{s_1=\pm 1} \cdots \sum_{s_N=\pm 1} s_k s_{k+1} \exp\Big[\sum_{i=1}^{N-1} \beta J_i s_i s_{i+1}\Big], \tag{5.51a}$$

$$= \frac{1}{Z_N} \frac{1}{\beta} \frac{\partial}{\partial J_k} \sum_{s_1=\pm 1} \cdots \sum_{s_N=\pm 1} \exp\Big[\sum_{i=1}^{N-1} \beta J_i s_i s_{i+1}\Big], \tag{5.51b}$$

$$= \frac{1}{Z_N} \frac{1}{\beta} \frac{\partial Z_N(J_1, \cdots, J_{N-1})}{\partial J_k}\bigg|_{J_i = J} \tag{5.51c}$$

$$= \frac{\sinh \beta J}{\cosh \beta J} = \tanh \beta J, \tag{5.51d}$$

where we have used the form (5.50) for Z_N. To obtain $G(r = 2)$, we use the fact that $s_{k+1}^2 = 1$ to write $s_k s_{k+2} = s_k (s_{k+1} s_{k+1}) s_{k+2} = (s_k s_{k+1})(s_{k+1} s_{k+2})$. We write

$$G(r = 2) = \frac{1}{Z_N} \sum_{\{s_j\}} s_k s_{k+1} s_{k+1} s_{k+2} \exp \Big[\sum_{i=1}^{N-1} \beta J_i s_i s_{i+1} \Big], \tag{5.52a}$$

$$= \frac{1}{Z_N} \frac{1}{\beta^2} \frac{\partial^2 Z_N(J_1, \cdots, J_{N-1})}{\partial J_k \, \partial J_{k+1}} = [\tanh \beta J]^2. \tag{5.52b}$$

It is clear that the method used to obtain $G(r = 1)$ and $G(r = 2)$ can be generalized to arbitrary r. We write

$$G(r) = \frac{1}{Z_N} \frac{1}{\beta^r} \frac{\partial}{\partial J_k} \frac{\partial}{J_{k+1}} \cdots \frac{\partial}{J_{k+r-1}} Z_N, \tag{5.53}$$

and use (5.50) for Z_N to find that

$$G(r) = \tanh \beta J_k \tanh \beta J_{k+1} \cdots \tanh \beta J_{k+r-1},$$

$$= \prod_{k=1}^{r} \tanh \beta J_{k+r-1}. \tag{5.54}$$

For a uniform interaction, $J_i = J$, and (5.54) reduces to the result for $G(r)$ in (5.43).

Problem 5.9. Calculation of $G(r)$ for four spins

Consider an Ising chain of $N = 4$ spins and calculate $G(r)$ by exact enumeration of the 2^4 microstates. Choose free boundary conditions and calculate $G(r)$ using the microstates that you enumerated in Problem 5.5. Assume that the system is in equilibrium with a heat bath at temperature T and in zero magnetic field.

5.4.3 Simulations of the Ising chain

Although we have found an exact solution for the one-dimensional Ising model, we can gain additional physical insight by doing simulations. As we will see, simulations are essential for the Ising model in higher dimensions.

As we discussed in Section 4.11, the Metropolis algorithm is the simplest and most common Monte Carlo algorithm for a system in equilibrium with a heat bath at temperature T. In the context of the Ising model, the Metropolis algorithm can be implemented as follows:

1. Choose an initial microstate of N spins. The two most common initial states are the ground state with all spins parallel or the $T = \infty$ state where each spin is chosen to be ± 1 at random.

2. Choose a spin at random and make a trial flip. Compute the change in energy of the system, ΔE, corresponding to the flip. The calculation is straightforward because the change in energy is determined by only the two nearest neighbor spins. If $\Delta E < 0$, then accept the change. If $\Delta E > 0$, accept the change with probability $p = e^{-\beta \Delta E}$. To do so, generate a random number r uniformly distributed in the unit interval. If $r \leq p$, accept the new microstate; otherwise, retain the previous microstate.

3. Repeat step (2) many times choosing spins at random.

4. Compute the averages of the quantities of interest such as $\overline{E}$, $\overline{M}$, C, and χ after the system has reached equilibrium.

In the following two problems we explore some of the qualitative properties of the Ising chain.

Problem 5.10. Qualitative properties of the Ising chain

Use the applet/application at `<stp.clarku.edu/simulations/ising/ising1d.html>` to simulate the one-dimensional Ising model. It is convenient to measure the temperature in units such that $J/k = 1$. For example, a temperature of $T = 2$ really means that $T = 2J/k$. The "time" is measured in terms of Monte Carlo steps per spin, where in one Monte Carlo step per spin, N spins are chosen at random for trial changes. (On the average each spin will be chosen equally, but during any finite interval, some spins might be chosen more than others.) Choose $H = 0$.

(a) Choose $N = 200$ spins and start the system at $T = 2$ and observe the evolution of the magnetization and energy per spin to equilibrium. The initial state is chosen to be the ground state. What is the approximate time for the system to reach equilibrium? What is your criterion for equilibrium? What is the mean energy, magnetization, heat capacity, and susceptibility? Estimate the mean size of the domains of parallel spins.

(b) Consider $T = 1.0$ and $T = 0.5$ and observe the size of the domains of parallel spins. Estimate the mean size of the domains at these temperatures.

Problem 5.11. Thermodynamic properties of the Ising chain

The thermodynamic quantities of interest for the Ising model include the mean energy E, the heat capacity C, and the isothermal susceptibility χ_{T}. We are especially interested in the temperature-dependence of these quantities near $T = 0$.

(a) Why is the mean value of the magnetization of little interest for the one-dimensional Ising model?

(b) How can the heat capacity and susceptibility be computed during the simulation at a given temperature?

(c) Use the applet at `<stp.clarku.edu/simulations/ising/ising1d.html>` to estimate these quantities and determine the qualitative-dependence of χ and the correlation length ξ on T at low temperatures.

(d) Why does the Metropolis algorithm become inefficient at low temperatures?

5.4.4 *Transfer matrix

So far we have considered the Ising chain only in zero external magnetic field. As might be expected, the solution for $H \neq 0$ is more difficult. We next apply the *transfer matrix* method to solve for the thermodynamic properties of the Ising chain in nonzero magnetic field. The transfer matrix method is very general and can be applied to various magnetic systems and to seemingly unrelated quantum mechanical systems. The transfer matrix method also is of historical interest because it led to the exact solution of the two-dimensional Ising model in the absence of a magnetic field.

Problem 5.12. Transfer matrix method in zero magnetic field

Show that the partition function for a system of $N = 3$ spins with toroidal boundary conditions can be expressed as the the product of two matrics:

$$\begin{pmatrix} e^{\beta J} & e^{-\beta J} \\ e^{-\beta J} & e^{\beta J} \end{pmatrix} \begin{pmatrix} e^{\beta J} & e^{-\beta J} \\ e^{-\beta J} & e^{\beta J} \end{pmatrix}. \tag{5.55}$$

To apply the transfer matrix method to the one-dimensional Ising model, it is necessary to adopt toroidal boundary conditions so that the chain becomes a ring with $s_{N+1} = s_1$. This boundary condition enables us to write the energy as:

$$E = -J \sum_{i=1}^{N} s_i s_{i+1} - \frac{1}{2} H \sum_{i=1}^{N} (s_i + s_{i+1}). \quad \text{(toroidal boundary conditions)} \tag{5.56}$$

The use of toroidal boundary conditions implies that each spin is equivalent.

The transfer matrix $\mathbf{T}$ is defined by its four matrix elements which are given by

$$T_{s,s'} = e^{\beta[Jss' + \frac{1}{2}H(s+s')]}. \tag{5.57}$$

The explicit form of the matrix elements is

$$T_{++} = e^{\beta(J+H)} \tag{5.58a}$$

$$T_{--} = e^{\beta(J-H)} \tag{5.58b}$$

$$T_{-+} = T_{+-} = e^{-\beta J}, \tag{5.58c}$$

or

$$\mathbf{T} = \begin{pmatrix} T_{++} & T_{+-} \\ T_{-+} & T_{--} \end{pmatrix} = \begin{pmatrix} e^{\beta(J+H)} & e^{-\beta J} \\ e^{-\beta J} & e^{\beta(J-H)} \end{pmatrix}. \tag{5.59}$$

The definition (5.57) of $\mathbf{T}$ allows us to write Z_N in the form

$$Z_N(T, H) = \sum_{s_1} \sum_{s_2} \cdots \sum_{s_N} T_{s_1,s_2} T_{s_2,s_3} \cdots T_{s_N,s_1}. \tag{5.60}$$

The form of (5.60) is suggestive of our interpretation of $\mathbf{T}$ as a transfer function.

The rule for matrix multiplication that we need for the transfer matrix method is

$$(\mathbf{T}^2)_{s_1,s_3} = \sum_{s_2} T_{s_1,s_2} T_{s_2,s_3}. \tag{5.61}$$

If we multiply N matrices together, we obtain:

$$(\mathbf{T}^N)_{s_1,s_{N+1}} = \sum_{s_2} \sum_{s_3} \cdots \sum_{s_N} T_{s_1,s_2} T_{s_2,s_3} \cdots T_{s_N,s_{N+1}}. \tag{5.62}$$

This result is very close to what we have in (5.60). To make it identical, we use toroidal boundary conditions and set $s_{N+1} = s_1$, and sum over s_1:

$$\sum_{s_1} (\mathbf{T}^N)_{s_1,s_1} = \sum_{s_1} \sum_{s_2} \sum_{s_3} \cdots \sum_{s_N} T_{s_1,s_2} T_{s_2,s_3} \cdots T_{s_N,s_1} = Z_N. \tag{5.63}$$

Because $\sum_{s_1} (\mathbf{T}^N)_{s_1,s_1}$ is the definition of the trace (the sum of the diagonal elements) of $(\mathbf{T}^N)$, we have

$$Z_N = \text{trace}(\mathbf{T}^N). \tag{5.64}$$

Because the trace of a matrix is independent of the representation of the matrix, the trace in (5.64) may be evaluated by bringing $\mathbf{T}$ into diagonal form:

$$\mathbf{T} = \begin{pmatrix} \lambda_+ & 0 \\ 0 & \lambda_- \end{pmatrix}. \tag{5.65}$$

The matrix $\mathbf{T}^N$ is diagonal with the diagonal matrix elements λ_+^N, λ_-^N. If we choose the diagonal representation fo $\mathbf{T}$ in (5.65), we have

$$\text{trace}\,(\mathbf{T}^N) = \lambda_+^N + \lambda_-^N, \tag{5.66}$$

where λ_+ and λ_- are the eigenvalues of $\mathbf{T}$. Hence, we can express Z_N as

$$Z_N = \lambda_+^N + \lambda_-^N. \tag{5.67}$$

The fact that Z_N is the trace of the Nth power of a matrix is a consequence of our assumption of toroidal boundary conditions.

The eigenvalues $\lambda_{\pm}$ are given by the solution of the determinant equation

$$\begin{vmatrix} e^{\beta(J+H)} - \lambda & e^{-\beta J} \\ e^{-\beta J} & e^{\beta(J-H)} - \lambda \end{vmatrix} = 0. \tag{5.68}$$

The roots of (5.68) are

$$\lambda_{\pm} = e^{\beta J} \cosh \beta H \pm \left[e^{-2\beta J} + e^{2\beta J} \sinh^2 \beta H \right]^{1/2}. \tag{5.69}$$

It is easy to show that $\lambda_+ > \lambda_-$ for all H and β, and consequently $(\lambda_-/\lambda_+)^N \to 0$ as $N \to \infty$. In the thermodynamic limit $(N \to \infty)$, we obtain from (5.67) and (5.69)

$$\frac{1}{N} \ln Z_N(T, H) = \ln \lambda_+ + \ln \left[1 + \left(\frac{\lambda_-}{\lambda_+} \right)^N \right] \xrightarrow[N \to \infty]{} \ln \lambda_+, \tag{5.70}$$

and the free energy per spin is given by

$$\frac{1}{N} F(T, H) = -kT \ln \left[e^{\beta J} \cosh \beta J + \left(e^{2\beta J} \sinh^2 \beta H + e^{-2\beta J} \right)^{1/2} \right]. \tag{5.71}$$

We can use (5.71) to find the magnetization M at nonzero T and H:

$$M = \frac{\partial F}{\partial H} = N \frac{\sinh \beta H}{(\sinh^2 \beta H + e^{-4\beta J})^{1/2}}. \tag{5.72}$$

A system is paramagnetic if $M \neq 0$ only for $H \neq 0$, and is ferromagnetic if $M \neq 0$ for $H = 0$. For the one-dimensional Ising model, we see from (5.72) that $M = 0$ for $H = 0$, and there is no spontaneous magnetization at nonzero temperature. (Recall that $\sinh x \approx x$ for small x.) That is, the one-dimensional Ising model undergoes a phase transition from the paramagnetic to the ferromagnetic state only at $T = 0$. In the limit of low temperature $(\beta J \gg 1$ and $\beta H \gg 1)$, $\sinh \beta H \approx \frac{1}{2} e^{\beta H} \gg e^{-2\beta J}$ and $m = M/N \approx 1$ for $H \neq 0$. Hence, at low temperatures only a small field is needed to produce saturation, corresponding to $m = 1$.

Problem 5.13. Isothermal susceptibility of the Ising chain

More insight into the properties of the Ising chain can be found by calculating the isothermal susceptibility χ_T.

(a) Calculate the susceptibility using (5.72).

(b) What is the limiting behavior of the susceptibility in the limit $T \to 0$ for $H > 0$?

(c) Show that the limiting behavior of the zero field susceptibility in the limit $T \to 0$ is $\chi_T \sim e^{2\beta J}$. Express this limiting behavior in terms of the correlation length ξ. Why does χ_T diverge as $T \to 0$?

   Because the zero field susceptibility diverges as $T \to 0$, the fluctuations in the magnetization also diverge in this limit. As we will see, the divergence of the fluctuations of the magnetization is one of the characteristics of the critical point in the Ising model. That is, the phase transition from a paramagnet ($m = 0$ for $H = 0$) to a ferromagnet ($m \neq 0$ for $H = 0$) occurs at zero temperature for the one-dimensional Ising model. We will see that the critical point occurs at $T > 0$ for the Ising model in two and higher dimensions.

5.4.5   Absence of a phase transition in one dimension

We learned in Section 5.4.4 that the one-dimensional Ising model does not have a phase transition for $T > 0$. We now argue that a phase transition in one dimension is impossible if the interaction is short-range, that is, if only a finite number of spins interact with one another.

   At $T = 0$ the energy is a minimum with $E = -(N - 1)J$ (for free boundary conditions), and the entropy $S = 0$.[9] Consider all the excitations at $T > 0$ obtained by flipping all the spins to the right of some site (see Figure 5.5(a)). The energy cost of creating such a domain wall is $2J$. Because there are $N - 1$ sites where the wall may be placed, the entropy increases by $\Delta S = k \ln(N - 1)$. Hence, the free energy cost associated with creating one domain wall is

$$\Delta F = 2J - kT \ln(N - 1). \tag{5.73}$$

We see from (5.73) that for $T > 0$ and $N \to \infty$, the creation of a domain wall lowers the free energy. Hence, more domain walls will be created until the spins are completely randomized and the net magnetization is zero. We conclude that $M = 0$ for $T > 0$ in the limit $N \to \infty$.

Problem 5.14. Compare the energy of the configuration in Figure 5.5(a) with the energy of the configuration shown in Figure 5.5(b) and discuss why the number of spins in a domain in one dimension can be changed without the cost of energy.

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[9]The ground state for $H = 0$ corresponds to all spins up or all spins down. It is convenient to break this symmetry by assuming that $H = 0^+$ and letting $T \to 0$ before setting $H = 0$.
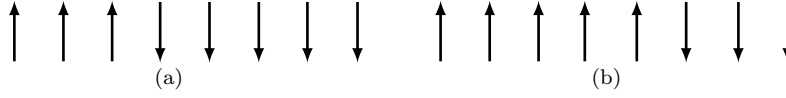
Figure 5.5: A domain wall in one dimension for a system of $N = 8$ spins. In (a) the energy of the system is $E = -5J$ for free boundary conditions. The energy cost for forming a domain wall is 2J (recall that the ground state energy is $-7J$. In (b) the domain wall has moved with no cost in energy.
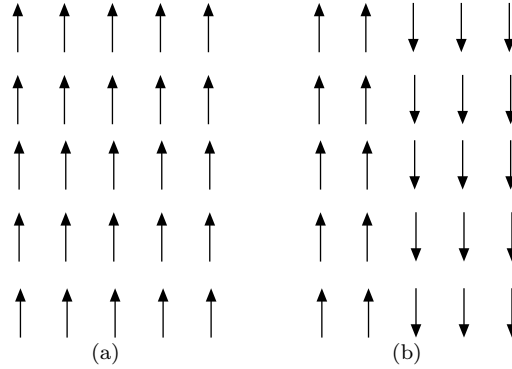
Figure 5.6: (a) The ground state of a 5×5 Ising model. (b) Example of a domain wall. The energy cost of the domain is $5J$ assuming free boundary conditions.

5.5   The Two-Dimensional Ising Model

We first give an argument similar to the one that given in Section 5.4.1 to suggest the existence of a phase transition (to ferromagnetism) in two dimensions. We will show that the mean value of the magnetization is nonzero at low, but nonzero temperatures and in zero magnetic field.

The key difference between the one and two-dimensional case is that in one dimension, the existence of one domain wall allows the system to have regions of up and down spins, and the size of each region can be changed without any cost of energy. So on the average the number of up and down spins is the same. In two dimensions the existence of one domain does not make the magnetization zero. The regions of down spins cannot grow at low temperature because their growth requires longer boundaries and hence more energy.

From Figure 5.6 we see that the energy cost of one domain in two dimensions is given by JL (for free boundary conditions). Because the domain wall can be at any of the L columns, the entropy is at least order $\ln L$. Hence the free energy cost of creating one domain is $\Delta F \sim JL - T \ln L$. In the limit $L \to \infty$, $\Delta F > 0$. Therefore most of the spins will remain positive, and the magnetization remains positive. Hence $M > 0$ for $T > 0$, and the system is ferromagnetic.

We will find in the following that M becomes zero at a critical temperature $T_c > 0$.

5.5.1 Onsager solution

The two-dimensional Ising model was solved exactly in zero magnetic field for a rectangular lattice by Lars Onsager in 1944. Onsager's calculation was the first exact solution that exhibited a phase transition in a model with short-range interactions. Before his calculation, some people believed that statistical mechanics was not capable of yielding a phase transition.

Although Onsager's solution is of much historical interest, the mathematical manipulations are very involved. Moreover, the manipulations are special to the Ising model and cannot be generalized to other systems. For these reasons few workers in statistical mechanics have gone through the Onsager solution in great detail.[10] In the following, we give only the results of the two-dimensional solution for a square lattice.

The critical temperature T_c is given by

$$\sinh \frac{2J}{kT_c} = 1, \tag{5.74}$$

or

$$kT_c/J = \frac{2}{\ln(1 + \sqrt{2})} \approx 2.269. \tag{5.75}$$

It is convenient to express the mean energy in terms of the dimensionless parameter κ defined as

$$\kappa = 2\frac{\sinh 2\beta J}{(\cosh 2\beta J)^2}. \tag{5.76}$$

A plot of the parameter κ versus βJ is given in Figure 5.7. Note that κ is zero at low and high temperatures and has a maximum of unity at $T = T_c$.

The exact solution for the energy E can be written in the form

$$E = -2NJ \tanh 2\beta J - NJ\frac{\sinh^2 2\beta J - 1}{\sinh 2\beta J \cosh 2\beta J}\Big[\frac{2}{\pi}K_1(\kappa) - 1\Big], \tag{5.77}$$

where

$$K_1(\kappa) = \int_0^{\pi/2} \frac{d\phi}{\sqrt{1 - \kappa^2 \sin^2 \phi}}. \tag{5.78}$$

K_1 is known as the complete elliptic integral of the first kind. The first term in (5.77) is similar to the result (5.38) for the energy of the one-dimensional Ising model with a doubling of the exchange interaction J for two dimensions. The second term in (5.77) vanishes at low and high temperatures (because of the term in brackets) and at $T = T_c$ because of the vanishing of the term $\sinh^2 2\beta J - 1$. The function $K_1(\kappa)$ has a logarithmic singularity at $T = T_c$ at which $\kappa = 1$. Hence, the second term behaves as $(T - T_c) \ln |T - T_c|$ in the vicinity of T_c. We conclude that $E(T)$ is continuous at $T = T_c$ and at all other temperatures.

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[10]It is probably true that fewer people understand the Onsager solution of the two-dimensional Ising model than understand Einstein's theory of general relativity.
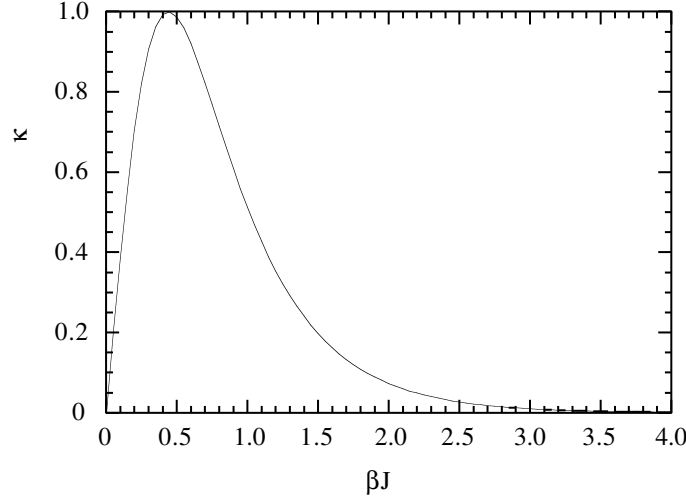
Figure 5.7: Plot of the function κ defined in (5.76) as a function of J/kT.

The heat capacity can be obtained by differentiating $E(T)$ with respect to temperature. It can be shown after some tedious algebra that

$$C(T) = Nk\frac{4}{\pi}(\beta J \coth 2\beta J)^2 \big[K_1(\kappa) - E_1(\kappa)$$
$$- (1 - \tanh^2 2\beta J)\big(\frac{\pi}{2} + (2\tanh^2 2\beta J - 1)K_1(\kappa)\big)\big], \tag{5.79}$$

where

$$E_1(\kappa) = \int_0^{\pi/2} d\phi \sqrt{1 - \kappa^2 \sin^2 \phi}. \tag{5.80}$$

E_1 is the complete elliptic integral of the second kind. Near T_c, C is given by

$$C \approx -Nk\frac{2}{\pi}\left(\frac{2J}{kT_c}\right)^2 \ln\big|1 - \frac{T}{T_c}\big| + \text{constant}. \qquad (T \text{ near } T_c) \tag{5.81}$$

The most important property of the Onsager solution is that the heat capacity diverges logarithmically at $T = T_c$:

$$C(T) \sim \ln|\epsilon|, \tag{5.82}$$

where the reduced temperature difference is given by

$$\epsilon = (T_c - T)/T_c. \tag{5.83}$$

A major test of the approximate treatments that we will develop in Section 5.6 and in Chapter 9 is whether they can yield a heat capacity that diverges as in (5.82).

To know whether the logarithmic divergence of the heat capacity at $T = T_c$ is associated with a phase transition, we need to know if there is a spontaneous magnetization. That is, is there a
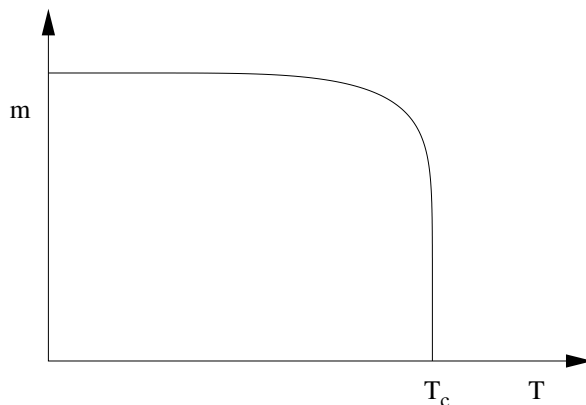
Figure 5.8: The temperature-dependence of the spontaneous magnetization of the two-dimensional Ising model.

range of $T > 0$ such that $M \neq 0$ for $H = 0$? Onsager's solution is limited to zero magnetic field. To calculate the spontaneous magnetization, we need to calculate the derivative of the free energy with respect to H for finite H and then let $H = 0$. The exact behavior of the two-dimensional Ising model as a function of the magnetic field H is not known. In 1952, Yang was able to calculate the magnetization for $T < T_c$ and the zero-field susceptibility.[11] Yang's exact result for the magnetization per spin can be expressed as

$$m(T) = \begin{cases} 0 & T > T_c \\ \left(1 - [\sinh 2\beta J]^{-4}\right)^{1/8} & T < T_c \end{cases} \tag{5.84}$$

A graph of m is shown in Figure 5.8. We see that m vanishes near T_c as $m \sim \epsilon^{1/8}$. The magnetization m is an example of an *order parameter*. The order parameter provides a signature of the order, that is, $m = 0$ for $T > T_c$ (disordered state) and $m \neq 0$ for $T \leq T_c$ (ordered state).

The behavior of the zero-field susceptibility as $T \to T_c$ is given by

$$\chi_T \sim |\epsilon|^{-7/4}. \tag{5.85}$$

The most important results of the exact solution of the two-dimensional Ising model are that the energy (and the free energy and the entropy) are continuous functions for all T, m vanishes continuously at $T = T_c$, the heat capacity diverges logarithmically at $T = T_c$, and the zero-field susceptibility diverges as a power law. When we discuss phase transitions in more detail in Chapter 9, we will understand that the paramagnetic $\leftrightarrow$ ferromagnetic transition in the two-dimensional Ising model is *continuous*. That is, the order parameter m vanishes continuously rather than discontinuously. Because the transition occurs only at $T = T_c$ and $H = 0$, the transition occurs at a *critical point*.

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[11]The result (5.84) was first announced by Onsager at a conference in 1944 but not published. Yang is the same person who together with Lee shared the 1957 Nobel Prize in Physics for work on parity violation. See <nobelprize.org/physics/laureates/1957/>.

The spin-spin correlation function $G(r)$ cannot be expressed in terms of simple analytical expressions for all r and all T. However, the general behavior of $G(r)$ for T near T_c is given by

$$G(r) \sim \frac{1}{r^{d-2+\eta}} e^{-r/\xi} \qquad (r \gg 1 \text{ and } |\epsilon| \ll 1), \tag{5.86}$$

where d is the spatial dimension and η is another critical exponent. The correlation length ξ diverges as

$$\xi \sim |\epsilon|^{-\nu}. \tag{5.87}$$

The exact result for the critical exponent ν for the two-dimensional Ising model is $\nu = 1$. At $T = T_c$, $G(r)$ decays as a power law:

$$G(r) = \frac{1}{r^\eta}. \qquad (r \gg 1, \, T = T_c, \text{ and } d = 2) \tag{5.88}$$

The power-law behavior in (5.88). For the two-dimensional Ising model $\eta = 1/4$. The value of the various critical exponents for the Ising model in two and three dimensions is summarized in Table 5.1.

quantity	exponent	$d = 2$ (exact)	$d = 3$	mean-field
specific heat	α	0 (logarithmic)	0.113	0 (jump)
order parameter	β	1/8	0.324	1/2
susceptibility	γ	7/4	1.238	1
equation of state $(T = T_c)$	δ	15	4.82	3
power law decay at $T = T_c$	η	1/4	0.031 (5)	0
correlation length	ν	1	0.629 (4)	1/2

Table 5.1: Values of the static critical exponents for the Ising model in two and three dimensions.

There is a fundamental difference between the exponential behavior of $G(r)$ for $T \neq T_c$ in (5.86) and the power law behavior of $G(r)$ for $T = T_c$ in (5.88). Systems with correlation functions that decay as a power law are said to be *scale invariant*. That is, power laws look the same on all scales. The replacement $x \to ax$ in the function $f(x) = Ax^{-\eta}$ yields a function $g(x)$ that is indistinguishable from $f(x)$ except for a change in the amplitude A by the factor $a^{-\eta}$. In contrast, this invariance does not hold for functions that decay exponentially because making the replacement $x \to ax$ in the function $e^{-x/\xi}$ changes the correlation length ξ by the factor a. The fact that the critical point is scale invariant is the basis for the renormalization group method considered in Chapter 9.

We stress that the phase transition in the Ising model is the result of the *cooperative* interactions between the spins. Phase transitions are of special interest in physics. Although phase transitions are commonplace, they are remarkable from a microscopic point of view. How does the behavior of the system change so remarkably with a small change in the temperature even though the interactions between the spins remain unchanged and short-range? The study of phase transitions in relatively simple systems such as the Ising model has helped us begin to understand phenomena as diverse as the distribution of earthquakes, the shape of snow flakes, and the transition from a boom economy to a recession.

5.5.2   Computer simulation of the two-dimensional Ising model

The implementation of the Metropolis algorithm for the two-dimensional model proceeds as in one dimension. The only difference is that an individual spin interacts with four nearest neighbors on a square lattice rather than only two nearest neighbors as in one dimension. Simulations of the Ising model in two dimensions allow us to compare our approximate results with the known exact results. Moreover, we can determine properties that cannot be calculated analytically. We explore some of the properties of the two-dimensional Ising model in Problem 5.15.

Problem 5.15. Simulation of the two-dimensional Ising model

Use the applet at `<stp.clarku.edu/simulations/ising/ising2d.html>` to simulate the two-dimensional Ising model at a given temperature. First choose $N = L^2 = 32^2$. Set the external magnetic field $H = 0$ and take $T = 10$. (Remember that we are measuring T in terms of J/k.) For simplicity, the initial orientation of the spins is all spins parallel.

(a) After equilibrium has been established is the orientation of the spins random, that is, is the mean magnetization equal to zero? What is a typical size of a domain, a region of parallel spins?

(b) Choose a low temperature such as $T = 0.5$. Are the spins still random or do a majority choose a preferred direction?

(c) Choose $L = 4$ and $T = 2.0$. Does the sign of the magnetization change during the simulation? Choose a larger value of L and observe if the sign of the magnetization changes.

(d) You probably noticed that $M = 0$ for sufficient high T and is nonzero for sufficiently low T. Hence, there is an intermediate value of T at which M first becomes nonzero. Choose $L = 32$ and start with $T = 4$ and gradually lower the temperature. Note the groups of aligned spins that grow as T is decreased. Estimate the value of T at which the mean magnetization first becomes nonzero.

(e) We can use the applet to obtain more quantitative information. Choose $L = 32$ and set $H = 0$. Start from $T = 4$ and determine the temperature-dependence of the magnetization M, the zero-field susceptibility χ, the mean energy E, and the specific heat C. Decrease the temperatures in intervals of 0.2 until about $T = 1.6$. Describe the qualitative behavior of these quantities.

*****Problem 5.16.** Ising antiferromagnet

So far we have considered only the ferromagnetic Ising model for which the energy of interaction between two nearest neighbor spins is $J > 0$. Hence the ground state in the ferromagnetic Ising model is all spins parallel. In contrast, if $J < 0$, two nearest neighbor spins need to be antiparallel to minimize their energy of interaction.

(a) Sketch the ground state of the one-dimensional antiferromagnetic Ising model.
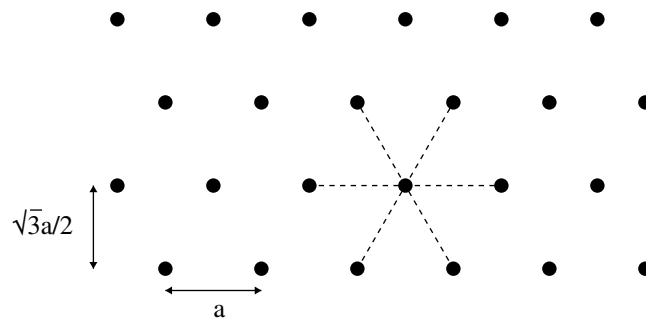
Figure 5.9: Each spin has six nearest neighbors on a triangular lattice.
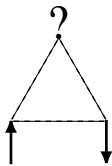
Figure 5.10: The top spin is frustrated because it cannot be antiparallel to both of its neighbors.

(b) Sketch the ground state of the antiferromagnetic Ising model on a square lattice. Use the applet/application at `<stp.clarku.edu/simulations/ising/antiferromagnetic.html>` to simulate the antiferromagnetic Ising model on a square lattice at various temperatures and describe its qualitative behavior. Does the system have a phase transition at $T > 0$?

(c) Consider the Ising antiferromagnetic model on a triangular lattice (see Fig. 5.9). On this lattice each spin has six nearest neighbors. However, the ground state in this case is not unique because of *frustration* (see Fig. 5.10). Convince yourself that there are multiple ground states. Is the entropy zero or nonzero at $T = 0$?[12] Use the applet/application at `<stp.clarku.edu/simulations/ising/triangularlattice.html>` to simulate the antiferromagnetic Ising model on a triangular lattice at various temperatures and describe its qualitative behavior. Does this system have a phase transition at $T > 0$?

5.6   Mean-Field Theory

Because we cannot solve the thermodynamics of the Ising model exactly in three dimensions and the exact solution of the two-dimensional Ising model is limited to zero external magnetic field, we need to develop approximate theories. In this section we develop an approximate theory known as *mean-field* or Weiss molecular field theory. Mean-field theories are relatively easy to treat and usually yield qualitatively correct results. We will see that their main disadvantage is that they

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[12]It has been shown rigorously that the entropy at zero temperature is $S(T = 0) = 0.3383kN$. See G. H. Wannier, "Antiferromagnetism. The triangular Ising net," Phys. Rev. **79**, 357–364 (1950), errata, Phys. Rev. B **7**, 5017 (1973).

ignore fluctuations and are insensitive to the spatial dimension. In Section 8.10 we will learn how to apply similar ideas to gases and liquids and in Section 9.4 we consider more sophisticated versions of mean-field theory to Ising systems.

In its simplest form mean-field theory assumes that each spin interacts with the same effective magnetic field. The effective field is due to the external magnetic field plus the internal field due to all the neighboring spins. That is, spin i "feels" an effective field H_{eff} given by

$$H_{\text{eff}} = J \sum_{j=1}^{q} s_j + H, \tag{5.89}$$

where the sum over j in (5.89) is over the q nearest neighbors of i. Because the orientation of the neighboring spins depends on the orientation of spin i, H_{eff} fluctuates from its mean

$$\overline{H}_{\text{eff}} = J \sum_{j=1}^{q} \overline{s}_j + H = Jqm + H, \tag{5.90}$$

where $\overline{s}_j = m$. In mean-field theory, we ignore the deviations of H_{eff} from $\overline{H}_{\text{eff}}$ and assume that the field at i is $\overline{H}_{\text{eff}}$, independent of the orientation of s_i. This assumption is an approximation because if s_i is up, then its neighbors are more likely to be up. This correlation is ignored in mean-field theory.

The form of the mean effective field in (5.90) is the same throughout the system. Hence, the result of the simple approximation that we have made has reduced the system of N interacting spins to a system of one spin interacting with an effective field (which depends on all the other spins).

The partition function for one spin in the effective field H_{eff} is

$$Z_1 = \sum_{s_1 = \pm 1} e^{\beta s_1 H_{\text{eff}}} = 2 \cosh \beta (Jqm + H). \tag{5.91}$$

The free energy per spin is

$$f = -\frac{1}{\beta} \ln Z_1 = -kT \ln \left[2 \cosh \beta (Jqm + H) \right], \tag{5.92}$$

and the magnetization is

$$m = -\frac{\partial f}{\partial H} = \tanh \beta (Jqm + H). \tag{5.93}$$

Equation (5.93) is a *self-consistent* transcendental equation whose solution yields m. We see that the mean-field that influences the mean value of m depends on the mean value of m.

Problem 5.17. Numerical solutions

Use the applet/application at `<stp.clarku.edu/simulations/ising/meanFieldSolution.html>` to find several numerical solutions of (5.93),

(a) Set $H = 0$ and $q = 4$ and determine the value of the mean-field approximation to the critical temperature T_c of the Ising model on a square lattice. The critical temperature satisfies the condition that $m \neq 0$ for $T \leq T_c$ and $m = 0$ for $T > T_c$. Start with $T = 10$ ($\beta = 0.1$) and then proceed to lower temperatures. Plot the temperature dependence of m.

(b) Choose $H = 1$ and plot $m(T)$ by solving (5.93) numerically.

(c) Determine $m(T)$ for the one-dimensional Ising model ($q = 2$) and $H = 0$ and $H = 1$ and compare your values with the exact solution in one dimension (see (5.72)).

From Figure 5.11 we find that nonzero solutions for m exist for $H = 0$ when $\beta q J \geq 1$. Thus the critical temperature T_c is given by

$$kT_c = Jq. \tag{5.94}$$

That is, $m \neq 0$ for $T \leq T_c$ and $m = 0$ for $T > T_c$ for $H = 0$. Near T_c the magnetization is small, and we can expand $\tanh \beta Jqm$ ($\tanh x \approx x - x^3/3$) to find

$$m = \beta Jqm - \frac{1}{3}(\beta Jqm)^3 + \ldots \tag{5.95}$$

Equation (5.95) has two solutions:

$$m(T > T_c) = 0, \tag{5.96a}$$

and

$$m(T < T_c) = \frac{3^{1/2}}{(\beta Jq)^{3/2}}(\beta Jq - 1)^{1/2}. \tag{5.96b}$$

The solution in (5.96a) corresponds to the high temperature disordered paramagnetic state ($m = 0$) and the solution in (5.96b) corresponds to the low temperature ordered ferromagnetic state ($m \neq 0$). How do we know which solution to choose? The answer can be found by calculating the free energy for both solutions and choosing the solution that gives the smaller free energy (see Problem 5.19).

If we set $kT_c = Jq$ in (5.96b) we can write the spontaneous magnetization as

$$m(T < T_c) = 3^{1/2}\left(\frac{T}{T_c}\right)\left(\frac{T_c - T}{T_c}\right)^{1/2}. \tag{5.97}$$

We see from (5.97) that m approaches zero as a power law as T approaches from T_c from below. As mentioned following (5.84), the quantity m is the order parameter of the system.

In terms of the dimensionless temperature difference $\epsilon = |T_c - T|/T_c$, we can express the behavior of the order parameter near T_c as

$$m(T) \sim \epsilon^\beta, \tag{5.98}$$

where we have introduced the critical exponent β (not to be confused with the inverse temperature). From (5.97) we see that mean-field theory predicts that $\beta = 1/2$. What is the value of β for the two-dimensional Ising model (see Table 5.1)?
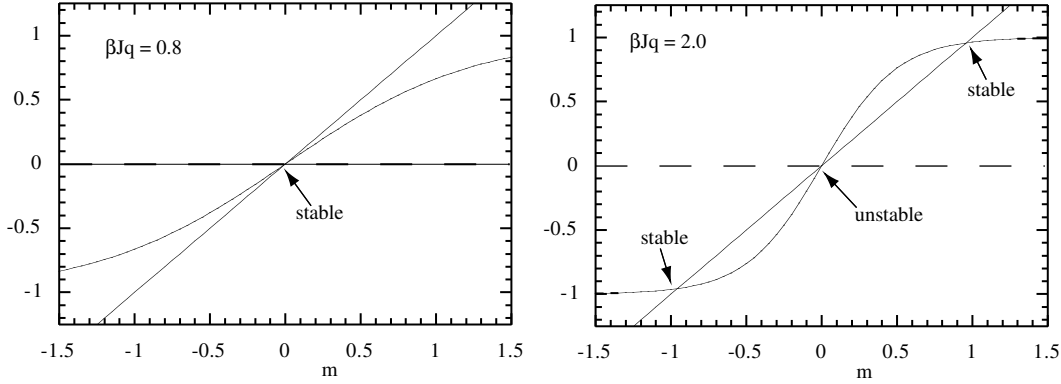
Figure 5.11: Graphical solution of the self-consistent equation (5.93). The solution $m = 0$ exists for all T, but the stable solutions $m = \pm m_0$ exists only for T sufficiently small that the initial slope of $\tanh \beta q J$ is larger than one.

We now find the behavior of other important physical properties near T_c. The zero field isothermal susceptibility (per spin) is given by

$$\chi_{\mathrm{T}} = \lim_{H \to 0} \frac{\partial m}{\partial H} = \frac{\beta(1 - \tanh^2 \beta J q m)}{1 - \beta J q(1 - \tanh^2 \beta J q m)}. \tag{5.99}$$

As expected, for high temperatures ($\beta J \ll 1$), we see that χ_{T} from (5.99) approaches the Curie law (5.21) for noninteracting spins. For $T > T_c$ we write

$$\chi_{\mathrm{T}} = \frac{\beta(1 - m^2)}{1 - \beta J q(1 - m^2)} = \frac{1}{k(T - T_c)}, \qquad (T > T_c, \, H \to 0) \tag{5.100}$$

where we have used the relation (5.93) with $H = 0$ and the fact that $m = 0$ for $T > T_c$. The result (5.100) for χ_{T} is known as the Curie-Weiss law. For $T \lesssim T_c$ we have from (5.97) that $m^2 \approx 3(T_c - T)/T_c$, $1 - m^2 = (3T - 2T_c)/T_c$, and

$$\chi_{\mathrm{T}} \approx \frac{1}{k[T - T_c(1 - m^2)]} = \frac{1}{k[T - 3T + 2T_c]} \tag{5.101a}$$

$$= \frac{1}{2k(T_c - T)}. \qquad (T \lesssim T_c, \, H \to 0) \tag{5.101b}$$

We can characterize the divergence of the zero-field susceptibility as the critical point is approached from either the low or high temperature side as

$$\chi_{\mathrm{T}} \sim |\epsilon|^{-\gamma}. \qquad (T \approx T_c) \tag{5.102}$$

The mean-field prediction for the critical exponent γ is $\gamma = 1$.

The magnetization at T_c as a function of H can be calculated by expanding (5.93) to third order in H with $\beta = \beta_c = 1/qJ$:

$$m = m + \beta_c H - \frac{1}{3}(m + \beta_c H)^3 + \dots \tag{5.103}$$

If we assume that $\beta_c H \ll m$, we find

$$m = (3\beta_c H)^{1/3}, \qquad (T = T_c) \tag{5.104}$$

which is consistent with our assumption that $\beta_c H \ll m$. In general, we write

$$m \sim H^{1/\delta} \qquad (T = T_c) \tag{5.105}$$

The mean-field prediction is $\delta = 3$.

The energy per spin in the mean-field approximation is

$$E = -\frac{1}{2} J q m^2, \tag{5.106}$$

which is the average value of the interaction energy divided by two to account for double counting. Because $m = 0$ for $T > T_c$, the energy vanishes for all $T > T_c$ and thus the heat capacity also vanishes according to mean-field theory. Below T_c the energy is given by

$$E = -\frac{1}{2} J q \big[\tanh(\beta(Jqm + H)) \big]^2. \tag{5.107}$$

The specific heat can be calculated from (5.107) for $T < T_c$. As shown in Problem 5.108, $C \to 3k/2$ for $T \to T_c$ from below. Hence, mean-field theory predicts predicts that there is a jump (discontinuity) in the specific heat.

Problem 5.18. Specific heat

Use the fact that $m^2 \approx 3(T_c - T)/T_c$ for $T \lesssim T_c$ to show that the specific heat according to mean-field theory is

$$C(T \to T_c^-) = 3k/2. \tag{5.108}$$

****Problem 5.19.** A more formal derivation of mean-field theory

We write $s_i s_j$ as

$$s_i s_j = (s_i - m + m)(s_j - m + m) \tag{5.109a}$$

$$= m^2 + m(s_i - m) + m(s_j - m) + (s_i - m)(s_j - m). \tag{5.109b}$$

Note that we have ordered the terms in (5.109b) in powers of their deviation from the mean. If we neglect the last term, which is quadratic in the fluctuations from the mean, we obtain

$$s_i s_j \approx m^2 + m(s_i - m) + m(s_j - m) = -m^2 + m(s_i + s_j). \tag{5.110}$$

Show that we can approximate the energy of interaction in the Ising model as

$$-J \sum_{i,j=\text{nn}(i)} s_i s_j = +J \sum_{i,j=\text{nn}(i)} m^2 - Jm \sum_{i,j=\text{nn}(i)} (s_i + s_j) \tag{5.111a}$$

$$= \frac{JqNm^2}{2} - Jqm \sum_{i=1}^{N} s_i. \tag{5.111b}$$

Use the fact that there are $qN(N-1)/2$ terms in the sums and $N(N-1)/2 \to N^2/2$ for $N \gg 1$. Show that the partition function $Z(T, H, N)$ can be expressed as

$$Z(T, H, N) = e^{-\beta N q J m^2/2} \sum_{s_1 = \pm 1} \cdots \sum_{s_N = \pm 1} e^{\beta(Jqm+h)\sum_i s_i} \tag{5.112a}$$

$$= e^{-\beta N q J m^2/2} \left(\sum_{\sigma = \pm 1} e^{\beta(qJm+h)\sigma} \right)^N \tag{5.112b}$$

$$= e^{-\beta N q J m^2/2} \left[2 \cosh \beta(qJm + H) \right]^N. \tag{5.112c}$$

Hence, the free energy per spin $f(T, H) = -\ln Z(T, H, N)\beta/N$ is given by

$$f(T, H) = \frac{1}{2} Jqm^2 - \frac{1}{\beta} \ln \left[2 \cosh \beta(qJm + H) \right]. \tag{5.113}$$

Problem 5.20. Minima of the free energy

(a) To see the physical meaning of the various solutions, expand the free energy in (5.113) about $m = 0$ with $H = 0$ and show that

$$f(m) = a + bJ(1 - \beta qJ)m^2 + cm^4. \tag{5.114}$$

Determine a, b, and c.

(b) If $H \neq 0$ but small, show that there is an additional term $-Hm$ in (5.114).

(c) Show that $m = 0$ provides a lower free energy for $T > T_c$, and that $m = \pm m_0$, $m_0 > 0$, provides a lower free energy for $T < T_c$.

(d) Use the applet at `<stp.clarku.edu/simulations/ising/meanFieldSolution.html>` to plot $f(m)$ as a function of m for $T > T_c$ and $H = 0$. For what value of m does f have a minimum?

(e) Plot $f(m)$ for $T = 1$ and $H = 0$. Where are the minima of $f(m)$? Do they have the same depth? If so, what is the meaning of this result?

(f) Choose $H = 0.5$ and $T = 1$. Do the two minima have the same depth? The equilibrium or stable phase corresponds to the global minimum. We will explore the significance of the other (local) free energy minimum in Section 5.9.5.

We now compare the results of mean-field theory near the phase transition with the exact results for the one and two-dimensional Ising models. The fact that the mean-field result (5.94) for T_c depends only on q, the number of nearest neighbors, and not the spatial dimension d is one of the inadequacies of the theory. The simple mean-field theory even predicts a phase transition in one dimension, which we know is qualitatively incorrect. In Table 5.2 the mean-field predictions for T_c are compared to the best known estimate of the critical temperatures for the Ising model on two and three-dimensional lattices. We see that for each dimension the mean-field theory prediction improves as the number of neighbors increases. Another limitation is that the mean

lattice	d	q	T_{mf}/T_c
square	2	4	1.763
triangular	2	6	1.648
diamond	3	4	1.479
simple cubic	3	6	1.330
bcc	3	8	1.260
fcc	3	12	1.225

Table 5.2: Comparison of the mean-field predictions for the critical temperature of the Ising model with exact results and the best known estimates for different spatial dimensions d and lattice symmetries.

energy vanishes above T_c, a result that is clearly incorrect. The source of this difficulty is that the correlation between the spins has been ignored.

In addition to the fact that the predictions of mean-field theory improve with increasing dimension, mean-field theory predicts that various thermodynamic properties exhibit power law behavior near T_c as given in (5.98), (5.102), and (5.105) in agreement with the corresponding exact results and simulations. The mean-field predictions for the critical exponents are $\beta = 1/2$, $\gamma = 1$, and $\delta = 3$ respectively (see Table 5.1). These values of the critical exponents do not agree with the results of the Onsager solution of the two-dimensional Ising model, but are not terribly wrong. Note that the mean-field results for the critical exponents are independent of dimension. Also mean-field theory predicts a jump in the specific heat, whereas the Onsager solution predicts a logarithmic divergence. Similar disagreements are found in three dimensions. However, the mean-field predictions do yield the correct results for the critical exponents in four and higher dimensions. In Section 9.4 we discuss more sophisticated treatments of mean-field theory that yield better results for the temperature and magnetic field dependence of the magnetization and other thermodynamic quantities. In Section 9.5 we discuss the Landau theory of phase transitions, a more general version of mean-field theory, which is applicable to a wide variety of systems. However, all mean-field theories predict the same (incorrect) values for the critical exponents. In Sections 9.8 and 9.9 we introduce the renormalization group method, a powerful method for calculating critical exponents and other properties of critical points.

Problem 5.21. Improvement of mean-field theory with dimension

From Table 5.1 we see that the predictions of mean-field theory increase in accuracy with increasing dimension. Why is this trend reasonable?

When mean-field theory fails*. We have seen that mean-field theory gives reasonable qualitative but not quantitative results. The limitations of mean-field theory can also be seen from the following qualitative argument. We will see that mean-field theory does not treat fluctuations consistently, and this failure leads to the demise of mean-field theory near the critical point where fluctuations become very important.

The main assumption in our development of mean-field theory is that each spin feels the same effective magnetic field due to all the other spins (and the external magnetic field). That is, we ignored the fluctuations in the effective field. But if we have ignored fluctuations, why does the susceptibility diverge near the critical point? (Recall that the susceptibility is a measure of the

fluctuations of the magnetization.) Because the fluctuations are ignored in one context, but not another, we see that mean-field theory carries with it the seeds of its own destruction. That is, mean-field theory does not treat the fluctuations consistently. This inconsistency is unimportant if the fluctuations are not too important.

A useful criterion for the applicability of mean-field theory is that the fluctuations of the magnetization M averaged over the distance ξ should be much less than the mean value of M, that is,

$$\overline{(\Delta M)^2} \ll \overline{M}^2. \qquad \text{(averaged over the distance } \xi) \tag{5.115}$$

It can be shown that the left-hand side of (5.115) is proportional to $\xi^{-d}\chi_{\mathrm{T}}$. We thus write

$$\xi^{-d}\chi \ll m^2. \tag{5.116}$$

The inequality in (5.116) is called the Ginzburg criterion. If we substitute $m \sim \epsilon^\beta$, $\chi_{\mathrm{T}} \sim \epsilon^{-\gamma}$, and $\xi \sim \epsilon^{-\nu}$, we can write (5.116) as

$$\epsilon^{d\nu-\gamma} \ll \epsilon^{2\beta}, \tag{5.117}$$

or

$$\epsilon^{(d/2)-2} \ll 1, \tag{5.118}$$

where we have substituted $\nu = 1/2$, $\beta = 1/2$, and $\gamma = 1$. We see that the inequality in (5.118) is always satisfied for $d > 4$ near the critical point where $\epsilon \ll 1$. That is, the mean-field exponents are exact in dimensions greater than four. (In four dimensions the power law behavior is modified by logarithmic factors.) The mean-field theory estimates for the critical temperature become exact only in the limit $d \to \infty$ or for an infinite-range interaction.

For $d < 4$ the inequality (5.118) can be satisfied if ϵ is not too small. If we include the constants that we ignored in obtaining (5.118), the criterion (5.116) can be expressed in three dimensions as

$$[(\Delta C/k)\xi_0^3]^{-1} \ll \epsilon^{1/2}, \tag{5.119}$$

where ΔC is the jump in the specific heat (per unit volume) and ξ_0 is the correlation length at $T = 0$. Some numerical factors have been omitted in (5.119) for simplicity. We define the crossover (reduced) temperature $\epsilon_\times$ as

$$\epsilon_\times^2 \propto [(\Delta C/k)\xi_0^3]^{-2}. \tag{5.120}$$

Hence, mean-field theory is valid provided that $|T - T_c| \geq |T_\times - T_c|.$[13]

5.7 *Infinite-Range Interactions

We might expect that mean-field theory would become exact in a system for which every spin interacts equally strongly with every other spin because the fluctuations of the effective field would

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[13]There are systems such as the conventional (BCS) superconductors for which ξ_0 is so large and hence $\epsilon_\times$ is so small that mean-field theory is applicable at all temperatures that are experimentally accessible. For example, for tin $\xi_0 \approx 2.3 \times 10^{-7}$ m and $\Delta C \approx 800$ J/m^3. In this case mean-field theory should be applicable until ϵ becomes as small as 10^{-14}. There are other systems, such as carbon dioxide and a modified Ising model with longer range interactions, for which crossover behavior is observed from mean-field behavior to fluctuation-dominated behavior closer to the critical point.

go to zero in this limit. We will refer to this model as the infinite-range Ising model, although the interaction range becomes infinite only in the limit $N \to \infty$. In Problem 5.22 we will show that for such a system of N spins, the energy is given by

$$E = \frac{J_N}{2}(N - M^2), \tag{5.121}$$

where M is the magnetization and J_N is the interaction between any two spins. Note that E depends only on M. In the same problem we will also show that the number of states with magnetization M is given by

$$g(M) = \frac{N!}{n!(N-n)!}, \tag{5.122}$$

where n is the number of up spins. As before, $n = N/2 + M/2$ and $N - n = N/2 - M/2$.

Problem 5.22. Energy and density of states of infinite-range Ising model

(a) Show that the energy of a system for which every spin interacts with every other spin is given by (5.121). One way to do so is to consider a small system, say $N = 9$ and to work out the various possibilities. As you do so, you will see how to generalize your results to arbitrary N.

(b) Use similar considerations as in part (a) to find the number of states as in (5.122).

We have to scale the energy of interaction J_N to obtain a well-behaved thermodynamic limit. If we did not, the energy change associated with the flip of a spin would grow linearly with N and a well-defined thermodynamic limit would not exist. We will choose

$$J_N = \frac{qJ}{N}, \tag{5.123}$$

so that $kT_c/J = q$ when $N \to \infty$.

Given the energy in (5.121) and the number of states in (5.122), we can write the partition function as

$$Z_N = \sum_M \frac{N!}{(\frac{N}{2} + \frac{M}{2})!(\frac{N}{2} - \frac{M}{2})!} e^{-\beta J_N(N-M^2)/2} e^{-\beta HM}, \tag{5.124}$$

where we have included the interaction with an external magnetic field. For N not too large, we can evaluate the sum over M numerically. For $N \gg 1$ we can convert the sum to an integral. We write

$$Z_N = \int_{-\infty}^{\infty} Z(M)\, dM, \tag{5.125}$$

where

$$Z(M) = \frac{N!}{n!(N-n)!} e^{-\beta E} e^{\beta HM}, \tag{5.126}$$

where $n = (M + N)/2$. A plot of $Z(M)$ shows that it is peaked about a particular value of M. So let us do our usual trick of expanding $\ln Z_M$ about its maximum.

We will first find the value of M for which $Z(M)$ is a maximum. We write

$$\ln Z(M) = \ln N! - \ln n! - \ln(N-n)! - \beta E + \beta hM. \tag{5.127}$$

We then use Stirling's approximation (3.103) and the fact that $d(\ln x!)/dx = \ln x$, $dn/dM = 1/2$, and $d(N-n)/dM = -1/2$ and obtain

$$\frac{d\ln Z(M)}{dM} = -\frac{1}{2}\ln n + \frac{1}{2}\ln(N-n) + \beta J_N M + \beta H \tag{5.128a}$$

$$= -\frac{1}{2}\ln\frac{N}{2}(1+m) + \frac{1}{2}\ln\frac{N}{2}(1-m) + q\beta Jm + \beta H \tag{5.128b}$$

$$= -\frac{1}{2}\ln(1+m) + \frac{1}{2}\ln(1-m) + q\beta Jm + \beta H = 0. \tag{5.128c}$$

We set $d(\ln Z(M))/dM = 0$ to find the value of M that maximizes $Z(M)$. We have

$$\frac{1}{2}\ln\frac{1-m}{1+m} = -\beta(qJm + H), \tag{5.129}$$

so that

$$\frac{1-m}{1+m} = e^{-2\beta(qJm+H)} = x \tag{5.130}$$

Finally we solve (5.130) for m in terms of x and obtain $1 - m = x(1+m)$, $m(-1-x) = -1+x$, and hence

$$m = \frac{1-x}{1+x} = \frac{1 - e^{-2\beta(Jqm+H)}}{e^{-2\beta(Jqm+H)} + 1} \tag{5.131a}$$

$$= \frac{e^{\beta(Jqm+H)} - e^{-\beta(Jqm+H)}}{e^{-\beta(Jqm+H)} + e^{\beta(Jqm+H)}} \tag{5.131b}$$

$$= \tanh(\beta(Jqm + H). \tag{5.131c}$$

Note that (5.131c) is identical to the mean-field result in (5.93).[14]

*__Problem 5.23.__ Show that $Z(M)$ can be written as a Gaussian and then do the integral over M in (5.125) to find the mean-field form of Z. Use this form of Z to find the mean-field result for the free energy F.

5.8   *Density of States

The probability that a system in equilibrium with a heat bath at a temperature T has energy E is given by

$$P(E,\beta) = \Omega(E)e^{-\beta E}/Z, \tag{5.132}$$

where Z is the partition function and $\Omega(E)$ is the number of states with energy E. If $\Omega(E)$ were known, we could calculate the mean energy (and other thermodynamic quantities) at any temperature from the relation

$$\overline{E} = (1/Z)\sum_E E\Omega(E)e^{-\beta E}. \tag{5.133}$$

---

[14] Mean-field theory corresponds to taking the limit $N \to \infty$ before letting the range of interaction go to infinity. In contrast, the infinite-range Ising model corresponds to taking both limits simultaneously. Although the infinite-range Ising model gives the same results for m as mean-field theory, the two approaches can yield different results in other contexts.

Hence, the quantity $\Omega(E)$ is of much interest.

In the following we discuss an algorithm for directly computing $\Omega(E)$ for the two-dimensional Ising model. In this case the energy is a discrete variable and hence the quantity we wish to compute is the number of spin configurations with the same energy.

Suppose that we were to try to compute $\Omega(E)$ by doing a random walk in energy space by flipping the spins at random and accepting all configurations that we obtain in this way. The histogram of the energy, $H(E)$, the number of visits to each possible energy E of the system, would converge to $\Omega(E)$ if the walk visited all possible configurations. In practice, it would be impossible to realize such a long random walk given the extremely large number of configurations. For example, the Ising model on a $L = 10$ square lattice has $2^{100} \approx 1.3 \times 10^{30}$ spin configurations.

An even more important limitation of doing a simple random walk to determine $\Omega(E)$ is that the walk would spend most of its time visiting the same energy values over and over again and would not reach the values of E that are less probable. The idea of the Wang-Landau algorithm is to do a random walk in energy space by flipping single spins at random and accepting the changes with a probability that is proportional to the reciprocal of the density of states. In this way energy values that would be visited often using a simple random walk would be visited less often because they have a larger density of states. There is only one problem – we don't know the density of states. We will see that the Wang-Landau algorithm estimates the density of states at the same time that it does a random walk in phase space.

The algorithm starts with an initial arbitrary spin configuration a guess for the density of states. The simplest guess is to set $\Omega(E) = 1$ for all possible energies E. The algorithm can be summarized by the follow steps.

1. Choose a spin at random and make a trial flip. Compute the energy before, E_1, and after the flip, E_2, and accept the change with probability

$$p(E_1 \rightarrow E_2) = \min(\tilde{\Omega}(E_1)/\tilde{\Omega}(E_2), 1), \tag{5.134}$$

where $\tilde{\Omega}(E)$ is the current estimate of $\Omega(E)$. Equation (5.134) implies that if $\tilde{\Omega}(E_2) \leq \tilde{\Omega}(E_1)$, the state with energy E_2 is always accepted; otherwise, it is accepted with probability $\tilde{\Omega}(E_1)/\tilde{\Omega}(E_2)$. That is, the state with energy E_2 is accepted if a random number $r \leq \tilde{\Omega}(E_1)/\tilde{\Omega}(E_2)$.

2. After the trial flip the energy of the system is E. ($E = E_2$ if the change is accepted or remains at E_1 if the change is not accepted.) The other part of the Wang-Landau algorithm is to multiply the current value of $\tilde{\Omega}(E)$ by the modification factor $f > 1$

$$\tilde{\Omega}(E) = f\tilde{\Omega}(E). \tag{5.135}$$

We also update the existing entry for $H(E)$ in the energy histogram: $H(E) \rightarrow H(E) + 1$. Because $\tilde{\Omega}(E)$ becomes very large, in practice we must work with the logarithm of the density of states, so that $\ln(\tilde{\Omega}(E))$ will fit into double precision numbers. Therefore, each update of the density of states is implemented as $\ln(\tilde{\Omega}(E)) \rightarrow \ln(\tilde{\Omega}(E)) + \ln(f)$, and the ratio of the density of states is computed as $\exp[\ln(\tilde{\Omega}(E_1)) - \ln(\tilde{\Omega}(E_2))]$. A reasonable choice of the initial modification factor is $f = f_0 = e \approx 2.71828\ldots$. If f_0 is too small, the random walk will need a very long time to reach all possible energies. Too large a choice of f_0 will lead to large statistical errors.

3. We proceed with the random walk in energy space until a flat histogram $H(E)$ is obtained, that is, until all the possible energy values are visited an approximately equal number of times. Because it is impossible to obtain a perfectly flat histogram, we will say that $H(E)$ is "flat" when $H(E)$ for all possible E is not less than p of the average histogram $\overline{H(E)}$; p is chosen according to the size and the complexity of the system and the desired accuracy of the density of states. For the two-dimensional Ising model on small lattices, p can be chosen to be as high as 0.95, but for large systems the criterion for flatness may never be satisfied if p is too close to unity.

4. Once the flatness criterion has been satisfied, we reduce the modification factor f using a function such as $f_1 = \sqrt{f_0}$, reset the histogram to $H(E) = 0$ for all values of E, and begin the next iteration of the random walk during which the density of states is modified by f_1 at each trial flip. The density of states is not reset during the simulation. We continue performing the random walk until the histogram $H(E)$ is again flat. We then reduce the modification factor, $f i + 1 = \sqrt{f_i}$, reset the histogram to $H(E) = 0$ for all values of E, and continue the random walk.

5. The simulation is stopped when f is smaller than a predefined value (such as $f_{\text{final}} = \exp(10^{-8}) \approx 1.00000001$). The modification factor acts as a control parameter for the accuracy of the density of states during the simulation and also determines how many Monte Carlo sweeps are necessary for the entire simulation.

At the end of the simulation, the algorithm provides only a relative density of states. To determine the normalized density of states $\Omega(E)$, we can either use the fact that the total number of states for the Ising model is

$$\sum_E \Omega(E) = 2^N, \tag{5.136}$$

or that the number of ground states (for which $E = -2NJ$) is two. The latter normalization guarantees the accuracy of the density of states at low energies which is important in the calculation of thermodynamic quantities at low temperatures. If we apply (5.136), we cannot guarantee the accuracy of $\Omega(E)$ for energies at or near the ground state, because the rescaling factor is dominated by the maximum density of states. We can use one of these two normalization conditions to obtain the absolute density of states, and use the other normalization condition to check the accuracy of our result.

*Problem 5.24. Wang-Landau algorithm

Use the applet/application at `<stp.clarku.edu/simulations/ising/wanglandau.html>` which implements the Wang-Landau algorithm for the Ising model on a square lattice.

(a) Choose $L = 2$. How many states are there for each value of E? Run the simulation and verify that the computed density of states is close to your exact answer.

(b) Choose larger values of L, for example, $L = 16$, and describe the qualitative energy dependence of $\Omega(E)$.

(c) The program computes the specific heat as a function of temperature using the estimated value of $\tilde{\Omega}(E)$. Describe the qualitative temperature dependence of the specific heat.

5.9 Supplementary Notes

5.9.1 How does magnetism occur in matter?

Classical electromagnetic theory tells us that magnetic fields are due to electrical currents and changing electric fields, and that the magnetic fields far from the currents are described by a magnetic dipole. It is natural to assume that magnetic effects in matter are due to microscopic current loops created by the motion of electrons in atoms. However, it was shown by Niels Bohr in his doctoral thesis of 1911 and independently by Johanna H. van Leeuwen in her 1919 doctoral thesis that diamagnetism does not exist in classical physics (see Problem 6.75). Hence, magnetism is a quantum phenomena.

In the context of magnetism the most obvious new physics due to quantum mechanics is the existence of an intrinsic magnetic moment. The intrinsic magnetic moment is proportional to the intrinsic spin, another quantum mechanical property. The interaction energy between a single spin and an externally applied magnetic field $\mathbf{B}$ is given by

$$E = -\boldsymbol{\mu} \cdot \mathbf{B}. \tag{5.137}$$

There is a distinction between the magnetic field produced by currents external to the material and the field produced internally by the magnetic moments within the material. The applied field is denoted as $\mathbf{H}$ and the total field is denoted as $\mathbf{B}$. The fields $\mathbf{B}$ and $\mathbf{H}$ are related to the magnetization per unit volume $\mathbf{m} = \mathbf{M}/V$ by

$$\mathbf{B} = \mu_0(\mathbf{H} + \mathbf{m}). \tag{5.138}$$

The energy due to the external magnetic field $\mathbf{H}$ coupled to $\mathbf{M}$ is

$$E = -\mathbf{M} \cdot \mathbf{H}. \tag{5.139}$$

The origin of the interaction energy between magnetic moments must be due to quantum mechanics. Because the electrons responsible for magnetic behavior are localized near the atoms of a regular lattice in most magnetic materials, we consider the simple case of two localized electrons. Each electron has a spin $1/2$ which can point either up or down along the axis that is specified by the applied magnetic field. The electrons interact with each other and with nearby atoms and are described in part by the spatial wavefunction $\psi(\mathbf{r}_1, \mathbf{r}_2)$. This wavefunction must be multiplied by the spin eigenstates to obtain the actual state of the two electron system. We denote the basis for these states as

$$|\uparrow\uparrow\rangle, |\downarrow\downarrow\rangle, |\uparrow\downarrow\rangle, |\downarrow\uparrow\rangle, \tag{5.140}$$

where the arrows corresponds to the spin of the electrons. These states are eigenstates of the z-component of the total spin angular momentum S_z such that S_z operating on any of the states in (5.140) has an eigenvalue equal to the sum of the spins in the z direction. For example, $S_z|\uparrow\uparrow\rangle = 1|\uparrow\uparrow\rangle$ and $S_z|\uparrow\downarrow\rangle = 0|\uparrow\downarrow\rangle$. Similarly, S_x or S_y give zero if either operator acts on these states.

Because electrons are fermions, the basis states in (5.140) are not physically meaningful, because if two electrons are interchanged, the new wavefunction must either be the same or differ

by a minus sign. The simplest normalized linear combinations of the states in (5.140) that satisfy this condition are

$$\frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle) \tag{5.141a}$$

$$|\uparrow\uparrow\rangle \tag{5.141b}$$

$$\frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle) \tag{5.141c}$$

$$|\downarrow\downarrow\rangle \tag{5.141d}$$

The state in (5.141a) is antisymmetric, because interchanging the two electrons leads to minus the original state. This state has a total spin, $S = 0$, and is called the singlet state. The collection of the last three states is called the triplet state and has $S = 1$. Because the states of fermions must be antisymmetric, the spin state is antisymmetric when the spatial part of the wavefunction $\psi(\mathbf{r}_1, \mathbf{r}_2)$ is symmetric and vice versa. That is, if the spins are parallel, then $\psi(\mathbf{r}_1, \mathbf{r}_2) = -\psi(\mathbf{r}_2, \mathbf{r}_1)$. Similarly, if the spins are antiparallel, then $\psi(\mathbf{r}_1, \mathbf{r}_2) = +\psi(\mathbf{r}_2, \mathbf{r}_1)$. Hence, when $\mathbf{r}_1 = \mathbf{r}_2$, ψ is zero for parallel spins and is nonzero for antiparallel spins. We conclude that if the spins are parallel, the separation between the two electrons will rarely be small and their average electrostatic energy will be less than it is for antiparallel spins. We denote E_{triplet} and E_{singlet} as the triplet energy and the singlet energy, respectively, and write the interaction energy in terms of the spin operators. We write

$$(\mathbf{S}_1 + \mathbf{S}_2)^2 = \mathbf{S}_1{}^2 + \mathbf{S}_2{}^2 + 2\,\mathbf{S}_1{\cdot}\mathbf{S}_2. \tag{5.142}$$

For spin $1/2$, $\mathbf{S}_1{}^2 = \mathbf{S}_1(\mathbf{S}_1 + 1) = 3/4 = \mathbf{S}_2{}^2$. The total spin, $\mathbf{S} = \mathbf{S}_1 + \mathbf{S}_2$ equals zero for the singlet state and is unity for the triplet state. Hence, $S^2 = S(S + 1) = 0$ for the singlet state and $S^2 = 2$ for the triplet state. These results lead to $\mathbf{S}_1 \cdot \mathbf{S}_2 = -3/4$ for the singlet state and $\mathbf{S}_1 \cdot \mathbf{S}_2 = 1/4$ for the triplet state and allows us to write

$$E = \frac{1}{4}(E_{\text{singlet}} + 3E_{\text{triplet}}) - J\mathbf{S}_1 \cdot \mathbf{S}_2, \tag{5.143}$$

where $J = E_{\text{singlet}} - E_{\text{triplet}}$. The term (5.143) in parenthesis is a constant and can be omitted by suitably defining the zero of energy. The second term represents a convenient form of the interaction between two spins.

Can we write the total effective interaction of a system of three spins as $-J_{12}\,\mathbf{S}_1 \cdot \mathbf{S}_2 - J_{23}\,\mathbf{S}_2 \cdot \mathbf{S}_3 - J_{13}\,\mathbf{S}_1 \cdot \mathbf{S}_3$? In general, the answer is no, and we can only hope that this simple form is a reasonable approximation. The total energy of the most common model of magnetism is based on the form (5.143) for the spin-spin interaction and is expressed as

$$\hat{H} = -\sum_{i<j=1}^{N} J_{ij}\,\mathbf{S}_i \cdot \mathbf{S}_j - g\mu_0\mathbf{H}{\cdot}\sum_{i=1}^{N}\mathbf{S}_i, \qquad \text{(Heisenberg model)} \tag{5.144}$$

where $g\mu_0$ is the magnetic moment of the electron. The *exchange interaction J_{ij}* can be positive or negative. The form (5.144) of the interaction energy is known as the *Heisenberg model*. Note that $\mathbf{S}$ as well as the Hamiltonian $\hat{H}$ is an operator, and that the Heisenberg model is quantum mechanical in nature. The distinction between the operator $\hat{H}$ and the magnetic field $\mathbf{H}$ will be clear from the context.

As we have seen, the Heisenberg model assumes that we can treat all interactions in terms of pairs of spins. This assumption means that the magnetic ions in the crystal must be sufficiently far apart that the overlap of their wavefunctions is small. We also have neglected any orbital contribution to the total angular momentum. In addition, dipolar interactions can be important and lead to a coupling between the spin degrees of freedom and the relative displacements of the magnetic ions. In general, it is very difficult to obtain the exact Hamiltonian from first principles, and the Heisenberg form of the Hamiltonian should be considered as a reasonable approximation with the details buried into the exchange constant J.

The Heisenberg model is the starting point for most microscopic models of magnetism. We can go to the classical limit $S \to \infty$, consider spins with one, two, or three components, place the spins on lattices of any dimension and any crystal structure, and allow J to be positive, negative, random, nearest-neighbor, long-range, etc. In addition, we can include other interactions such as the interaction of an electron with an ion. The theoretical possibilities are very rich as are the types of magnetic materials of interest experimentally.

5.9.2 The thermodynamics of magnetism

[xx not written xx]

5.9.3 Low temperature expansion

The existence of exact analytical solutions for systems with nontrivial interactions is the exception. In general, we must be satisfied with approximate solutions with limited ranges of applicability. To understand the nature of one class of approximations, we reconsider the one-dimensional Ising model at low temperatures.

Suppose that we are interested in the behavior of the Ising model at low temperatures in the presence of a magnetic field H. We know that the state of lowest energy (the ground state) corresponds to all spins completely aligned. What happens when we raise the temperature slightly above $T = 0$? The only way that the system can raise its energy is by flipping one or more spins. At a given temperature we can consider the excited states corresponding to 1, 2, ..., f flipped spins. These f spins may be connected or may consist of disconnected groups.

As an example, consider a system of $N = 5$ spins with toroidal boundary conditions. The ground state is shown in Figure 5.12. The energy cost of flipping a single spin is $4J + 2H$. (The energy of interaction of the flipped spin with its two neighbors changes from $-2J$ to $+2J$.) A typical configuration with one spin flipped is shown in Figure 5.13. Because the flipped spin can be at $N = 5$ different sites, we write

$$Z = [1 + 5\,e^{-\beta(4J+2H)} + \ldots]e^{-\beta E_0}, \tag{5.145}$$

where $E_0 = -5(J + H)$.

The next higher energy excitation consists of a pair of flipped spins with one contribution arising from pairs that are not nearest neighbors and the other contribution arising from nearest neighbor pairs (see Figure 5.14). We will leave it as an exercise (see Problem 5.25) to determine the corresponding energies and the number of different ways that this type of excitation occurs.

Figure 5.12: The ground state of $N = 5$ Ising spins in an external magnetic field. For toroidal boundary conditions, the ground state energy is $E_0 = -5J - 5H$.

Figure 5.13: The flip of a single spin of $N = 5$ Ising spins. The corresponding energy cost is $4J + 2H$.

Problem 5.25. Low temperature expsnsion for five spins

Use the microstates that were enumerated in Problem 5.5 to find the low temperature expansion of Z for a system of $N = 5$ spins in one dimension. Use toroidal boundary conditions. Write your result for Z in terms of the variables

$$u = e^{-2\beta J}, \tag{5.146}$$

and

$$w = e^{-2\beta H}. \tag{5.147}$$

****Problem 5.26.** Generalize the low temperature expansion to find higher order contributions to Z_N. Convince yourself that the low temperature series can be summed exactly in one dimension. (The low temperature series of the Ising model can only be summed approximately in higher dimensions using what are known as Padé approximants.)

5.9.4   High temperature expansion

At high temperatures for which $J/kT \ll 1$, the effects of the interactions between the spins become small. We can develop a perturbation method that is based on expanding Z in terms of the small parameter J/kT. For simplicity, we consider the Ising model in zero magnetic field. We write

$$Z_N = \sum_{s=\pm 1} \prod_{i,j=\mathrm{nn}(i)} e^{\beta J s_i s_j}, \tag{5.148}$$

where the sum is over all states of the N spins, and the product is restricted to nearest neighbor pairs of sites $\langle ij \rangle$ in the lattice. We first apply the identity

$$e^{\beta J s_i s_j} = \cosh \beta J + s_i s_j \sinh \beta J = \cosh \beta J (1 + v s_i s_j), \tag{5.149}$$

where

$$v = \tanh \beta J. \tag{5.150}$$

Figure 5.14: Configurations corresponding to two flipped spins. In (a) the flipped spins are not nearest neighbors and in (b) the flipped spins are neighbors.

The identity (5.149) can be demonstrated by considering the various cases $s_i, s_j = \pm 1$ (see Problem 5.34). The variable v approaches zero as $T \to \infty$ and will be used as an expansion parameter instead of J/kT for reasons that will become clear later. Equation (5.148) can now be written as

$$Z_N = (\cosh \beta J)^p \sum_s \prod_{\langle ij \rangle} (1 + v s_i s_j), \tag{5.151}$$

where p is the total number of nearest neighbor pairs in the lattice, that is, the total number of interactions. For a lattice with toroidal boundary conditions

$$p = \frac{1}{2} N q, \tag{5.152}$$

where q is the number of nearest neighbor sites of a given site; $q = 2$ for an Ising chain.

To make the above procedure explicit, consider the case $N = 3$ with toroidal boundary conditions. For this case $p = 3(2)/2 = 3$, and there are three factors in the product in (5.151): $(1 + v s_1 s_2)(1 + v s_2 s_3)(1 + v s_3 s_1)$. If we expand this product in powers of v, we obtain the $2^p = 8$ terms in the partition function:

$$\begin{aligned}
Z_{N=3} = (\cosh \beta J)^3 \sum_{s_1=-1}^{1} \sum_{s_2=-1}^{1} \sum_{s_3=-1}^{1} &\Big[1 + v(s_1 s_2 + s_2 s_3 + s_3 s_1) \\
&+ v^2(s_1 s_2 s_2 s_3 + s_1 s_2 s_3 s_1 + s_2 s_3 s_3 s_1) + v^3 s_1 s_2 s_2 s_3 s_3 s_1 \Big].
\end{aligned} \tag{5.153}$$

It is convenient to introduce a one-to-one correspondence between each of the eight terms in the bracket in (5.153) and a diagram on the lattice. The set of eight diagrams is shown in Figure 5.15. Because v enters into the product in (5.153) as $v s_i s_j$, a diagram of order v^n has n v-bonds. We can use the topology of the diagrams to help us to keep track of the terms in (5.153). The term of order v^0 is simply $2^{N=3} = 8$. Because $\sum_{s_i=\pm 1} s_i = 0$, each of the terms of order v vanish. Similarly, each of the three terms of order v^2 contains at least one of the spin variables raised to an odd power so that these terms also vanish. For example, $s_1 s_2 s_2 s_3 = s_1 s_3$, and both s_1 and s_3 enter to first-order. In general, we have

$$\sum_{s_i=-1}^{1} s_i{}^n = \begin{cases} 2 & n \text{ even} \\ 0 & n \text{ odd} \end{cases} \tag{5.154}$$

From (5.154) we see that only terms of order v^0 and v^3 contribute so that

$$Z_{N=3} = \cosh^3 \beta J [8 + 8v^3] = 2^3 (\cosh^3 \beta J + \sinh^3 \beta J). \tag{5.155}$$
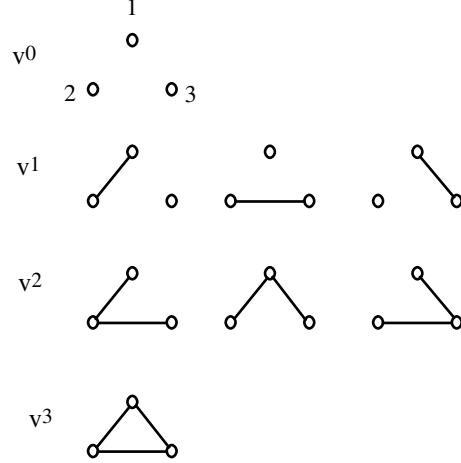
Figure 5.15: The eight diagrams that correspond to the eight terms in the Ising model partition function for the $N = 3$ Ising chain. The term $s_i s_j$ is represented by a line is represented by a line between the neighboring sites i and j.

We now generalize the above analysis to arbitrary N. We have observed that the diagrams that correspond to nonvanishing terms in Z are those that have an even number of bonds from each vertex; these diagrams are called *closed*. The reason is that a bond from site i corresponds to a product of the form $s_i s_j$. An even number of bonds from site i implies that s_i to an even power enters into the sum in (5.151). Hence, only diagrams with an even number of bonds from each vertex yield a nonzero contribution to Z_N.

For the Ising chain, only two bonds can come from a given site. Hence, we see that although there are 2^N diagrams for a Ising chain of N spins with toroidal boundary conditions, only the diagrams of order v^0 (with no bonds) and of order v^N will contribute to Z_N. We conclude that

$$Z_N = (\cosh \beta J)^N [2^N + 2^N v^N]. \tag{5.156}$$

Problem 5.27. Draw the diagrams that correspond to the terms in the high temperature expansion of the Ising model partition function for the $N = 4$ Ising chain.

Problem 5.28. The form of Z_N in (5.156) is not identical to the form of Z_N given in (5.28). Use the fact that $v < 1$ and take the thermodynamic limit $N \to \infty$ to show the equivalence of the two results for Z_N.

5.9.5   Metastable states and nucleation

We first consider the simulations in Problem 5.29 to introduce the concepts of metastability and nucleating droplets.

Problem 5.29. Simulations of metastable states

(a) Use the applet at `<stp.clarku.edu/simulations/ising/ising2d.html>` to simulate the Ising model on a square lattice. Choose $L = 64$, $T = 1$, and $H = 0.7$. Run the simulation until the systems reaches equilibrium. You will notice that most of the spins are aligned (up) with the magnetic field.

(b) Pause the simulation and let $H = -0.7$; we say that we have "flipped" the field. Continue the simulation after the changed field and watch the configuration of spins. Do the spins align themselves with the magnetic field immediately after the flip? What is the equilibrium state of the system?

You probably noticed that spins did not immediately flip to align themselves with the magnetic field. Instead most of the spins remain up and the mean values of the magnetization and energy do not change for many Monte Carlo steps per spin. We say that the system is in a *metastable* state. The reason that the spins do not flip as soon as the field is flipped is that if the field is not too large, it costs energy for a spin to flip because it would likely no longer be parallel with its neighbors. If we wait long enough, we will see isolated "droplets" of spins pointing in the stable) (down) direction. If a droplet is too small, it will likely shrink and vanish. In contrast, if the droplet is bigger than a certain critical size (see Figure 5.16), it will grow and the system will quickly reach its equilibrium state. If the droplet is a certain critical size, then it will grow with probability 50%. This droplet is called the *critical droplet* or the *nucleating droplet*. The initial decay of the metastable state is called *nucleation*.
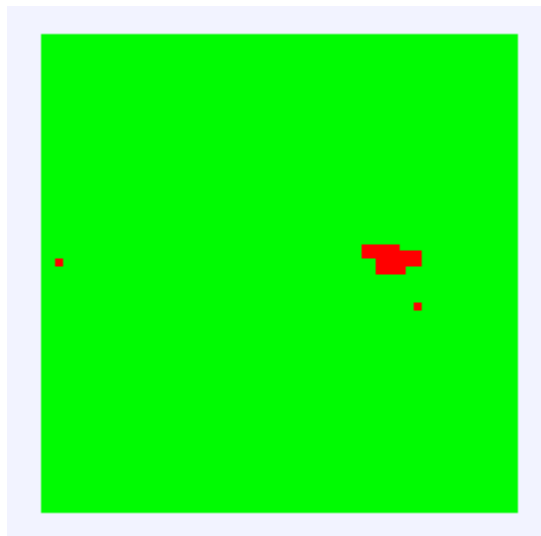
Figure 5.16: Example of a nucleating droplet.

Metastable states occur often in nature and in the laboratory. For example, if you take a container of distilled (very pure) water with no dirt, pollen, or other impurities), you can super-

cool it below the freezing temperature of $0°C$. The supercooled water will remain a liquid unless there is a spontaneous density fluctuation. More likely, an external disturbance will create the necessary fluctuation. Search `<youtube.com>` for supercooled water to see some great demonstrations. Metastable states are important in forming crystalline metals from a molten liquid, and are important in biological systems, and in the inflationary scenario of the early universe.

Lets consider nucleation at low temperatures so that we can ignore the entropy. A compact droplet (circular in two dimensions and spherical in three dimensions) minimizes the energy cost of creating a droplet of down spins. The energy is decreased by aligning the spins of a droplet with the field. This energy decrease is proportional to the area (volume in three dimensions of the droplet. Hence,

$$\Delta E_{\text{bulk}} = -aHr^d, \tag{5.157}$$

where r is the radius of the droplet, d is the spatial dimension, and a is a constant.

However, creating a surface costs energy. The associated cost energy cost is proportional to the circumference of the droplet, and hence

$$\Delta E_{\text{surface}} = \sigma H r^{d-1}, \tag{5.158}$$

where σ is the energy cost per spin. This quantity is known as the surface tension.

The total energy cost of creating a droplet of radius r is

$$\Delta E = aHr^d + \sigma H r^{d-1}. \tag{5.159}$$

We see that the energy cost of the droplet increases as a function of r until a critical radius r_c (see Figure 5.17).
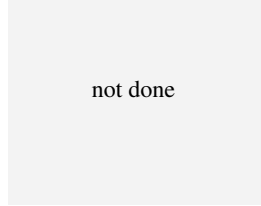
Figure 5.17: The energy cost of a droplet of radius r.

The radius of the critical droplet can be obtained by determining where E has a maximum:

$$\left.\frac{dE}{dr}\right|_{r=r_c} = -adHr_c^{d-1} + (d-1)\sigma r_c^{d-2} = 0, \tag{5.160}$$

or

$$-adHr_c + (d-1)\sigma = 0, \tag{5.161}$$

and

$$r_c = \frac{(d-1)\sigma}{adH} \tag{5.162}$$

The energy cost of creating the critical droplet is $E_c = b\sigma^d/H^{d-1}$, where b depends on d. The probability of creating the droplet is proportional to $e^{-\beta E_c}$. The lifetime of the metastable state, that is the time before the critical droplet occurs, is proportional to the inverse of this probability.

Note that we used equilibrium considerations to estimate the size of the droplet and the lifetime of the metastable state. This assumption of equilibrium is justified only if the lifetime of the metastable state is long. Hence, we must have $\beta/H \gg 1$, that is, small fields or low temperatures.

In Problem 5.20f you found that the free energy of the Ising model has two minima for $T < T_c$ and $H \neq 0$. It can be shown that in the thermodynamic limit $N \to \infty$, the system will be found in the lowest free energy minimum, the global minimum. The other minimum corresponds to the metastable phase.

Vocabulary

magnetization m, zero field susceptibility χ

Ising model, exchange constant J

correlation function $G(r)$, correlation length ξ, domain wall

order parameter, continuous phase transition, critical point

critical temperature T_c, critical exponents α, β, δ, γ, ν, η

exact enumeration

mean-field theory

low and high temperature expansions

Additional problems

Problem 5.30. Thermodynamics of classical spins

The energy of interaction of a classical magnetic dipole with an external magnetic field $\mathbf{B}$ is given by

$$E = -\boldsymbol{\mu} \cdot \mathbf{B} = -\mu H \cos\theta, \tag{5.163}$$

where θ is the continuously variable angle between $\boldsymbol{\mu}$ and $\mathbf{B}$. In the absence of an external field, the dipoles (or spins as they are commonly called) are randomly oriented so that the mean magnetization is zero. If $H \neq 0$, the mean magnetization is given by

$$M = \mu N \overline{\cos\theta}. \tag{5.164}$$

The direction of the magnetization is parallel to $\mathbf{B}$. Show that the partition function for one spin is given by

$$Z_1 = \int_0^{2\pi} \int_0^{\pi} e^{\beta\mu H \cos\theta} \sin\theta \, d\theta \, d\phi. \tag{5.165}$$

Table 5.3: Listing of inline problems.

How is $\overline{\cos\theta}$ related to Z_1? Show that

$$M = N\mu L\big(\beta\mu H\big), \tag{5.166}$$

where the Langevin function $L(x)$ is given by

$$L(x) = \frac{e^x + e^{-x}}{e^x - e^{-x}} - \frac{1}{x} = \coth x - \frac{1}{x}. \tag{5.167}$$

For $|x| < \pi$, $L(x)$ can be expanded as

$$L(x) = \frac{x}{3} - \frac{x^3}{45} + \ldots + \frac{2^{2n}B_{2n}}{(2n)!} + \ldots, \qquad (x \ll 1) \tag{5.168}$$

where B_n is the Bernoulli number of order n (see Appendix A). What is M and the susceptibility in the limit of high T? For large x, $L(x)$ is given by

$$L(x) \approx 1 - \frac{1}{x} + 2e^{-2x}. \qquad (x \gg 1) \tag{5.169}$$

What is the behavior of M in the limit of low T?

Problem 5.31. *Arbitrary spin*

The magnetic moment of an atom or nucleus is associated with its angular momentum which is quantized. If the angular momentum is J, the magnetic moment along the direction of **B** is restricted to $(2J + 1)$ orientations. We write the energy of an individual atom as

$$E = -g\mu_0\,\mathbf{J}\cdot\mathbf{B} = -g\mu_0 J_z B. \tag{5.170}$$

The values of μ_0 and g depend on whether we are considering a nucleus, an atom, or an electron. The values of J_z are restricted to $-J, -J+1, -J+2, \ldots, J-1, J$. Hence, the partition function for one atom contains $(2J+1)$ terms:

$$Z_1 = \sum_{m=-J}^{J} e^{-\beta(-g\mu_0 mH)}. \tag{5.171}$$

The summation index m ranges from $-J$ to J in integral steps.

To simplify the notation, we let $\alpha = \beta g\mu_0 B$, and write Z_1 as a finite geometrical series:

$$Z_1 = \sum_{m=-J}^{J} e^{m\alpha}, \tag{5.172a}$$

$$= e^{-\alpha J}(1 + e^{\alpha} + e^{2\alpha} + \ldots + e^{2J\alpha}). \tag{5.172b}$$

The sum of a finite geometrical series is given by

$$S_n = \sum_{p=0}^{n} x^p = \frac{x^{n+1} - 1}{x - 1}. \tag{5.173}$$

Given that there are $(2J+1)$ terms in (5.172b), show that

$$Z = e^{-\alpha J} \frac{e^{(2J+1)\alpha} - 1}{e^{\alpha} - 1} = e^{-\alpha J} \frac{[1 - e^{(2J+1)\alpha}]}{1 - e^{\alpha}}. \tag{5.174}$$

Use the above relations to show that

$$M = Ng\mu_0 J B_J(\alpha), \tag{5.175}$$

where the Brillouin function $B_J(\alpha)$ is defined as

$$B_J(\alpha) = \frac{1}{J}\left[(J + 1/2)\coth(J + 1/2)\alpha - \frac{1}{2}\coth\alpha/2\right]. \tag{5.176}$$

What is the limiting behavior of M for high and low T for fixed B? What is the limiting behavior of M for $J = \frac{1}{2}$ and $J \gg 1$?

Problem 5.32. The five configurations shown in Figure 5.18 for the Ising chain were generated using the Metropolis algorithm (see Section 5.4.3) at $\beta J = 1$ using toroidal boundary conditions. On the basis of this limited sample, estimate the mean value of E/J, the specific heat per spin, and the spin correlation $G(r)$ for $r = 1$, 2, and 3. For simplicity, take only one of the spins to be the origin.

Problem 5.33. Use the applet at <stp.clarku.edu/simulations/ising/ising2d.html> to determine $P(E)$, the probability that the system has energy E, for the two-dimensional Ising model. (For the Ising model the energy is a discrete variable.) What is the approximate form of the probability distribution at $T = 4$? What is its width? Then take $T = T_c \approx 2.269$. Is the form of $P(E)$ similar? If not, why?
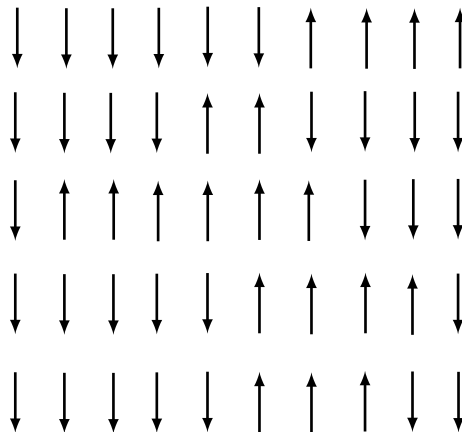
Figure 5.18: Five configurations of the $N = 10$ Ising chain with toroidal boundary conditions generated by the Metropolis algorithm at $\beta J = 1$ and $H = 0$.

Problem 5.34. Verify the validity of the identity (5.149) by considering the different possible values of $s_i s_j$ and using the identities $2 \cosh x = e^x + e^{-x}$ and $2 \sinh x = e^x - e^{-x}$.

Problem 5.35. Explore the analogy between the behavior of the Ising model and the behavior of a large group of people. Under what conditions would a group of people act like a collection of individuals doing their "own thing?" Under what conditions might they act as a group? What factors could cause such a transition?

*__Problem 5.36.__ The demon algorithm and the Ising chain

(a) Write a program that uses the demon algorithm to generate a representative sample of microstates for the Ising chain at fixed energy. The easiest trial change is to flip a single spin. Show that for such a flip the possible changes in the energy in zero magnetic field are 0 and $\pm 4J$. Confirm that the possible energies of the spins are $E = -NJ, -NJ+4J, -NJ+8J \ldots +NJ$, and that the possible demon energies are $E_d = 4nJ$, where $n = 0, 1, 2, \ldots$

(b) Calculate the mean demon energy as a function of the temperature of the system.

(c) The most difficult part of the program is choosing the initial state so that it has the desired energy. (Choose J to be the unit of energy.) One way is to begin with all the spins parallel and randomly flip spins until the desired energy is reached. (Remember to choose the desired energy that is compatible with what you found in part (a).)

(d) Choose $N = 20$ and $E_d = 0$. Collect data for the mean energy of the system, the mean demon energy, and the probability $P(E_d)$ that the demon has energy E_d for about ten different energies. Equilibrate the spins for about 100 flips per spin before taking averages for each value of the total energy. Average over approximately 1000 flips per spin. Discuss the qualitative behavior of $P(E_d)$ and show that your results are consistent with what you found in part (b).
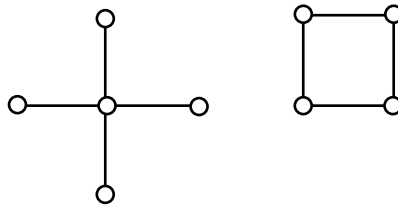
Figure 5.19: Two examples of possible diagrams on the square lattice. The only term that contributes to Z corresponds to the square.

*__Problem 5.37.__ Consider a one-dimensional Ising-type model defined by the usual Hamiltonian with $H = 0$, but with $s_i = 0, \pm 1$. Use the transfer matrix method to calculate the dependence of the energy on T. The solution requires the differentiation of the root of a cubic equation that you might wish to do numerically.

__Problem 5.38.__ Exact calculation of the partition function

Calculate the partition function for the Ising model on a square lattice for $N = 4$ and $N = 9$ in the presence of an external magnetic field. Assume that the system is in equilibrium with a heat bath at temperature T. You might find it easier to write a short program to enumerate all the microstates. Choose either toroidal or open boundary conditions. Calculate the corresponding values of the mean energy, the heat capacity, and the zero field susceptibility.

__Problem 5.39.__ Low temperature behavior in mean-field theory

(a) Write (5.93) in the form $\beta q J m = \tanh^{-1} m = (1/2) \ln[(1+m)/(1-m)]$ and show that

$$m(T) \approx 1 - 2e^{-\beta q J} \text{ as } T \to 0. \tag{5.177}$$

(b) Determine the low temperature behavior of χ_{T}. Does it approach zero for $T \ll T_c$?

*__Problem 5.40.__ The high temperature expansion we discussed for the Ising chain in Section 5.9.4 is very general and can be readily applied to the two and three-dimensional Ising model. We write

$$Z_N = (\cosh \beta J)^{Nq/2} \, 2^N \sum_{b=0}^{Nq/2} g(b) v^b, \tag{5.178}$$

where $g(b)$ is the number of diagrams with b bonds such that each vertex of the diagram is even. It is understood that $g(0) = 1$. The form of (5.178) implies that we have reduced the calculation of the Ising model partition function to the problem of counting closed diagrams on a lattice. For the Ising model on the square lattice ($q = 4$), the first nontrivial contribution to Z_N comes from loops made up of four bonds (see Figure 5.19) and is given by

$$(\cosh \beta J)^{2N} \, 2^N g(4) v^4, \tag{5.179}$$

where $g(4) = N$. It is possible to sum many terms in the high temperature expansion of Z_N and other quantities and determine the thermodynamic behavior for all temperatures including the vicinity of the phase transition.

To make the high temperature expansion more explicit, work out the first several terms in (5.178) for a two-dimensional Ising model with $N = 4$ and $N = 9$.

Suggestions for further reading

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Chapter 6

Noninteracting Particle Systems

21 August 2007

We apply the general formalism of statistical mechanics to classical and quantum systems of noninteracting particles and discuss the equipartition theorem, the Maxwell velocity distribution, the Fermi-Dirac and Bose-Einstein distributions, blackbody radiation, the ideal Fermi and Bose gases, and the specific heat of a crystalline solid among other applications.

6.1   Introduction

Noninteracting systems are important for several reasons. For example, the interactions between the atoms in a gas can be ignored in the limit of low densities. In the limit of high temperatures, the interaction between the spins in an Ising model can be neglected because the mean energy exchanged with the heat bath is much larger than the potential energy of interaction. Another reason for studying systems of noninteracting particles is that there are many cases for which the equilibrium properties of a system of interacting particles can be reformulated as a collection of noninteracting modes or *quasiparticles*. We will see such an example when we study the harmonic model of a crystal.

6.2   The Ideal Classical Gas

An ideal (or perfect) gas is an idealized system of identical particles for which the interactions between them can be neglected.[1] In Sections 4.4 and 4.5 we derived the thermodynamic properties of the ideal classical gas[2] using the microcanonical ensemble. If the gas is in thermal equilibrium with a heat bath at temperature T, it is more natural and convenient to treat the ideal gas in the

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[1]An ideal gas is a good approximation to a real gas at low densities where the mean interparticle distance is much larger than the range of the interparticle interactions.

[2]The theme music for this section can be found at <www.classicalgas.com/>.

canonical ensemble. However, because the particles are not localized, they cannot be distinguished from each other as were the harmonic oscillators considered in Example 4.4 and the spins in Chapter 5. Hence, we cannot simply focus our attention on one particular particle. For this reason we will later find it more convenient to derive the thermodynamic properties of the ideal classical gas using the grand canonical ensemble (see Section 6.8).

If the temperature is sufficiently high, we expect that we can treat a system of particles semiclassically. To do so, the de Broglie wavelength associated with the particles must be small. That is, for the semiclassical description to be valid, the mean de Broglie wavelength λ must be smaller than any other length in the system. For an ideal gas, the only two lengths are L, the linear dimension of the system, and the mean distance between particles. As shown in Problem 6.1, the mean distance between particles in three dimensions is $\rho^{-1/3}$. Because we are interested in the thermodynamic limit for which $L \gg \lambda$, the semiclassical limit requires that

$$\lambda \ll \rho^{-1/3} \quad \text{or} \quad \rho\lambda^3 \ll 1. \qquad \text{(semiclassical limit)} \tag{6.1}$$

Problem 6.1. Mean distance between particles

(a) Consider a system of N particles confined to a line of length L. What is the definition of the particle density ρ? The mean distance between particles is N/L. How does this distance depend on ρ?

(b) Consider a system of N particles confined to a square of linear dimension L. In this case the mean distance between particles is $A/N = L^2/N$. How does the mean distance between particles depend on ρ?

(c) Use similar considerations to determine the density dependence of the mean distance between particles in three dimensions.

To estimate the magnitude of λ, we need to know the typical value of the momentum of a particle. For a nonrelativistic system we know from (4.65) that $\overline{p^2}/2m = 3kT/2$. (We will rederive this result more generally in Section 6.3.) Hence $\overline{p^2} \sim mkT$ and $\lambda \sim h/\sqrt{\overline{p^2}} \sim h/\sqrt{mkT}$. We will find it is convenient to define the *thermal de Broglie wavelength* λ as

$$\lambda = \Big(\frac{h^2}{2\pi mkT}\Big)^{1/2} = \Big(\frac{2\pi\hbar^2}{mkT}\Big)^{1/2}. \qquad \text{(thermal de Broglie wavelength)} \tag{6.2}$$

This form of λ with the factor of $\sqrt{2\pi}$ will allow us to express the partition function in a convenient form (see (6.11)).

The calculation of the partition function of an ideal gas in the semiclassical limit proceeds as follows. First, we assume that $\lambda \ll \rho^{-1/3}$ so that we could pick out one particle from another if the particles were distinguishable. (If $\lambda \sim \rho^{-1/3}$, the wave functions of the particles would overlap.) Of course, identical particles are intrinsically indistinguishable, so we will have to correct for overcounting later.

With these considerations in mind we now calculate Z_1, the partition function for one particle, in the semiclassical limit. As we found in (4.42), the energy eigenvalues of a particle in a cube of side L are given by

$$\epsilon_n = \frac{h^2}{8mL^2}(n_x{}^2 + n_y{}^2 + n_z{}^2), \tag{6.3}$$

where the subscript n represents the set of quantum numbers n_x, n_y, and n_z, each of which can be any nonzero, positive integer. The corresponding partition function is given by

$$Z_1 = \sum_n e^{-\beta \epsilon_n} = \sum_{n_x=1}^{\infty} \sum_{n_y=1}^{\infty} \sum_{n_z=1}^{\infty} e^{-\beta h^2 (n_x{}^2 + n_y{}^2 + n_z{}^2)/8mL^2}. \tag{6.4}$$

Because the sum over each quantum number is independent of the other two quantum numbers, we can rewrite (6.4) as

$$Z_1 = \Big[\sum_{n_x=1}^{\infty} e^{-\alpha^2 n_x{}^2} \Big] \Big[\sum_{n_y=1}^{\infty} e^{-\alpha n_y{}^2} \Big] \Big[\sum_{n_z=1}^{\infty} e^{-\alpha n_z{}^2} \Big] \tag{6.5a}$$

$$= Z_x Z_y Z_z = Z_x^3, \tag{6.5b}$$

where

$$\alpha^2 = \frac{\beta h^2}{8mL^2} = \frac{\pi}{4} \frac{\lambda^2}{L^2}, \tag{6.6}$$

and

$$Z_x = \sum_{n_x=1}^{\infty} e^{-\alpha^2 n_x{}^2}. \tag{6.7}$$

The functions Z_y and Z_z have the same form as Z_x. (We could have known beforehand that Z_1 in (6.5b) would factor into three terms. Why?)

It remains to evaluate the sum over n_x in (6.7). Because the linear dimension L of the container is of macroscopic size, we have $\lambda \ll L$ and α in (6.7) is much less than one (unless T is very small). Hence because the difference between successive terms in the sum is very small, we can convert the sum in (6.7) to an integral:

$$Z_x = \sum_{n_x=1}^{\infty} e^{-\alpha^2 n_x{}^2} = \sum_{n_x=0}^{\infty} e^{-\alpha^2 n_x{}^2} - 1 \rightarrow \int_0^{\infty} e^{-\alpha^2 n_x^2} \, dn_x - 1. \tag{6.8}$$

We have accounted for the fact that the sum over n_x in (6.7) is from $n_x = 1$ rather than $n_x = 0$. We next make a change of variables and write $x^2 = \alpha^2 n_x^2$. We have that

$$Z_x = \frac{1}{\alpha} \int_0^{\infty} e^{-x^2} dx - 1 = L \Big(\frac{2\pi m}{\beta h^2} \Big)^{1/2} - 1. \tag{6.9}$$

The Gaussian integral in (6.9) gives a factor of $\pi^{1/2}/2$ (see Appendix A). Because the first term in (6.9) is order $L/\lambda \gg 1$, we can ignore the second term. The expressions for Z_y and Z_z are identical, and hence we obtain

$$Z_1 = Z_x Z_y Z_z = V \Big(\frac{2\pi m}{\beta h^2} \Big)^{3/2}. \tag{6.10}$$

The result (6.10) is the partition function associated with the translational motion of one particle in a box. Note that Z_1 can be conveniently expressed as

$$Z_1 = \frac{V}{\lambda^3}. \tag{6.11}$$

It is straightforward to find the mean pressure and energy for one particle in a box. We take the logarithm of both sides of (6.10) and find

$$\ln Z_1 = \ln V - \frac{3}{2} \ln \beta + \frac{3}{2} \ln \frac{2\pi m}{h^2}. \tag{6.12}$$

Hence the mean pressure due to one particle is given by

$$\bar{p} = \frac{1}{\beta} \frac{\partial \ln Z_1}{\partial V} \Big|_{T,N} = \frac{1}{\beta V} = \frac{kT}{V}, \tag{6.13}$$

and the mean energy is

$$\bar{e} = -\frac{\partial \ln Z_1}{\partial \beta} \Big|_{V,N} = \frac{3}{2\beta} = \frac{3}{2} kT. \tag{6.14}$$

The mean energy and pressure of an ideal gas of N particles is N times that of the corresponding quantities for one particle. Hence, we obtain for an ideal classical gas the equations of state

$$PV = NkT, \tag{6.15}$$

and

$$E = \frac{3}{2} NkT. \tag{6.16}$$

The heat capacity at constant volume of an ideal gas of N particles is

$$C_V = \frac{\partial E}{\partial T} \Big|_V = \frac{3}{2} Nk. \tag{6.17}$$

We have derived the mechanical and thermal equations of state for an ideal classical gas for a second time! The derivation of the equations of state is much easier in the canonical ensemble than in the microcanonical ensemble. The reason is that we were able to consider the partition function of one particle because the only constraint is that the temperature is fixed instead of the total energy.

Problem 6.2. The volume dependence of Z_1 should be independent of the shape of the box. Show that the same result for Z_1 is obtained if the box has linear dimensions L_x, L_y, and L_z.

Problem 6.3. We obtained the semiclassical limit of the partition function Z_1 for one particle in a box by writing it as a sum over single particle states and then converting the sum to an integral. Show that the semiclassical partition Z_1 for a particle in a one-dimensional box can be expressed as

$$Z_1 = \int \frac{dp \, dx}{h} \, e^{-\beta p^2 / 2m}. \qquad \text{(one dimension)} \tag{6.18}$$

The integral over p in (6.18) extends from $-\infty$ to $+\infty$.

The entropy of an ideal classical gas of N particles. Although it is straightforward to calculate the mean energy and pressure of an ideal classical gas by considering the partition function for one particle, the calculation of the entropy is more subtle. To understand the difficulty, consider the calculation of the partition function of an ideal gas of three particles. Because there are no

interactions between the particles, we can write the total energy as a sum of the single particle energies $\epsilon_1 + \epsilon_2 + \epsilon_3$, where ϵ_i is the energy of the ith particle. The partition function Z_3 is

$$Z_3 = \sum_{\text{all states}} e^{-\beta(\epsilon_1+\epsilon_2+\epsilon_3)}. \tag{6.19}$$

The sum over all states in (6.19) is over the states of the three particle system. If the three particles were distinguishable, there would be no restriction on the number of particles that could be in any single particle state, and we could sum over the possible states of each particle separately. Hence, the partition function for a system of three distinguishable particles has the form

$$Z_3 = Z_1^3. \qquad \text{(distinguishable particles)} \tag{6.20}$$

It is instructive to show the origin of the relation (6.20) for an specific example. Suppose the three particles are red, white, and blue and are in equilibrium with a heat bath at temperature T. For simplicity, we assume that each particle can be in one of only three states with energy ϵ_1, ϵ_2, or ϵ_3. The partition function for one particle is given by

$$Z_1 = e^{-\beta\epsilon_1} + e^{-\beta\epsilon_2} + e^{-\beta\epsilon_3}. \tag{6.21}$$

In Table 6.2 we show the twenty-seven possible states of the system of three distinguishable particles. The corresponding partition function is given by

$$\begin{aligned}
Z_3 = {}& e^{-3\beta\epsilon_1} + e^{-3\beta\epsilon_2} + e^{-3\beta\epsilon_3} \\
& + 3\big[e^{-\beta(2\epsilon_1+\epsilon_2)} + e^{-\beta(\epsilon_1+2\epsilon_2)} + e^{-\beta(2\epsilon_1+\epsilon_3)} \\
& + e^{-\beta(2\epsilon_2+\epsilon_3)} + e^{-\beta(\epsilon_1+2\epsilon_3)} + e^{-\beta(\epsilon_2+2\epsilon_3)}\big] \\
& + 6\,e^{-\beta(\epsilon_1+\epsilon_2+\epsilon_3)}. \qquad \text{(three distinguishable particles)}
\end{aligned} \tag{6.22}$$

It is easy to see that Z_3 in (6.22) can be factored and expressed as

$$Z_3 = Z_1^3. \tag{6.23}$$

In contrast, if the three particles are indistinguishable, many of the microstates shown in Table 6.2 would be impossible. In this case we cannot assign the states of the particles independently, and the sum over all states in (6.19) cannot be factored as in (6.20). For example, the state 1, 2, 3 could not be distinguished from the state 1, 3, 2.

As discussed in Section 4.3.7, the semiclassical limit assumes that states with multiple occupancy such as 1, 1, 2 and 1, 1, 1 can be ignored because there are many more single particle states than there are particles (see Problem 4.19). (In our simple example, each particle can be in one of only three states and the number of states is comparable to the number of particles.) If we assume that the particles are indistinguishable and that microstates with multiple occupancy can be ignored, then Z_3 is given by

$$Z_3 = e^{-\beta(\epsilon_1+\epsilon_2+\epsilon_3)}. \qquad \text{(indistinguishable, multiple occupancy ignored)} \tag{6.24}$$

However, if the particles are *distinguishable*, there are 3! states (states 22–27 in Table 6.2) with energy $\epsilon_1 + \epsilon_2 + \epsilon_3$ (again ignoring states with multiple occupancy). Thus if we count microstates

state s	red	white	blue	E_s
1	ϵ_1	ϵ_1	ϵ_1	$3\epsilon_1$
2	ϵ_2	ϵ_2	ϵ_2	$3\epsilon_2$
3	ϵ_3	ϵ_3	ϵ_3	$3\epsilon_3$
4	ϵ_2	ϵ_1	ϵ_1	$2\epsilon_1 + \epsilon_2$
5	ϵ_1	ϵ_2	ϵ_1	$2\epsilon_1 + \epsilon_2$
6	ϵ_1	ϵ_1	ϵ_2	$2\epsilon_1 + \epsilon_2$
7	ϵ_1	ϵ_2	ϵ_2	$\epsilon_1 + 2\epsilon_2$
8	ϵ_2	ϵ_1	ϵ_2	$\epsilon_1 + 2\epsilon_2$
9	ϵ_2	ϵ_2	ϵ_1	$\epsilon_1 + 2\epsilon_2$
10	ϵ_3	ϵ_1	ϵ_1	$2\epsilon_1 + \epsilon_3$
11	ϵ_1	ϵ_3	ϵ_1	$2\epsilon_1 + \epsilon_3$
12	ϵ_1	ϵ_1	ϵ_3	$2\epsilon_1 + \epsilon_3$
13	ϵ_3	ϵ_2	ϵ_2	$2\epsilon_2 + \epsilon_3$
14	ϵ_2	ϵ_3	ϵ_2	$2\epsilon_2 + \epsilon_3$
15	ϵ_2	ϵ_2	ϵ_3	$2\epsilon_2 + \epsilon_3$
16	ϵ_1	ϵ_3	ϵ_3	$\epsilon_1 + 2\epsilon_3$
17	ϵ_3	ϵ_1	ϵ_3	$\epsilon_1 + 2\epsilon_3$
18	ϵ_3	ϵ_3	ϵ_1	$\epsilon_1 + 2\epsilon_3$
19	ϵ_2	ϵ_3	ϵ_3	$\epsilon_2 + 2\epsilon_3$
20	ϵ_3	ϵ_2	ϵ_3	$\epsilon_2 + 2\epsilon_3$
21	ϵ_3	ϵ_3	ϵ_2	$\epsilon_2 + 2\epsilon_3$
22	ϵ_1	ϵ_2	ϵ_3	$\epsilon_1 + \epsilon_2 + \epsilon_3$
23	ϵ_1	ϵ_3	ϵ_2	$\epsilon_1 + \epsilon_2 + \epsilon_3$
24	ϵ_2	ϵ_1	ϵ_3	$\epsilon_1 + \epsilon_2 + \epsilon_3$
25	ϵ_2	ϵ_3	ϵ_1	$\epsilon_1 + \epsilon_2 + \epsilon_3$
26	ϵ_3	ϵ_1	ϵ_2	$\epsilon_1 + \epsilon_2 + \epsilon_3$
27	ϵ_3	ϵ_2	ϵ_1	$\epsilon_1 + \epsilon_2 + \epsilon_3$

Table 6.1: The twenty-seven microstates of an ideal gas of three distinguishable particles (red, white, and blue). Each particle can be in one of three states with energy ϵ_1, ϵ_2, or ϵ_3.

assuming that the three particles are distinguishable, we overcount the number of states by the number of permutations of the particles. Hence, in the semiclassical limit we can write

$$Z_3 = \frac{Z_1^3}{3!}. \qquad \text{(correction for overcounting)} \tag{6.25}$$

In general, if we begin with the fundamental quantum mechanical description of matter, then identical particles are indistinguishable at all temperatures. However, if we make the assumption that single particle states with multiple occupancy can be ignored, we can express Z_N, the partition function of N noninteracting identical particles, as

$$Z_N = \frac{Z_1{}^N}{N!}. \qquad \text{(semiclassical limit)} \tag{6.26}$$

If we substitute for Z_1 from (6.10), we obtain

$$Z_N = \frac{V^N}{N!} \left(\frac{2\pi mkT}{h^2} \right)^{3N/2}. \tag{6.27}$$

If we take the logarithm of both sides of (6.27) and use Stirling's approximation (3.103), we can write the free energy of a noninteracting classical gas as

$$F = -kT \ln Z_N = -kTN \left[\ln \frac{V}{N} + \frac{3}{2} \ln \left(\frac{2\pi mkT}{h^2} \right) + 1 \right]. \tag{6.28}$$

In Section 6.8 we will use the grand canonical ensemble to obtain the entropy of an ideal classical gas without any ad hoc assumptions such as assuming that the particles are distinguishable and then introducing the factor of $N!$. That is, in the grand canonical ensemble we will be able to automatically satisfy the condition that the particles are indistguishable.

Problem 6.4. Equations of state of an ideal gas

Use the result (6.28) to find the pressure equation of state and the mean energy of an ideal gas. Do these relations depend on whether the particles are indistinguishable or distinguishable?

Problem 6.5. Entropy of an ideal gas

(a) The entropy can be found from the relations, $F = E - TS$ or $S = -\partial F/\partial T$. Show that

$$S(T, V, N) = Nk \left[\ln \frac{V}{N} + \frac{3}{2} \ln \left(\frac{2\pi mkT}{h^2} \right) + \frac{5}{2} \right]. \tag{6.29}$$

The form of S in (6.29) is known as the *Sackur-Tetrode equation* (see Problem 4.25). Is this form of S applicable in the limit of low temperatures?

(b) Express kT in terms of E and show that $S(E, V, N)$ can be expressed as

$$S(E, V, N) = Nk \left[\ln \frac{V}{N} + \frac{3}{2} \ln \left(\frac{4\pi mE}{3Nh^2} \right) + \frac{5}{2} \right], \tag{6.30}$$

in agreement with the result (4.63) found by using the microcanonical ensemble. The form (6.30) of S in terms of its natural variables E, V, and N is known as the *fundamental relation* for an ideal classical gas.

Problem 6.6. The chemical potential of an ideal classical gas

(a) Use the relation $\mu = \partial F/\partial N$ and the result (6.28) to show that the chemical potential of an ideal classical gas is given by

$$\mu = -kT \ln \left[\frac{V}{N} \left(\frac{2\pi mkT}{h^2} \right)^{3/2} \right]. \tag{6.31}$$

(b) We will see in Problem 6.45 that if two systems are placed into contact with different initial chemical potentials, particles will go from the system with high chemical potential to the system with low chemical potential. (This behavior is analogous to energy going from high to low temperatures.) Does "high" chemical potential for an ideal classical gas imply "high" or "low" density?

(c) Calculate the entropy and chemical potential of one mole of helium gas at standard temperature and pressure. Take $V = 2.24 \times 10^{-2} \, \text{m}^3$, $N = 6.02 \times 10^{23}$, $m = 6.65 \times 10^{-27} \, \text{kg}$, and $T = 273 \, \text{K}$.

Problem 6.7. Entropy as an extensive quantity

(a) Because the entropy is an extensive quantity, we know that if we double the volume and double the number of particles (thus keeping the density constant), the entropy must double. This condition can be written formally as $S(T, \lambda V, \lambda N) = \lambda S(T, V, N)$. Although this behavior of the entropy is completely general, there is no guarantee that an approximate calculation of S will satisfy this condition. Show that the Sackur-Tetrode form of the entropy of an ideal gas of identical particles, (6.29), satisfies this general condition.

(b) Show that if the $N!$ term were absent from (6.27) for Z_N, S would be given by

$$S = Nk\left[\ln V + \frac{3}{2}\ln\left(\frac{2\pi mkT}{h^2}\right) + \frac{3}{2}\right]. \tag{6.32}$$

Is this form of S proportional to N for V/N constant?

(c) The fact that (6.32) yields an entropy that is not extensive does *not* indicate that identical particles must be indistinguishable. Instead the problem arises from our identification of S with $\ln Z$ as discussed in Section 4.6. Recall that we considered a system with fixed N and made the identification (see (4.105))

$$dS/k = d(\ln Z + \beta E). \tag{6.33}$$

It is straightforward to integrate (6.33) and obtain

$$S = k(\ln Z + \beta E) + g(N), \tag{6.34}$$

where $g(N)$ is an arbitrary function of N only. Although we usually set $g(N) = 0$, it is important to remember that $g(N)$ is arbitrary. What must be the form of $g(N)$ in order that the entropy of an ideal classical gas be extensive?

Entropy of mixing. Suppose that we have two containers A and B with two different gases (for example, Argon and Oxygen) at the same temperature T. What is the change of the entropy of the combined system if we remove the partition separating them and allow the two gases to mix (see Figure 6.1)? Because particles of type A are different than the particles of type B, we lose information about the system and therefore the entropy must increase. (We knew initially that the type A particles were in container A and particles of type B were in container B.) We conclude that the entropy of mixing satisfies

$$\Delta S > 0 \qquad \text{(entropy of mixing)} \tag{6.35}$$

N_A, V_A	N_B, V_B

Figure 6.1: The composite system is prepared such that there N_A particles of type A in container A and N_B particles of type B in container B. The two containers are at the same temperature T. What is the entropy of mixing if the partition is removed?

Alternatively, we know that there would the entropy must increase because removing the partition between the two containers is an irreversible process. (Reinserting the partition would not separate the two gases.)

If the two gases are identical and at originally at the same density, is there any change of entropy when the partition is removed? Because we lose no information in this case, we should have $\Delta S = 0$. In the following, we will derive these results for the special case of an ideal gas.

Consider two ideal gases at the same temperature T with N_A and N_B particles in containers of volume V_A and V_B, respectively. The gases are initially separated by a partition. If we use (6.29) for the entropy, we find

$$S_A = N_A k \left[\ln \frac{V_A}{N_A} + f(T) \right], \tag{6.36a}$$

$$S_B = N_B k \left[\ln \frac{V_B}{N_B} + f(T) \right], \tag{6.36b}$$

where the function $f(T) = 3/2 \ln(2\pi mkT/h^2) + 5/2$. We then allow the particles to mix so that they fill the entire volume $V = V_A + V_B$. If the particles are identical, the total entropy after the removal of the partition is given by

$$S = k(N_A + N_B) \left[\ln \frac{V_A + V_B}{N_A + N_B} + f(T) \right], \tag{6.37}$$

and the change in the value of S, the *entropy of mixing*, is given by

$$\Delta S = k \left[(N_A + N_B) \ln \frac{V_A + V_B}{N_A + N_B} - N_A \ln \frac{V_A}{N_A} - N_B \ln \frac{V_B}{N_B} \right]. \qquad \text{(identical gases)} \tag{6.38}$$

Problem 6.8. Entropy of mixing

(a) Use (6.38) to show that $\Delta S = 0$ if the two gases have equal densities before separation. Write $N_A = \rho V_A$ and $N_B = \rho V_B$.

(b) Why is the entropy of mixing nonzero if the two gases initially have different densities even though the particles are identical?

If the two gases are not identical, the total entropy after mixing is

$$S = k \left[N_A \ln \frac{V_A + V_B}{N_A} + N_B \ln \frac{V_A + V_B}{N_B} + (N_A + N_B) f(T) \right]. \tag{6.39}$$

Then the entropy of mixing becomes

$$\Delta S = k\Big[N_A \ln \frac{V_A + V_B}{N_A} + N_B \ln \frac{V_A + V_B}{N_B} - N_A \ln \frac{V_A}{N_A} - N_B \ln \frac{V_B}{N_B}\Big]. \qquad \text{(entropy of mixing)}$$

(6.40)

For the special case of $N_A = N_B = N$ and $V_A = V_B = V$, we find

$$\Delta S = 2Nk \ln 2. \tag{6.41}$$

Problem 6.9. More on mixing

(a) Explain the result (6.41) in simple terms.

(b) What would be the result for the entropy of mixing if we had used the result (6.32) for S instead of (6.29)? Consider the special case of $N_A = N_B = N$ and $V_A = V_B = V$.

6.3 Classical Systems and the Equipartition Theorem

We have used the microcanonical and canonical ensembles to show that the mean energy of an ideal classical gas in three dimensions is given by $E = 3kT/2$. Similarly, we have found that the mean energy of a one-dimensional harmonic oscillator is given by $E = kT$ in the limit of high temperatures. These results are special cases of the *equipartition theorem* which can be stated as follows:

> For a classical system in equilibrium with a heat bath at temperature T, the mean value of each contribution to the total energy that is quadratic in a coordinate equals $\frac{1}{2}kT$.

Note that the equipartition theorem holds regardless of the coefficients of the quadratic terms and is valid only for a classical system. If all the contributions to the energy are quadratic, the mean energy is distributed equally to each term (hence the name "equipartition").

We first consider a single particle in a region with potential $U(\mathbf{r})$ in equilibrium with a heat bath at temperature T. Because the position and momentum of the particle are continuous variables, the probability of finding the particle in a small volume d^3r about $\mathbf{r}$ with a momentum in a small volume d^3p about $\mathbf{p}$ is proportional to the Boltzmann factor and the volume $d^3r\, d^3p$ in phase space:

$$e^{-\beta(p^2/2m + U(\mathbf{r}))} d^3r\, d^3p. \tag{6.42}$$

To normalize the probability we have to integrate rather than sum over all the possible values of $\mathbf{r}$ and $\mathbf{p}$.

To derive the equipartition theorem, we generalize these considerations for a single particle to a system of N particles. We use the canonical ensemble and the fact that the probability density of a particular microstate is proportional to the Boltzmann probability $e^{-\beta E}$, where E is the energy of a particular microstate. Because a microstate is defined by the positions and momenta of every particle, we can express the average of any physical quantity $f(\mathbf{r}, \mathbf{p})$ in a classical system by

$$\overline{f} = \frac{\int f(\mathbf{r}_1, \ldots, \mathbf{r}_N, \mathbf{p}_1, \ldots, \mathbf{p}_N)\, e^{-\beta E(\mathbf{r}_1, \ldots, \mathbf{r}_N, \mathbf{p}_1, \ldots, \mathbf{p}_N)}\, d\mathbf{r}_1 \ldots d\mathbf{r}_N\, d\mathbf{p}_1 \ldots d\mathbf{p}_N}{\int e^{-\beta E(\mathbf{r}_1, \ldots, \mathbf{r}_N, \mathbf{p}_1, \ldots, \mathbf{p}_N)}\, d\mathbf{r}_1 \ldots d\mathbf{r}_N\, d\mathbf{p}_1 \ldots d\mathbf{p}_N}. \tag{6.43}$$

Note that we have replaced the sum over quantum states by an integration over phase space. We derived a special expression of this idea in Problem 6.3.[3]

Suppose that the total energy can be written as a sum of quadratic terms. For example, the kinetic energy of one particle in three dimensions in the nonrelativistic limit can be expressed as $(p_x^2 + p_y^2 + p_z^2)/2m$. Another example is the one-dimensional harmonic oscillator for which the total energy is $p_x^2/2m + kx^2/2$. Let us consider a one-dimensional system of two particles for simplicity, and suppose that the energy of the system can be written as

$$E = \epsilon_1(p_1) + \tilde{E}(x_1, x_2, p_2), \tag{6.44}$$

where $\epsilon_1 = bp_1^2$ with b a constant. We have separated out the quadratic dependence of the energy of particle 1 on its momentum. We use (6.43) and express the mean value of ϵ_1 as

$$\bar{\epsilon}_1 = \frac{\int_{-\infty}^{\infty} \epsilon_1 \, e^{-\beta E(x_1, x_2, p_1, p_2)} \, dx_1 dx_2 \, dp_1 dp_2}{\int_{-\infty}^{\infty} e^{-\beta E(x_1, x_2, p_1, p_2)} \, dx_1 dx_2 \, dp_1 dp_2} \tag{6.45a}$$

$$= \frac{\int_{-\infty}^{\infty} \epsilon_1 \, e^{-\beta[\epsilon_1 + \tilde{E}(x_1, x_2, p_2)]} \, dx_1 dx_2 \, dp_1 dp_2}{\int_{-\infty}^{\infty} e^{-\beta[\epsilon_1 + \tilde{E}(x_1, x_2, p_2, p_2)]} \, dx_1 dx_2 dp_1 dp_2} \tag{6.45b}$$

$$= \frac{\int_{-\infty}^{\infty} \epsilon_1 \, e^{-\beta \epsilon_1} \, dp_1 \int e^{-\beta \tilde{E}} \, dx_1 dx_2 \, dp_2}{\int_{-\infty}^{\infty} e^{-\beta \epsilon_1} \, dp_1 \int e^{-\beta \tilde{E}} \, dx_1 dx_2 \, dp_2}. \tag{6.45c}$$

The integrals over all the coordinates except p_1 cancel, and we have

$$\bar{\epsilon}_1 = \frac{\int_{-\infty}^{\infty} \epsilon_1 \, e^{-\beta \epsilon_1} \, dp_1}{\int_{-\infty}^{\infty} e^{-\beta \epsilon_1} \, dp_1}. \tag{6.46}$$

We could have written $\bar{\epsilon}_1$ in the form (6.46) directly without any intermediate steps because the probability density can be written as a product of two terms – one term that depends only on p_1 and another term that depends on x_1, x_2, and p_2.

As we have done in other contexts, we can write $\bar{\epsilon}_1$ as

$$\bar{\epsilon}_1 = -\frac{\partial}{\partial \beta} \ln \left(\int_{-\infty}^{\infty} e^{-\beta \epsilon_1} \, dp_1 \right). \tag{6.47}$$

If we substitute $\epsilon_1 = ap_1^2$, the integral in (6.47) becomes

$$Z = \int_{-\infty}^{\infty} e^{-\beta \epsilon_1} dp_1 = \int_{-\infty}^{\infty} e^{-\beta a p_1^2} \, dp_1 \tag{6.48a}$$

$$= (\beta a)^{-1/2} \int_{-\infty}^{\infty} e^{-x^2} dx, \tag{6.48b}$$

where we have let $x^2 = \beta a p^2$. Note that the integral in (6.48b) is independent of β, and its numerical value is irrelevant. Hence

$$\bar{\epsilon}_1 = -\frac{\partial}{\partial \beta} \ln Z(\beta) = \frac{1}{2} kT. \tag{6.49}$$

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[3]We could divide $d\mathbf{r}_1 \ldots d\mathbf{r}_N \, d\mathbf{p}_1 \ldots d\mathbf{p}_N$ by h^{3N} in the numerator and denominator so that we would obtain the correct number of microstates in the semiclassical limit, but this factor cancels.

Equation (6.49) is an example of the equipartition theorem of classical statistical mechanics.

Problem 6.10. Interpretation of results

(a) Explain why we could have written (6.46) directly.

(b) What is the physical interpretation of the integrand in the numerator and denominator of (6.46)?

The equipartition theorem is not really a new result, is applicable only when the system can be described classically, and is applicable only to each term in the energy that is proportional to a coordinate squared. This coordinate also must take on a continuum of values from $-\infty$ to $+\infty$.

Applications of the equipartition theorem. A system of particles in three dimensions has $3N$ quadratic contributions to the kinetic energy, three for each particle. From the equipartition theorem, we know that the mean kinetic energy is $3NkT/2$, independent of the nature of the interactions, if any, between the particles. Hence, the heat capacity at constant volume of an ideal classical monatomic gas is given by $C_V = 3Nk/2$ as found previously.

Another application of the equipartition function is to the one-dimensional harmonic oscillator in the classical limit. In this case there are two quadratic contributions to the total energy and hence the mean energy of a classical harmonic oscillator in equilibrium with a heat bath at temperature T is kT. In the harmonic model of a crystal each atom feels a harmonic or spring-like force due to its neighboring atoms. The N atoms independently perform simple harmonic oscillations about their equilibrium positions. Each atom contributes three quadratic terms to the kinetic energy and three quadratic terms to the potential energy. Hence, in the high temperature limit the energy of a crystal of N atoms is $E = 6NkT/2$ and the heat capacity at constant volume is

$$C_V = 3Nk. \qquad \text{(law of Dulong and Petit)} \qquad (6.50)$$

The result (6.50) is known as the law of Dulong and Petit. This result was first discovered empirically and is valid only at sufficiently high temperatures. At low temperatures the independence of C_V on T breaks down and a quantum treatment is necessary. The heat capacity of an insulating solid at low temperatures is discussed in Section 6.11.

The result (6.49) implies that the heat capacity of a monatomic ideal classical gas is $3NkT/2$. Let us consider a gas consisting of diatomic molecules. Its equation of state is still given by $PV = NkT$ assuming that the molecules do not interact. Why? However, its heat capacity differs in general from that of a monatomic gas because a diatomic molecule has additional energy associated with vibrational and rotational motion. We expect that the two atoms of a diatomic molecule can vibrate along the line joining them and rotate about their center of mass, in addition to the translational motion of their center of mass. Hence, we would expect that C_V for an ideal diatomic gas is greater than C_V for a monatomic gas. The heat capacity of a diatomic molecule is explored in Problem 6.47.

We have seen that it is convenient to do calculations for a fixed number of particles for classical systems. For this reason we usually calculate the heat capacity of a N particle system or the specific heat per particle. Experimental chemists usually give the specific heat as the heat capacity per mole and experimental physicists usually give the specific heat as the heat capacity per kilogram or gram. All three quantities are known as the specific heat and their precise meaning is clear from their units and the context.

6.4 Maxwell Velocity Distribution

We now find the distribution of particle velocities in a classical system that is in equilibrium with a heat bath at temperature T. We know that the total energy can be written as the sum of two parts: the kinetic energy $K(\mathbf{p}_1, \ldots, \mathbf{p}_N)$ and the potential energy $U(\mathbf{r}_1, \ldots, \mathbf{r}_N)$. The kinetic energy is a quadratic function of the momenta $\mathbf{p}_1, \ldots, \mathbf{p}_N$ (or velocities), and the potential energy is a function of the positions $\mathbf{r}_1, \ldots, \mathbf{r}_N$ of the particles. The total energy is $E = K + U$. The probability density of a configuration of N particles defined by $\mathbf{r}_1, \ldots, \mathbf{r}_N, \mathbf{p}_1, \ldots, \mathbf{p}_N$ is given in the canonical ensemble by

$$p(\mathbf{r}_1, \ldots, \mathbf{r}_N; \mathbf{p}_1, \ldots, \mathbf{p}_N) = A\, e^{-[K(\mathbf{p}_1, \mathbf{p}_2, \ldots, \mathbf{p}_N) + U(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N)]/kT} \tag{6.51a}$$

$$= A\, e^{-K(\mathbf{p}_1, \mathbf{p}_2, \ldots, \mathbf{p}_N)/kT} e^{-U(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N)/kT}, \tag{6.51b}$$

where A is a normalization constant. As we noted in Section 6.3 the probability density p is a product of two factors, one that depends only on the particle positions and the other that depends only on the particle momenta. This factorization implies that the probabilities of the momenta and positions are independent. The momentum of a particle is not influenced by its position and vice versa. The probability of the positions of the particles can be written as

$$f(\mathbf{r}_1, \ldots, \mathbf{r}_N)\, d\mathbf{r}_1 \ldots d\mathbf{r}_N = B\, e^{-U(\mathbf{r}_1, \ldots, \mathbf{r}_N)/kT} d\mathbf{r}_1 \ldots d\mathbf{r}_N, \tag{6.52}$$

and the probability of the momenta is given by

$$f(\mathbf{p}_1, \ldots, \mathbf{p}_N)\, d\mathbf{p}_1 \ldots d\mathbf{p}_N = C\, e^{-K(\mathbf{p}_1, \ldots, \mathbf{p}_N)/kT} d\mathbf{p}_1 \ldots d\mathbf{p}_N. \tag{6.53}$$

For notational simplicity, we have denoted the two probability densities by f, even though their functional form is different in (6.52) and (6.53). The constants B and C in (6.53) and (6.52) can be found by requiring that each probability is normalized.

We emphasize that the probability distribution for the momenta does not depend on the nature of the interaction between the particles and is the same for all classical systems at the same temperature. This statement might seem surprising because it might seem that the velocity distribution should depend on the density of the system. An external potential also does not affect the velocity distribution. These statements do not hold for quantum systems, because in this case the position and momentum operators do not commute. That is, $e^{-\beta(\hat{K} + \hat{U})} \neq e^{-\beta\hat{K}} e^{-\beta\hat{U}}$ for quantum systems. (We have denoted operators in quantum mechanics by ˆ.)

Because the total kinetic energy is a sum of the kinetic energy of each of the particles, the probability density $f(\mathbf{p}_1, \ldots, \mathbf{p}_N)$ is a product of terms that each depend on the momenta of only one particle. This factorization implies that the momentum probabilities of the various particles are independent, that is, the momentum of one particle does not affect the momentum of any other particle. These considerations imply that we can write the probability that a particle has momentum $\mathbf{p}$ in the range $d\mathbf{p}$ as

$$f(p_x, p_y, p_z)\, dp_x dp_y dp_z = c\, e^{-(p_x^2 + p_y^2 + p_z^2)/2mkT} dp_x dp_y dp_z. \tag{6.54}$$

The constant c is given by the normalization condition

$$c \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} e^{-(p_x^2 + p_y^2 + p_z^2)/2mkT} dp_x dp_y dp_z = c\left[\int_{-\infty}^{\infty} e^{-p^2/2mkT} dp\right]^3 = 1. \tag{6.55}$$

If we use the fact that $\int_{-\infty}^{\infty} e^{-\alpha x^2} dx = (\pi/\alpha)^{1/2}$ (see Appendix A), we find that $c = (2\pi mkT)^{-3/2}$. Hence the momentum probability distribution can be expressed as

$$f(p_x, p_y, p_z)\, dp_x dp_y dp_z = \frac{1}{(2\pi mkT)^{3/2}}\, e^{-(p_x^2+p_y^2+p_z^2)/2mkT} dp_x dp_y dp_z. \tag{6.56}$$

The corresponding velocity probability distribution is given by

$$f(v_x, v_y, v_z)\, dv_x dv_y dv_z = \left(\frac{m}{2\pi kT}\right)^{3/2} e^{-m(v_x^2+v_y^2+v_z^2)/2kT} dv_x dv_y dv_z. \tag{6.57}$$

Equation (6.57) is known as the *Maxwell velocity distribution.* Note that its form is a Gaussian. The probability distribution for the speed is discussed in Section 6.7.4.

Because $f(v_x, v_y, v_z)$ is a product of three independent factors, the probability of the velocity of a particle in a particular direction is independent of the velocity in any other direction. For example, the probability that a particle has a velocity in the x-direction in the range v_x to $v_x + dv_x$ is

$$f(v_x)\, dv_x = \left(\frac{m}{2\pi kT}\right)^{1/2} e^{-mv_x^2/2kT} dv_x. \tag{6.58}$$

Many textbooks derive the Maxwell velocity distribution for an ideal classical gas and give the mistaken impression that the distribution applies only if the particles are noninteracting. We stress that the Maxwell velocity (and momentum) distribution applies to any classical system regardless of the interactions, if any, between the particles.

Problem 6.11. Is there an upper limit to the velocity?

The upper limit to the velocity of a particle is the velocity of light. Yet the Maxwell velocity distribution imposes no upper limit to the velocity. Is this contradiction likely to lead to difficulties?

Problem 6.12. Alternative derivation of the Maxwell velocity distribution

We can also derive the Maxwell velocity distribution by making some plausible assumptions. We first assume that the probability density $f(\mathbf{v})$ for one particle is a function only of its speed $|\mathbf{v}|$ or equivalently v^2. We also assume that the velocity distributions of the components v_x, v_y, v_z are independent of each other.

(a) Given these assumptions, explain why we can write

$$f(v_x^2 + v_y^2 + v_z^2) = f(v_x^2)f(v_y^2)f(v_z^2). \tag{6.59}$$

(b) Show that the only mathematical function that satisfies the condition (6.59) is the exponential function

$$f(v^2) = c\,e^{-\alpha v^2}, \tag{6.60}$$

where c and α are independent of $\mathbf{v}$.

(c) Determine c in terms of α using the normalization condition $1 = \int_{-\infty}^{\infty} f(u)du$ for each component. Why must α be positive?

(d) Use the fact that $\frac{1}{2}kT = \frac{1}{2}m\overline{v_x^2}$ to find the result (6.57).

6.5 Occupation Numbers and Bose and Fermi Statistics

We now develop the formalism necessary for calculating the thermodynamic properties of ideal quantum systems. The absence of interactions between the particles of an ideal gas enables us to reduce the problem of determining the energy levels E_s of the gas as a whole to determining ϵ_k, the energy levels of a single particle. Because the particles are indistinguishable, we cannot specify the microstate of each particle. Instead a microstate of an ideal gas is specified by the *occupation numbers n_k*, the number of particles in each of the single particle energies ϵ_k. If we know the value of the occupation number for each state, we can write the total energy of the system as

$$E_s = \sum_k n_k \, \epsilon_k. \tag{6.61}$$

The set of n_k completely specifies a microstate of the system. The partition function for an ideal gas can be expressed in terms of the occupation numbers as

$$Z(V, T, N) = \sum_{\{n_k\}} e^{-\beta \sum_k n_k \epsilon_k}, \tag{6.62}$$

where the occupation numbers n_k satisfy the condition

$$N = \sum_k n_k. \tag{6.63}$$

As discussed in Section 4.3.7 one of the fundamental results of relativistic quantum mechanics is that all particles can be classified into two groups. Particles with zero or integral spin such as ^{4}He are *bosons* and have wave functions that are symmetric under the exchange of any pair of particles. Particles with half-integral spin such as electrons, protons, and neutrons are *fermions* and have wave functions that are antisymmetric under particle exchange. The Bose or Fermi character of composite objects can be found by noting that composite objects that have an even number of fermions are bosons and those containing an odd number of fermions are themselves fermions.[4] For example, an atom of ^{3}He is composed of an odd number of particles: two electrons, two protons, and one neutron each of spin $\frac{1}{2}$. Hence, ^{3}He has half-integral spin making it a fermion. An atom of ^{4}He has one more neutron so there are an even number of fermions and ^{4}He is a boson. What type of particle is a hydrogen molecule, H_2?

It is remarkable that all particles fall into one of two mutually exclusive classes with different spin. It is even more remarkable that there is a connection between the spin of a particle and its statistics. Why are particles with half-integral spin fermions and particles with integral spin bosons? The answer lies in the requirements imposed by Lorentz invariance on quantum field theory. This requirement implies that the form of quantum field theory must be the same in all inertial reference frames. Although most physicists believe that the relation between spin and statistics must have a simpler explanation, no such explanation yet exists.[5]

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[4] You might have heard of the existence of Bose-like bound pairs of electrons (Cooper pairs) in what is known as the BCS theory of superconductivity. However such pairs are not composite objects in the usual sense.

[5] In spite of its fundamental importance, it is only a slight exaggeration to say that "everyone knows the spin-statistics theorem, but no one understands it."

n_1	n_2	n_3	n_4
0	1	1	1
1	0	1	1
1	1	0	1
1	1	1	0

Table 6.2: Possible states of a three particle fermion system with four single particle energy states. The quantity n_k represents the number of particles in a single particle state k. Note that we have not specified which particle is in a particular state.

The difference between fermions and bosons is specified by the possible values of n_k. For fermions we have

$$n_k = 0 \text{ or } 1. \qquad \text{(fermions)} \tag{6.64}$$

The restriction (6.64) states the Pauli exclusion principle for noninteracting particles – two identical fermions cannot be in the same single particle state. In contrast, the occupation numbers n_k for identical bosons can take any positive integer value:

$$n_k = 0, 1, 2, \cdots \qquad \text{(bosons)} \tag{6.65}$$

We will see in the following sections that the nature of the statistics of a many particle system can have a profound effect on its properties.

Example 6.1. Calculate the partition function of an ideal gas of $N = 3$ identical fermions in equilibrium with a heat bath at temperature T. Assume that each particle can be in one of four possible states with energies, $\epsilon_1, \epsilon_2, \epsilon_3$, and ϵ_4.

Solution. The possible microstates of the system are summarized in Table 6.2. The spin of the fermions is neglected. Is it possible to reduce this problem to a one body problem as we did for a noninteracting classical system?

The partition function is given by

$$Z_3 = e^{-\beta(\epsilon_2+\epsilon_3+\epsilon_4)} + e^{-\beta(\epsilon_1+\epsilon_3+\epsilon_4)} + e^{-\beta(\epsilon_1+\epsilon_2+\epsilon_4)} + e^{-\beta(\epsilon_1+\epsilon_2+\epsilon_3)}. \tag{6.66}$$

Problem 6.13. Calculate $\bar{n}_1$, the mean number of fermions in the state with energy ϵ_1, for the system in Example 6.1.

Problem 6.14. Calculate the mean energy of an ideal gas of $N = 3$ identical bosons in equilibrium with a heat bath at temperature T, assuming that each particle can be in one of three states with energies, 0, Δ, and 2Δ. Is it possible to reduce this problem to a one body problem as we did for a noninteracting classical system?

*Problem 6.15.** Consider a single particle of mass m in a one-dimensional harmonic oscillator potential given by $V(x) = \frac{1}{2}kx^2$. As we found in Example 4.4, the partition function is given by $Z_1 = e^{-x/2}/(1 - e^{-x})$, where $x = \beta\hbar\omega$.

(a) What is the partition function Z_{2d} for two noninteracting distinguishable particles in the same potential?

(b) What is the partition function $Z_{2f,S=0}$ for two noninteracting fermions in the same potential assuming the fermions have no spin?

(c) What is the partition function Z_{2b} for two noninteracting bosons in the same potential? Assume the bosons have spin zero.

*Problem 6.16. Calculate the mean energy and entropy in the four cases considered in Problem 6.15. Plot E and S as a function of T and compare the behavior of E and S in the limiting cases of $T \to 0$ and $T \to \infty$.

6.6 Distribution Functions of Ideal Bose and Fermi Gases

The calculation of the partition function for an ideal gas in the semiclassical limit was straightforward because we were able to choose a single particle as the system. This choice is not possible for an ideal gas at low temperatures where the quantum nature of the particles cannot be ignored. So we need a different strategy. The key idea is that it is possible to distinguish the set of all particles in a *given single particle state* from the particles in any other single particle state. For this reason we choose the system of interest to be the *set of all particles that are in a given single particle state*. Because the number of particles in a given quantum state varies, we need to use the grand canonical ensemble and assume that each system is coupled to a particle reservoir independently of the other single particle states.

Because we have not yet applied the grand canonical ensemble, we briefly review it here. The thermodynamic potential in the grand canonical ensemble is denoted by $\Omega(T, V, \mu)$ and is equal to $-PV$ (see (2.172)). The connection of thermodynamics to statistical mechanics is given by $\Omega = -kT \ln \mathcal{Z}$, where the grand partition function $\mathcal{Z}$ is given by

$$\mathcal{Z} = \sum_n e^{-\beta(E_n - \mu N_n)}. \tag{6.67}$$

The goal is to calculate $\mathcal{Z}$, then Ω and the pressure equation of state $-PV$ (in terms of T, V, and μ), and then determine S from the relation

$$S = -\left(\frac{\partial \Omega}{\partial T}\right)_{V,\mu}, \tag{6.68}$$

and the mean number of particles from the relation

$$\overline{N} = -\left(\frac{\partial \Omega}{\partial \mu}\right)_{T,V} \tag{6.69}$$

The probability of a particular microstate is given by

$$P_n = \frac{1}{\mathcal{Z}} e^{-\beta(E_n - \mu N_n)}. \qquad \text{(Gibbs distribution)} \tag{6.70}$$

We will use these relations in the following.

Because the system of interest is all the particles in the kth single particle state, the first step is to calculate the grand partition function $\mathcal{Z}_k$ for this system. We write the energy of the n_k particles in the kth state as $n_k \epsilon_k$ and write $\mathcal{Z}_k$ as

$$\mathcal{Z}_k = \sum_{n_k} e^{-\beta n_k(\epsilon_k - \mu)}, \tag{6.71}$$

where the sum is over the possible values of n_k. For fermions this sum is straightforward because $n_k = 0$ and 1 (see (6.64)). Hence

$$\mathcal{Z}_k = 1 + e^{-\beta(\epsilon_k - \mu)}. \tag{6.72}$$

The corresponding thermodynamic or Landau potential Ω_k is given by

$$\Omega_k = -kT \ln \mathcal{Z}_k = -kT \ln[1 + e^{-\beta(\epsilon_k - \mu)}]. \tag{6.73}$$

We use the relation $\overline{n}_k = -\partial \Omega_k / \partial \mu$ (see (6.69)) to find the mean number of particles in the kth quantum state. The result is

$$\overline{n}_k = -\frac{\partial \Omega_k}{\partial \mu} = \frac{e^{-\beta(\mu - \epsilon_k)}}{1 + e^{-\beta(\mu - \epsilon_k)}}, \tag{6.74}$$

or

$$\overline{n}_k = \frac{1}{e^{\beta(\epsilon_k - \mu)} + 1}. \qquad \text{(Fermi-Dirac distribution)} \tag{6.75}$$

The result (6.75) for the mean number of particles in the kth state is known as the *Fermi-Dirac distribution*.

The integer values of n_k are unrestricted for bosons. We write (6.71) as

$$\mathcal{Z}_k = 1 + e^{-\beta(\epsilon_k - \mu)} + e^{-2\beta(\epsilon_k - \mu)} + \cdots = \sum_{n_k=0}^{\infty} \left[e^{-\beta(\epsilon_k - \mu)} \right]^{n_k}. \tag{6.76}$$

The geometrical series in (6.76) is convergent for $e^{-\beta(\epsilon_k - \mu)} < 1$. Because this condition must be satisfied for all values of ϵ_k, we require that $e^{\beta \mu} < 1$ or

$$\mu < 0. \qquad \text{(bosons)} \tag{6.77}$$

In contrast, the chemical potential may be either positive or negative for fermions. The summation of the geometrical series in (6.76) gives

$$\mathcal{Z}_k = \frac{1}{1 - e^{-\beta(\epsilon_k - \mu)}}, \tag{6.78}$$

and hence we obtain

$$\Omega_k = kT \ln \left[1 - e^{-\beta(\epsilon_k - \mu)} \right]. \tag{6.79}$$

The mean number of particles in the kth state is given by

$$\overline{n}_k = -\frac{\partial \Omega_k}{\partial \mu} = \frac{e^{-\beta(\epsilon_k - \mu)}}{1 - e^{-\beta(\epsilon_k - \mu)}} \tag{6.80}$$

or

$$\overline{n}_k = \frac{1}{e^{\beta(\epsilon_k - \mu)} - 1}. \qquad \text{(Bose-Einstein distribution)} \qquad (6.81)$$

The form (6.81) is known as the *Bose-Einstein distribution.*

It is frequently convenient to group the Fermi-Dirac and Bose-Einstein distributions together and to write

$$\boxed{\overline{n}_k = \frac{1}{e^{\beta(\epsilon_k - \mu)} \pm 1}. \qquad \begin{cases} + \text{ Fermi-Dirac distribution} \\ - \text{ Bose-Einstein distribution} \end{cases}} \qquad (6.82)$$

The convention is that the upper sign corresponds to Fermi statistics and the lower sign to Bose statistics.

The classical limit. The Fermi-Dirac and Bose-Einstein distributions must reduce to the classical limit under the appropriate conditions. In the classical limit $\overline{n}_k \ll 1$ for all k, that is, the mean number of particles in any single particle state must be small. Hence $\epsilon^{\beta(\epsilon_k - \mu)} \gg 1$ and in this limit both the Fermi-Dirac and Bose-Einstein distributions reduce to

$$\overline{n}_k = e^{-\beta(\epsilon_k - \mu)} \qquad \text{(Maxwell-Boltzmann distribution)} \qquad (6.83)$$

This result (6.83) is known as the *Maxwell-Boltzmann distribution.*

6.7 Single Particle Density of States

If we sum (6.82) over all single particle states, we obtain the mean number of particles in the system:

$$\overline{N}(T, V, \mu) = \sum_k \overline{n}_k = \sum_k \frac{1}{e^{\beta(\epsilon_k - \mu)} \pm 1}. \qquad (6.84)$$

For a given temperature T and volume V, (6.84) is an implicit equation for the chemical potential μ in terms of the mean number of particles. That is, the chemical potential determines the mean number of particles just as the temperature determines the mean energy. Similarly, we can write the mean energy of the system as

$$\overline{E}(T, V, \mu) = \sum_k \epsilon_k \, \overline{n}_k. \qquad (6.85)$$

Because the (grand) partition function $\mathcal{Z}$ is a product, $\mathcal{Z} = \prod_k \mathcal{Z}_k$, the Landau potential for the ideal gas is given by

$$\Omega(T, V, \mu) = \sum_k \Omega_k = \mp kT \sum_k \ln \left[1 \pm e^{-\beta(\epsilon_k - \mu)} \right]. \qquad (6.86)$$

For a macroscopic system the number of particles and the energy are well defined, and we will usually replace $\overline{n}$ and $\overline{E}$ by N and E respectively.

Because we have described the microscopic states at the most fundamental level, that is, by using quantum mechanics, the macroscopic averages of interest such as (6.84), (6.85) and (6.86) involve sums rather than integrals over the microscopic states. However, because the systems of

interest are macroscopic, the volume of the system is so large that the energies of the discrete microstates are very close together and for practical purposes indistinguishable from a continuum. As usual, it is easier to do integrals than to do sums over a very large number of states and we will replace the sums in (6.84)–(6.86) by integrals. For example, we wish to write for an arbitrary function $f(\epsilon)$

$$\sum_k f(\epsilon_k) \rightarrow \int_0^\infty f(\epsilon)\, g(\epsilon) d\epsilon, \tag{6.87}$$

where $g(\epsilon)\, d\epsilon$ is the number of single particle states between ϵ and $\epsilon + d\epsilon$. The quantity $g(\epsilon)$ is known as the *density of states*, although a better term would be the density of *single* particle states.

6.7.1   Density of states in k-space

Although we already have calculated the density of states $g(\epsilon)$ for a single particle in a box (see Section 4.3), we review the calculation here to emphasize its generality and the common aspects of the calculation for blackbody radiation, elastic waves in a solid, and electron waves. For convenience, we choose the box to be a cube of linear dimension L and assume that the wave function vanishes at the faces of the cube. This condition ensures that we will obtain standing waves. The condition for a standing wave in one dimension is that the wavelength satisfies the condition

$$\lambda = \frac{2L}{n} \qquad (n = 1,\ 2,\ \ldots) \tag{6.88}$$

where n is a nonzero positive integer. It is useful to define the *wave number k* as

$$k = \frac{2\pi}{\lambda}, \tag{6.89}$$

and write the standing wave condition as $k = n\pi/L$. Because the waves in the x, y, and z directions satisfy similar conditions, we can treat the wave number as a vector whose components satisfy

$$\mathbf{k} = (n_x, n_y, n_z)\frac{\pi}{L}, \tag{6.90}$$

where n_x, n_y, n_z are positive integers. Not all values of $\mathbf{k}$ are permissible and each combination of $\{n_x, n_y, n_z\}$ corresponds to a different state. In the "number space" defined by the three perpendicular axes labeled by n_x, n_y, and n_z, the possible values of states lie at the centers of cubes of unit edge length.

Because the energy of a wave depends only on the magnitude of $\mathbf{k}$, we want to know the number of states between k and $k + dk$. As we did in Section 4.3, it is easier to first find $\Gamma(k)$, the number of states with wave number less than or equal to k. We know that the volume in n-space of a single state is unity, and hence the number of states in number space that are contained in the positive octant of a sphere of radius n is given by $\Gamma(n) = \frac{1}{8}(4\pi n^3/3)$, where $n^2 = n_x^2 + n_y^2 + n_z^2$. Because $\mathbf{k} = \pi\mathbf{n}/L$, the number of states with wave vector less than or equal to k is

$$\Gamma(k) = \frac{1}{8}\frac{4\pi k^3/3}{(\pi/L)^3}. \tag{6.91}$$

If we use the relation

$$g(k)\,dk = \Gamma(k + dk) - \Gamma(k) = \frac{d\Gamma(k)}{dk}\,dk, \tag{6.92}$$

we obtain

$$g(k)\,dk = V\frac{k^2\,dk}{2\pi^2}, \tag{6.93}$$

where the volume $V = L^3$. Equation (6.93) gives the density of states in k-space between k and $k + dk$.

Although we obtained the result (6.93) for a cube, the result is independent of the shape of the enclosure and the nature of the boundary conditions (see Problem 6.58). That is, if the box is sufficiently large, the surface effects introduced by the box do not affect the physical properties of the system.

Problem 6.17. Find the form of the density of states in k-space for standing waves in a two-dimensional and in a one-dimensional box.

6.7.2   Photons

The result (6.93) for the density of states in k-space holds for any wave in a three-dimensional enclosure. Now we wish to find the number of states $g(\epsilon)\,d\epsilon$ as a function of the energy ϵ. For simplicity, we adopt the same symbol to represent the density of states in k-space and in ϵ-space because the interpretation of g will be clear from the context.

The dependence of $g(\epsilon)$ on ϵ depends on how the energy depends on k. For electromagnetic waves of frequency ν, we know that $\lambda\nu = c$, $\omega = 2\pi\nu$, and $k = 2\pi/\lambda$. Hence, $\omega = 2\pi c/\lambda$ or

$$\omega = ck. \tag{6.94}$$

The energy ϵ of a photon of frequency ω is

$$\epsilon = \hbar\omega = \hbar ck. \tag{6.95}$$

Because $k = \epsilon/\hbar c$, we find that

$$g(\epsilon)\,d\epsilon = V\frac{\epsilon^2}{2\pi^2\hbar^3 c^3}\,d\epsilon. \tag{6.96}$$

The result (6.96) requires one modification. The state of an electromagnetic wave or photon depends not only on its wave vector or momentum, but also on its polarization. There are two mutually perpendicular directions of polarization (right circularly polarized and left circularly polarized) for each electromagnetic wave of wave number $\mathbf{k}$.[6] Thus the number of photon states in which the photon has a energy in the range ϵ to $\epsilon + d\epsilon$ is given by

$$g(\epsilon)\,d\epsilon = V\frac{\epsilon^2\,d\epsilon}{\pi^2\hbar^3 c^3}. \qquad \text{(photons)} \tag{6.97}$$

We will use (6.97) frequently in the following sections.

---

[6]In the language of quantum mechanics we say that the photon has spin one and two helicity states. The fact that the photon has spin $S = 1$ and two helicity states rather than $(2S + 1) = 3$ states is a consequence of special relativity for massless particles.

6.7.3 Electrons

For a nonrelativistic particle of mass m, we know that

$$\epsilon = \frac{p^2}{2m}. \tag{6.98}$$

From the relations $p = h/\lambda$ and $k = 2\pi/\lambda$, we find that the momentum p of a particle is related to its wave vector k by $p = \hbar k$. Hence, the energy can be expressed as

$$\epsilon = \frac{\hbar^2 k^2}{2m}, \tag{6.99}$$

and

$$d\epsilon = \frac{\hbar^2 k}{m} dk. \tag{6.100}$$

If we use (6.93) and the relations (6.99) and (6.100), we find that the number of states in the interval ϵ to $\epsilon + d\epsilon$ is given by

$$g(\epsilon)\, d\epsilon = n_s \frac{V}{4\pi^2 \hbar^3} (2m)^{3/2}\, \epsilon^{1/2}\, d\epsilon. \tag{6.101}$$

We have included a factor of n_s, the number of spin states for a given value of k or ϵ. Because electrons have spin $1/2$, $n_s = 2$, and we can write (6.101) as

$$g(\epsilon)\, d\epsilon = \frac{V}{2\pi^2 \hbar^3} (2m)^{3/2}\, \epsilon^{1/2}\, d\epsilon. \qquad \text{(electrons)} \tag{6.102}$$

Because it is common to choose units such that $\hbar = 1$, we will express most of our results in the remainder of this chapter in terms of $\hbar$ instead of h.

Problem 6.18. Calculate the energy density of states for a nonrelativistic particle of mass m in $d = 1$ and $d = 2$ spatial dimensions (see Problem 6.17). Sketch $g(\epsilon)$ on one graph for $d = 1$, 2, and 3 and comment on the dependence of $g(\epsilon)$ on ϵ for different spatial dimensions.

Problem 6.19. Calculate the energy density of states for a relativistic particle of rest mass m for which $\epsilon^2 = p^2 c^2 + m^2 c^4$.

Problem 6.20. The relation between the energy and equation of state for an ideal gas

The mean energy E is given by

$$E = \int_0^\infty \epsilon\, \overline{n}(\epsilon)\, g(\epsilon)\, d\epsilon \tag{6.103a}$$

$$= n_s \frac{V}{4\pi^2 \hbar^3} (2m)^{3/2} \int_0^\infty \frac{\epsilon^{3/2} d\epsilon}{e^{\beta(\epsilon - \mu)} \pm 1}. \tag{6.103b}$$

Use (6.86) for the Landau potential and (6.101) for the density of states of nonrelativistic particles in three dimensions to show that Ω can be expressed as

$$\Omega = \mp kT \int_0^\infty g(\epsilon) \, \ln[1 \pm e^{-\beta(\epsilon-\mu)}] \, d\epsilon, \tag{6.104a}$$

$$= \mp kT \frac{n_s V}{4\pi^2 \hbar^3} (2m)^{3/2} \int_0^\infty \epsilon^{1/2} \ln[1 \pm e^{-\beta(\epsilon-\mu)}] \, d\epsilon. \tag{6.104b}$$

Integrate (6.104b) by parts with $u = \ln[1 \pm e^{-\beta(\epsilon-\mu)}]$ and $dv = \epsilon^{1/2} \, d\epsilon$ and show that

$$\Omega = -\frac{2}{3} n_s \frac{V}{4\pi^2 \hbar^3} (2m)^{3/2} \int_0^\infty \frac{\epsilon^{3/2} \, d\epsilon}{e^{\beta(\epsilon-\mu)} \pm 1}. \tag{6.105}$$

The form (6.103b) for E is the same as the general result (6.105) for Ω except for the factor of $-\frac{2}{3}$. Because $\Omega = -PV$ (see (2.172)), we obtain

$$PV = \frac{2}{3} E. \tag{6.106}$$

The relation (6.106) is exact and holds for an ideal gas with any statistics at any temperature T, and depends only on the nonrelativistic relation, $\epsilon = p^2/2m$.

Problem 6.21. The relation between the energy and equation of state for photons

Use similar considerations as in Problem 6.20 to show that for photons:

$$PV = \frac{1}{3} E. \tag{6.107}$$

Equation (6.107) holds at any temperature and is consistent with Maxwell's equations which implies that the pressure due to an electromagnetic wave is related to the energy density by $P = u(T)/3$.

6.7.4 Distribution of speeds

In Section 6.4 we found that the distribution of velocities in a classical system of particles was a Gaussian and given by (6.57). To determine the distribution of speeds we need to know the number of states between v and $v + \Delta v$. As we discussed in Section 6.7.1 this number is $4\pi(v + \Delta v)^3/3 - 4\pi v^3/3 =\rightarrow 4\pi v^2 \Delta v$ in the limit $\Delta v \rightarrow 0$. Hence, the probability that a particle has a speed between v and $v + dv$ is given by

$$f(v)dv = 4\pi A v^2 e^{-mv^2/2kT} dv, \tag{6.108}$$

where A is a normalization constant which we calculate in Problem 6.22.

Problem 6.22. Maxwell speed distribution

(a) Compare the form of the Maxwell speed distribution (6.108) with the form of the Maxwell velocity (6.93).

(b) Use the fact that $\int_0^\infty f(v)\, dv = 1$ to calculate A and show that

$$f(v)dv = 4\pi v^2 \left(\frac{m}{2\pi kT}\right)^{3/2} e^{-mv^2/2kT} dv. \qquad \text{(Maxwell speed distribution)} \qquad (6.109)$$

(c) Calculate the mean speed $\bar{v}$, the most probable speed $\tilde{v}$, and the root-mean square speed v_{rms} and discuss their relative magnitudes.

(d) Make the change of variables $u = v/\sqrt{(2kT/m)}$ and show that

$$f(v)dv = f(u)du = (4/\sqrt{\pi})u^2 e^{-u^2} du, \qquad (6.110)$$

where we have again used same the same notation for two different, but physically related probability densities. The (dimensionless) speed probability density $f(u)$ is shown in Figure 6.2.
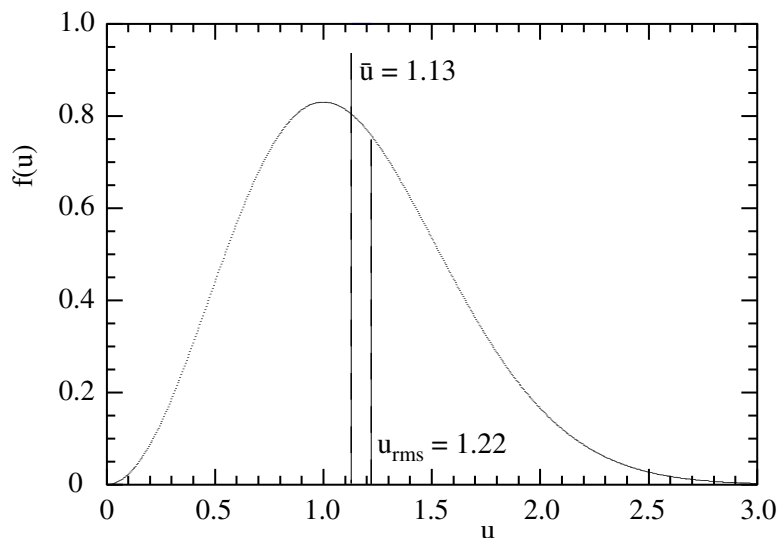
Figure 6.2: The probability density $f(u) = 4/\sqrt{\pi}u^2 e^{-u^2}$ that a particle has a speed u. Note the difference between the most probable speed $\tilde{u} = 1$, the mean speed $\bar{u} \approx 1.13$, and the root-mean-square speed $u_{\text{rms}} \approx 1.22$ in units of $(2kT/m)^{1/2}$.

6.8 The Equation of State of an Ideal Classical Gas

We have already seen how to obtain the equation of state and other thermodynamic quantities for the ideal classical gas in the microcanonical ensemble (fixed E, T, and N) and in the canonical ensemble (fixed T, V, and N). We now discuss how to use the grand canonical ensemble (fixed T, V, and μ) to find the analogous quantities under conditions for which the Maxwell-Boltzmann

distribution is applicable. The calculation in the grand canonical ensemble will automatically satisfy the condition that the particles are indistinguishable. For simplicity, we will assume that the particles are spinless.

As an example, we first compute the chemical potential from the condition that the mean number of particles is given by $\overline{N}$. If we use the Maxwell-distribution distribution (6.83) and the density of states (6.102) for spinless particles of mass m, we obtain

$$\overline{N} = \sum_k \overline{n}_k \to \int_0^\infty \overline{n}(\epsilon)\, g(\epsilon)\, d\epsilon \tag{6.111a}$$

$$= \frac{V}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} \int_0^\infty e^{-\beta(\epsilon-\mu)}\, \epsilon^{1/2}\, d\epsilon. \tag{6.111b}$$

We make the change of variables $x = \beta\epsilon$ and write (6.111b) as

$$\overline{N} = \frac{V}{4\pi^2}\left(\frac{2m}{\hbar^2\beta}\right)^{3/2} e^{\beta\mu} \int_0^\infty e^{-x}\, x^{1/2}\, dx. \tag{6.112}$$

The integral in (6.112) can be done analytically (make the change of variables $x = y^2$) and has the value $\pi^{\frac{1}{2}}/2$ (see Appendix A). Hence, the mean number of particles is given by

$$\overline{N}(T,V,\mu) = V\left(\frac{m}{2\pi\hbar^2\beta}\right)^{3/2} e^{\beta\mu}. \tag{6.113}$$

Because we cannot easily measure μ, we are not satisfied with knowing the function $\overline{N}(T,V,\mu)$. Instead, we can find the value of μ that yields the desired value of $\overline{N}$ by solving (6.113) for the chemical potential:

$$\mu = kT \ln\left[\frac{\overline{N}}{V}\left(\frac{2\pi\hbar^2\beta}{m}\right)^{3/2}\right]. \tag{6.114}$$

What is the difference, if any, between (6.113) and the result (6.31) for μ found in the canonical ensemble?

Problem 6.23. The chemical potential

(a) Estimate the chemical potential of a monatomic ideal classical gas at room temperature and show that $\mu \ll 0$.

(b) Show that $\overline{N}$ can be expressed as

$$\overline{N} = \frac{V}{\lambda^3}\, e^{\beta\mu}, \tag{6.115}$$

and hence

$$\mu(T,V) = -kT \ln\frac{1}{\rho\lambda^3}, \tag{6.116}$$

where $\rho = \overline{N}/V$.

(c) In Section 6.2 we argued that the semiclassical limit $\lambda \ll \rho^{-1/3}$ (see (6.1)) implies that $\overline{n}_k \ll 1$, that is, the mean number of particles that are in any single particle energy state is very small. Use the expression (6.116) for μ and (6.83) for $\overline{n}_k$ to show that the condition $\overline{n}_k \ll 1$ implies that $\lambda \ll \rho^{-1/3}$.

As we saw in Section 2.21, the chemical potential is the change in each of the thermodynamic potentials when one particle is added. It might be expected that $\mu > 0$, because it should cost energy to add a particle. But because the particles do not interact, perhaps $\mu = 0$? So why is $\mu \ll 0$ for an ideal classical gas? The reason is that we have to determine how much energy must be added to the system to keep the entropy and the volume fixed. Suppose that we add one particle with zero kinetic energy. Because the gas is ideal, there is no potential energy of interaction. However, because V is fixed, the addition of an extra particle leads to an increase in S. (S is an increasing function of N and V.) Because S also is an increasing function of the total energy, we have to reduce the energy.

The calculation of $\overline{N}(T, V, \mu)$ leading to (6.113) was not necessary because we can calculate the equation of state and all the thermodynamic quantities from the Landau potential Ω. We calculate Ω from (6.86) by noting that $e^{\beta\mu} \ll 1$ and approximating the argument of the logarithm by $\ln(1 \pm x) \approx \pm x$. We find that

$$\Omega = \mp kT \sum_k \ln\left[1 \pm e^{-\beta(\epsilon_k - \mu)}\right] \tag{6.117a}$$

$$\to -kT \sum_k e^{-\beta(\epsilon_k - \mu)}. \qquad \text{(semiclassical limit)} \tag{6.117b}$$

As expected, the form of Ω in (6.117b) is independent of whether we started with Bose or Fermi statistics.

As usual, we replace the sum over the single particle states by an integral over the density of states and find

$$\Omega = -kT\, e^{\beta\mu} \int_0^\infty g(\epsilon)\, e^{-\beta\epsilon}\, d\epsilon \tag{6.118a}$$

$$= -kT\, \frac{V}{4\pi^2 \hbar^3} \left(\frac{2m}{\beta}\right)^{3/2} e^{\beta\mu} \int_0^\infty x^{1/2}\, e^{-x}\, dx \tag{6.118b}$$

$$= -k\frac{V}{\beta^{5/2}} \left(\frac{m}{2\pi\hbar^2}\right)^{3/2} e^{\beta\mu}. \tag{6.118c}$$

If we substitute $\lambda = (2\pi\beta\hbar^2/m)^{1/2}$, we find

$$\Omega = -kT\frac{V}{\lambda^3}\, e^{\beta\mu}. \tag{6.119}$$

From the relation $\Omega = -PV$ (see (2.172)), we obtain

$$P = \frac{kT}{\lambda^3}\, e^{\beta\mu}. \tag{6.120}$$

If we use the thermodynamic relation (6.69), we obtain

$$\overline{N} = -\left.\frac{\partial\Omega}{\partial\mu}\right|_{V,T} = \frac{V}{\lambda^3}\, e^{\beta\mu}. \tag{6.121}$$

The classical equation of state, $PV = \overline{N}kT$, is obtained by using (6.121) to eliminate μ. The simplest way of finding the energy is to use the relation (6.106).

We can find the entropy $S(T, V, \mu)$ using (6.119) and (6.68):

$$S(T, V, \mu) = -\frac{\partial \Omega}{\partial T}\Big|_{V,\mu} = k\beta^2 \frac{\partial \Omega}{\partial \beta} \tag{6.122a}$$

$$= Vk\beta^2 \Big[\frac{5}{2\beta^{7/2}} - \frac{\mu}{\beta^{6/2}} \Big] \Big(\frac{m}{2\pi\hbar^2} \Big)^{3/2} e^{\beta\mu}. \tag{6.122b}$$

If we eliminate μ from (6.122b), we obtain the Sackur-Tetrode expression for the entropy of an ideal gas:

$$S(T, V, N) = Nk \Big[\frac{5}{2} - \ln \frac{N}{V} - \ln \Big(\frac{2\pi\hbar^2}{mkT} \Big)^{3/2} \Big]. \tag{6.123}$$

We have written N rather than $\overline{N}$ in (6.123). Note that we did not have to introduce any extra factors of $N!$ as we did in Section 6.2, because we already correctly counted the number of microstates.

Problem 6.24. Complete the missing steps and derive the ideal gas equations of state.

6.9 Blackbody Radiation

We can regard electromagnetic radiation as equivalent to a system of noninteracting bosons (photons), each of which has an energy $h\nu$, where ν is the frequency of the radiation. If the radiation is in an enclosure, equilibrium will be established and maintained by the interactions of the photons with the atoms of the wall in the enclosure. Because the atoms emit and absorb photons, the total number of photons is not conserved.

One of the important observations that led to the development of quantum theory was the consideration of the frequency spectrum of electromagnetic radiation from a blackbody. If a body in thermal equilibrium emits electromagnetic radiation, then this radiation is described as blackbody radiation and the object is said to be a blackbody. This statement does not mean that the body is actually black. The word "black" indicates that the radiation is perfectly absorbed and re-radiated by the object. The spectrum of light radiated by such an idealized black body is described by a universal spectrum called the Planck spectrum, which we will derive in the following (see (6.131)). The nature of the spectrum depends only on the absolute temperature T of the radiation.

The physical system that most closely gives the spectrum of a black body is the spectrum of the cosmic microwave background.[7] The observed cosmic microwave background spectrum fits the theoretical spectrum of a blackbody better than the best blackbody spectrum that we can make in a laboratory! In contrast, a piece of hot, glowing firewood is not really in thermal equilibrium,

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[7]The universe is filled with electromagnetic radiation with a distribution of frequencies given by (6.131) with $T \approx 2.73$ K. The existence of this background radiation is a remnant from a time when the universe was composed primarily of electrons and protons at a temperature of about 4000 K. This plasma of electrons and protons interacted strongly with the electromagnetic radiation over a wide range of frequencies, so that the matter and the radiation reached thermal equilibrium. By the time that the universe had cooled to 3000 K, the matter was primarily in the form of atomic hydrogen, which interacts with radiation only at the frequencies of the hydrogen spectral lines. As a result most of the radiation energy was effectively decoupled from matter. Electromagnetic radiation, such as starlight, radiated by matter since the decoupling, is superimposed on the cosmic blackbody radiation. More information about the cosmic microwave background can be found at `<www.astro.ubc.ca/people/scott/cmb.html>` and at many other sites.

and the spectrum of glowing embers is only a crude approximation to blackbody spectrum. The existence of the cosmic microwave background spectrum and its fit to the blackbody spectrum is compelling evidence that the universe experienced a Big Bang.

We can derive the Planck radiation law using either the canonical or grand canonical ensemble because the photons are continuously absorbed and emitted by the walls of the container and hence their number is not conserved. Let us first consider the canonical ensemble, and consider a gas of photons in equilibrium with a heat bath at temperature T. The total energy of the system is given by $E = n_1\epsilon_1 + n_2\epsilon_2 + \ldots$, where n_k is the number of photons with energy ϵ_k. Because there is no constraint on the total number of photons, we can write the canonical partition function as

$$Z(T,V) = \sum_s e^{-\beta E_s} = \sum_{n_1,n_2,\ldots=0}^{\infty} e^{-\beta(n_1\epsilon_1+n_2\epsilon_2+\ldots)} \tag{6.124a}$$

$$= \sum_{n_1=0}^{\infty} e^{-\beta n_1\epsilon_1} \sum_{n_2=0}^{\infty} e^{-\beta n_2\epsilon_2} \ldots \tag{6.124b}$$

$$= \prod_k \Big[\sum_{n_k=0}^{\infty} e^{-\beta n_k\epsilon_k} \Big]. \tag{6.124c}$$

The lack of a constraint means that we can do the sum over each occupation number separately. Because the term in brackets in (6.124c) is a geometrical series, we obtain

$$Z(T,V) = \prod_k \Big[\frac{1}{1-e^{-\beta\epsilon_k}} \Big]. \qquad \text{(photon gas)} \tag{6.125}$$

A quantity of particular interest is the mean number of photons in state k. In the canonical ensemble we have

$$\overline{n}_k = \frac{\sum_s n_k\, e^{-\beta E_s}}{\sum_s e^{-\beta E_s}} = \frac{\sum_{n_1,n_2,\ldots} n_k\, e^{-\beta(n_1\epsilon_1+n_2\epsilon_2+\ldots+n_k\epsilon_k+\ldots)}}{Z} \tag{6.126a}$$

$$= \frac{1}{Z} \Big[\frac{\partial}{\partial(-\beta\epsilon_k)} \sum_{n_1,n_2,\ldots} e^{-\beta(n_1\epsilon_1+n_2\epsilon_2+\cdots+n_k\epsilon_k+\ldots)} \Big] \tag{6.126b}$$

$$= \frac{\partial \ln Z}{\partial(-\beta\epsilon_k)}. \tag{6.126c}$$

Because the logarithm of a product of terms equals the sum of the logarithms of each term, we have from (6.125) and (6.126c)indexblackbody radiation!Planck distribution

$$\overline{n}_k = \frac{\partial}{\partial(-\beta\epsilon_k)} \Big[\sum_{k'} -\ln\left(1-e^{-\beta\epsilon_{k'}}\right) \Big] \tag{6.127a}$$

$$= \frac{e^{-\beta\epsilon_k}}{1-e^{-\beta\epsilon_k}}, \tag{6.127b}$$

or

$$\overline{n}_k = \frac{1}{e^{\beta\epsilon_k}-1}. \qquad \text{(Planck distribution)} \tag{6.127c}$$

The result (6.127c) can be understood by simple considerations. As we have mentioned, equilibrium is established and maintained by the interactions between the photons and the atoms of the wall in the enclosure. The number N of photons in the cavity cannot be imposed externally on the system and is fixed by the temperature T of the walls and the volume V enclosed. Hence, the free energy F for photons cannot depend on N because the latter is not a thermodynamic variable, and we have $\mu = \partial F/\partial N = 0$. If we substitute $\mu = 0$ into the general result (6.81) for the Bose-Einstein distribution, we find that the mean number of photons in state k is given by

$$\overline{n}_k = \frac{1}{e^{\beta h\nu} - 1}, \tag{6.128}$$

in agreement with (6.127c). That is, the photons in blackbody radiation are bosons whose chemical potential is zero.

The role of the chemical potential is to set the mean number of particles, just as the temperature sets the mean energy. Because the chemical potential has no role to play for a system of photons in blackbody radiation, we could have more simply started with (6.81) for $\overline{n}_k$ in the grand canonical ensemble and set $\mu = 0$.

Planck's theory of blackbody radiation follows from the form of the density of states for photons found in (6.97). The number of photons with energy in the range ϵ to $\epsilon + d\epsilon$ is given by

$$N(\epsilon)\, d\epsilon = \overline{n}(\epsilon)g(\epsilon)\, d\epsilon = \frac{V}{\pi^2 \hbar^3 c^3} \frac{\epsilon^2\, d\epsilon}{e^{\beta\epsilon} - 1}. \tag{6.129}$$

For simplicity, we have ignored the polarization of the electromagnetic radiation, and hence the spin of the photons. If we substitute $\epsilon = h\nu$ in the right-hand side of (6.129), we find that the number of photons in the frequency range ν to $\nu + d\nu$ is given by

$$N(\nu)\, d\nu = \frac{8\pi V}{c^3} \frac{\nu^2\, d\nu}{e^{\beta h\nu} - 1}. \tag{6.130}$$

The distribution of radiated energy is obtained by multiplying (6.130) by $h\nu$:

$$E(\nu)d\nu = h\nu N(\nu)\, d\nu = \frac{8\pi h V \nu^3}{c^3} \frac{d\nu}{e^{\beta h\nu} - 1}. \tag{6.131}$$

Equation (6.131) gives the energy radiated by a blackbody of volume V in the frequency range between ν and $\nu + d\nu$. The energy per unit volume $u(\nu)$ is given by

$$u(\nu) = \frac{8\pi h\nu^3}{c^3} \frac{1}{e^{\beta h\nu} - 1}. \qquad \text{(Planck's radiation law)} \tag{6.132}$$

We can change variables to $\epsilon = h\nu$ and write the energy density as

$$u(\epsilon) = \frac{8\pi}{(hc)^3} \frac{\epsilon^3}{e^{\epsilon/kT} - 1}. \tag{6.133}$$

The temperature dependence of $u(\epsilon)$ is shown in Figure 6.3.
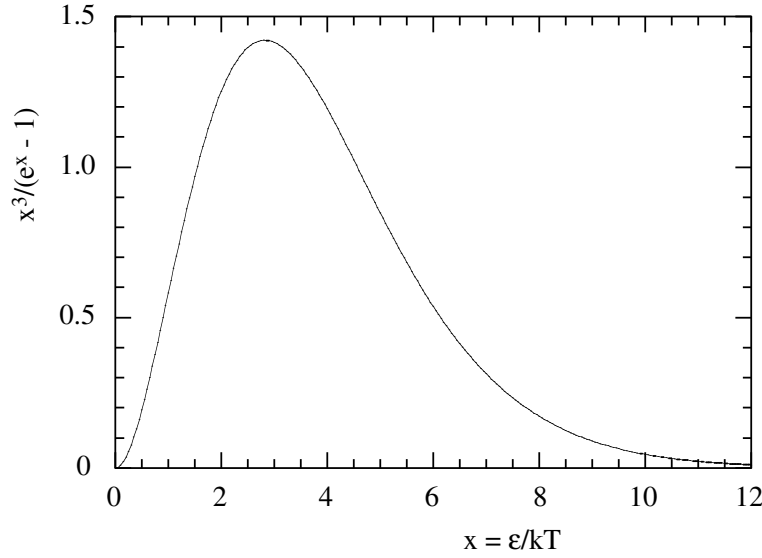
Figure 6.3: The Planck spectrum as a function of $x = \epsilon/kT$. The area under any portion of the curve multiplied by $8\pi(kT)^4/(hc)^3$ gives the energy of electromagnetic radiation within the corresponding energy or frequency range.

Problem 6.25. Wien's displacement law

The maximum of $u(\nu)$ shifts to higher frequencies with increasing temperature. Show that the maximum of u can be found by solving the equation

$$(3 - x)e^x = 3, \tag{6.134}$$

where $x = \beta h\nu_{\max}$. Solve (6.134) numerically for x and show that

$$\frac{h\nu_{\max}}{kT} = 2.822. \qquad \text{(Wien's displacement law)} \tag{6.135}$$

Problem 6.26. Derivation of the Rayleigh-Jeans and Wien's laws

(a) Use (6.132) to find the energy emitted by a blackbody at a wavelength between λ and $\lambda + d\lambda$.

(b) Determine the limiting behavior of your result in part a for long wavelengths. This limit is called the Rayleigh-Jeans law and is given by

$$u(\lambda)d\lambda = \frac{8\pi kT}{\lambda^4}d\lambda. \tag{6.136}$$

Does this form involve Planck's constant? The result in (6.136) was originally derived from purely classical considerations.

(c) Classical theory predicts the so-called ultraviolet catastrophe, namely that an infinite amount of energy is radiated at high frequencies. or short wavelengths. Explain how (6.136) would give an infinite result for the total energy that would be radiated.

(d) Determine the limiting behavior for short wavelengths. This behavior is called Wien's law.

Problem 6.27. Thermodynamic functions of blackbody radiation

Use the various thermodynamic relations to show that

$$E = V \int_0^\infty u(\nu)\, d\nu = \frac{4\sigma}{c} V T^4. \qquad \text{(Stefan-Boltzmann law)} \tag{6.137a}$$

$$F = -\frac{4\sigma}{3c} V T^4. \tag{6.137b}$$

$$S = \frac{16\sigma}{3c} V T^3. \tag{6.137c}$$

$$P = \frac{4\sigma}{3c} T^4 = \frac{1}{3}\frac{E}{V}. \tag{6.137d}$$

$$G = F + PV = 0. \tag{6.137e}$$

The free energy F in (6.137b) can be calculated from Z starting from (6.125) and using (6.97). The Stefan-Boltzmann constant σ is given by

$$\sigma = \frac{2\pi^5 k^4}{15 h^3 c^2}. \tag{6.138}$$

The integral

$$\int_0^\infty \frac{x^3\, dx}{e^x - 1} = \frac{\pi^4}{15}. \tag{6.139}$$

is evaluated in Appendix A.

The relation (6.137a) between the total energy and T is known as the Stefan-Boltzmann law. Because $G = N\mu$ and $N \neq 0$, we again find that the chemical potential equals zero for an ideal gas of photons.

Problem 6.28. Relations for blackbody radiation

(a) What is the relation between E and PV for blackbody radiation? Why is it not the same as (6.106) (see Problem 6.21)?

(b) Note that for a quasistatic adiabatic expansion or compression of the photon gas, the product $VT^3 = \text{constant}$. Why? How are P and V related for a quasistatic adiabatic process?

Problem 6.29. Show that the total mean number of photons in blackbody radiation is given by

$$N = \frac{V}{\pi^2 c^3} \int_0^\infty \frac{\omega^2 d\omega}{e^{\hbar\omega/kT} - 1} = \frac{V(kT)^3}{\pi^2 c^3 \hbar^3} \int_0^\infty \frac{x^2 dx}{e^x - 1}. \tag{6.140}$$

The integral in (6.140) can be expressed in terms of known functions (see Appendix A). The result is

$$\int_0^\infty \frac{x^2 dx}{e^x - 1} = 2 \times 1.202. \tag{6.141}$$

Hence

$$N = 0.244 V \left(\frac{kT}{\hbar c}\right)^3. \tag{6.142}$$

6.10 Ideal Fermi Gas

The properties of metals are dominated by the behavior of the conduction electrons. Given that there are Coulomb interactions between the electrons as well as interactions between the electrons and the positive ions of the lattice, it is remarkable that the *free electron model* in which the electrons are treated as an ideal gas of fermions near zero temperature is an excellent model of the conduction electrons in a metal under most circumstances.[8] In the following, we investigate the properties of an ideal Fermi gas and briefly discuss its applicability as a model of electrons in metals.

As we will see in Problem 6.30, the thermal de Broglie wavelength of the electrons in a typical metal is much larger than the mean interparticle spacing, and hence we must treat the electrons using Fermi statistics. When an ideal gas is dominated by quantum mechanical effects, it is said to be *degenerate*.

6.10.1 Ground-state properties

We first discuss the noninteracting Fermi gas at $T = 0$. From (6.75) we see that the zero temperature limit ($\beta \to \infty$) of the Fermi-Dirac distribution is

$$\overline{n}(\epsilon) = \begin{cases} 1 & \text{for } \epsilon < \mu \\ 0 & \text{for } \epsilon > \mu. \end{cases} \tag{6.143}$$

That is, all states whose energies are below the chemical potential are occupied, and all states whose energies are above the chemical potential are unoccupied. The Fermi distribution at $T = 0$ is shown in Figure 6.4.

The consequences of (6.143) are easy to understand. At $T = 0$, the system is in its *ground state*, and the particles are distributed among the single particle states so that the total energy of the gas is a minimum. Because we may place no more than one particle in each state, we need to construct the ground state of the system by adding a particle, one at a time, into the lowest available energy state until we have placed all the particles. To find the value of $\mu(T = 0)$, we write

$$N = \int_0^\infty \overline{n}(\epsilon) g(\epsilon) \, d\epsilon \xrightarrow[T \to 0]{} \int_0^{\mu(T=0)} g(\epsilon) \, d\epsilon = V \int_0^{\mu(T=0)} \frac{(2m)^{3/2}}{2\pi^2 \hbar^3} \epsilon^{1/2} \, d\epsilon. \tag{6.144}$$

We have substituted the electron density of states (6.102) in (6.144). The chemical potential at $T = 0$ is determined by requiring the integral to give the desired number of particles N. Because the value of the chemical potential at $T = 0$ will have special importance, it is common to denote it by ϵ_F:

$$\epsilon_F \equiv \mu(T = 0), \tag{6.145}$$

where ϵ_F, the energy of the highest occupied state, is called the *Fermi energy*.

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[8]The idea that a system of interacting electrons at low temperatures can be understood as a noninteracting gas of quasiparticles is called Fermi liquid theory and is due to Lev D. Landau (1908–1968), the same Landau for whom we named the thermodynamic potential in the grand canonical ensemble. Landau worked in many fields including low temperature physics, atomic and nuclear physics, condensed matter physics, and plasma physics. He was awarded the 1962 Nobel Prize for Physics for his work on superfluidity.
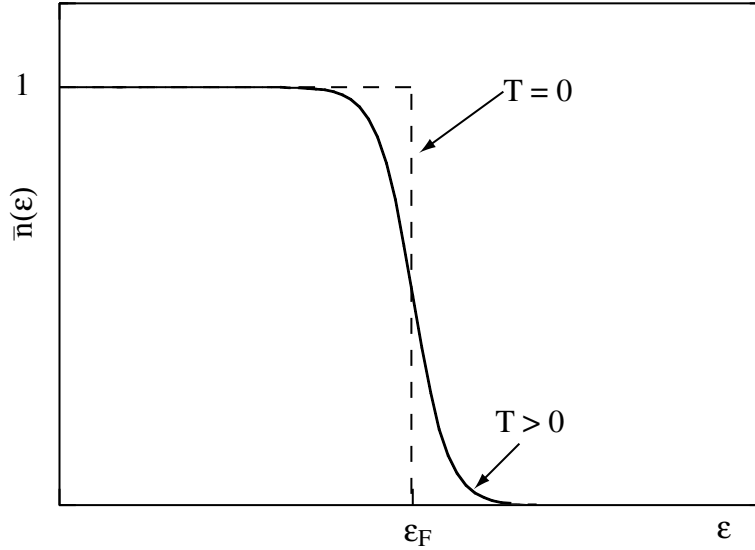
Figure 6.4: The Fermi-Dirac distribution at $T = 0$ (dotted line) and $T \ll T_F$ (solid line). The form of $\overline{n}(\epsilon)$ for $T > 0$ is based on the assumption that μ is unchanged for $T \ll T_F$. Also note that the area under the dotted line ($\overline{n}(\epsilon)$ at $T = 0$) is approximately equal to the area under the solid line ($\overline{n}(\epsilon)$ for $T \ll T_F$).

The integral on the right-hand side of (6.144) gives

$$N = \frac{V}{3\pi^2}\left(\frac{2m\epsilon_F}{\hbar^2}\right)^{3/2}. \tag{6.146}$$

From (6.146) we have that

$$\epsilon_F = \frac{\hbar^2}{2m}(3\pi^2\rho)^{2/3}, \qquad \text{(Fermi energy)} \tag{6.147}$$

where the density $\rho = N/V$. It is convenient to $\epsilon_F = p_F^2/2m$ where p_F is known as the *Fermi momentum*. It follows that the Fermi momentum p_F is given by

$$p_F = (3\pi^2\rho)^{1/3}\hbar. \qquad \text{(Fermi momentum)} \tag{6.148}$$

Note that the Fermi momentum can be estimated by using the de Broglie relation $p = h/\lambda$ and taking $\lambda \sim \rho^{-1/3}$, the mean distance between particles. That is, the particles are "localized" within a distance of order $\rho^{-1/3}$.

At $T = 0$ all the states with momentum less that p_F are occupied and all the states above this momentum are unoccupied. The boundary in momentum space between occupied and unoccupied states at $T = 0$ is called the *Fermi surface*. For an ideal Fermi gas, the Fermi surface is the surface of a sphere with radius p_F.

The chemical potential at $T = 0$ equals ϵ_F and is positive. In contrast, in Section 6.8 we argued in that μ should be less than zero for an ideal classical gas, because we have to subtract

energy to keep the entropy from increasing when we add a particle to the system. However, this argument depends on the possibility of adding a particle with zero energy. In a Fermi system at $T = 0$, no particle can be added with energy less than $\mu(T = 0)$, and hence $\mu(T = 0) > 0$.

We will find it convenient in the following to introduce a characteristic temperature, the Fermi temperature T_F, by

$$T_F = \epsilon_F/k. \tag{6.149}$$

The order of magnitude of T_F for typical metals is given in Table 6.3.

A direct consequence of the fact that the density of states in three dimensions is proportional to $\epsilon^{1/2}$ is that the mean energy per particle at $T = 0$ is $3\epsilon_F/5$:

$$\frac{\overline{E}}{N} = \frac{\int_0^{\epsilon_F} \epsilon\, g(\epsilon)\, d\epsilon}{\int_0^{\epsilon_F} g(\epsilon)\, d\epsilon} = \frac{\int_0^{\epsilon_F} \epsilon^{3/2} d\epsilon}{\int_0^{\epsilon_F} \epsilon^{1/2} d\epsilon} \tag{6.150a}$$

$$= \frac{\frac{2}{5}\epsilon_F^{5/2}}{\frac{2}{3}\epsilon_F^{3/2}} = \frac{3}{5}\epsilon_F. \tag{6.150b}$$

The total energy is given by

$$E = \frac{3}{5}N\epsilon_F = \frac{3}{5}N(3\pi^2)^{2/3}\frac{\hbar^2}{2m}\rho^{2/3}. \tag{6.151}$$

The pressure can be immediately found from the general relation $PV = 2E/3$ (see (6.106)) for an noninteracting, nonrelativistic gas at any temperature. Alternatively, the pressure can be found either from the relation

$$P = -\frac{\partial F}{\partial V} = \frac{2}{3}\frac{E}{V}, \tag{6.152}$$

because the the free energy is equal to the total energy at $T = 0$, or from the Landau potential $\Omega = -PV$ as discussed in Problem 6.31. The result is that the pressure at $T = 0$ is given by

$$P = \frac{2}{5}\rho\epsilon_F. \tag{6.153}$$

The fact that the pressure is nonzero even at zero temperature is a consequence of the Pauli exclusion principle, which allows only one particle to have zero momentum (two electrons if the spin is considered). All other particles have finite momentum and hence give rise to a zero-point pressure.

One way to understand the relation (6.153) is to recall the classical pressure equation of state, $P = \rho kT$. At $T = 0$ we can effectively replace T by the Fermi temperature T_F. Then $P = \rho kT \to \rho kT_F = \rho\epsilon_F$, which is the same as (6.153) except for a numerical factor.

Problem 6.30. Order of magnitude estimates

(a) Compare the values of T_F in Table 6.3 to room temperature.

(b) Given the data in Table 6.3 verify that the electron density for Li and Cu is $\rho = 4.7 \times 10^{28}\,\text{m}^{-3}$ and $\rho = 8.6 \times 10^{28}\,\text{m}^{-3}$, respectively.

element	ϵ_F (eV)	T_F (10^4 K)
Li	4.7	5.5
Na	3.2	3.8
Al	11.7	13.6
Cu	7	8.2
Ag	5.5	6.4

Table 6.3: Values of the Fermi energy and Fermi temperature for several metals at room temperature and atmospheric pressure.

(c) What is the mean distance between the electrons for Li and Cu?

(d) Use the fact that the mass of an electron is 9.1×10^{-31} kg to estimate the de Broglie wavelength corresponding to an electron with Fermi energy, $\lambda_F = h/p_F$.

(e) Compare your result for de Broglie wavelength which you found in part (d) to the mean interparticle spacing which found in part (c).

Problem 6.31. The Landau potential for an ideal Fermi gas at arbitrary T can be expressed as

$$\Omega = -kT \int_0^\infty g(\epsilon) \ln[1 + e^{-\beta(\epsilon - \mu)}] \, d\epsilon. \tag{6.154}$$

To obtain the $T = 0$ limit of Ω, we have that $\epsilon < \mu$ in (6.154), $\beta \to \infty$, and hence $\ln[1 + e^{-\beta(\epsilon - \mu)}] \to \ln e^{-\beta(\epsilon - \mu)} = -\beta(\epsilon - \mu)$. Hence, show that

$$\Omega = \frac{(2m)^{3/2} V}{2\pi^2 \hbar^2} \int_0^{\epsilon_F} d\epsilon \, \epsilon^{1/2} (\epsilon - \epsilon_F). \tag{6.155}$$

Calculate Ω and determine the pressure at $T = 0$.

Problem 6.32. Show that the limit (6.143) for $\overline{n}(\epsilon)$ at $T = 0$ follows only if $\mu > 0$.

6.10.2 Low temperature thermodynamic properties

One of the greatest successes of the free electron model and Fermi-Dirac statistics is the explanation of the temperature dependence of the heat capacity of a metal. If the electrons behaved like a classical noninteracting gas, we would expect a contribution to the heat capacity equal to $3Nk/2$, even in the limit that $T \to 0$. Instead, we typically find a very small contribution to the heat capacity which is linear in the temperature, a result that cannot be explained by classical statistical mechanics. Before we derive this result, we first give a qualitative argument for the low temperature dependence of the heat capacity of an ideal Fermi gas.

As we saw in Table 6.3, the Fermi temperature for the conduction electrons in a metal is much greater than room temperature, that is, $T \ll T_F$. Hence, at sufficiently low temperature, we should be able to understand the behavior of an ideal Fermi gas in terms of its behavior at zero

temperature. Because there is only one characteristic energy in the system (the Fermi energy), the criterion for low temperature is that $T \ll T_F$. Hence the conduction electrons in a metal are effectively at absolute zero even though the metal is at room temperature.

For $0 < T \ll T_F$, the electrons that are within order kT below the Fermi surface have enough energy to occupy states with energies that are order kT above the Fermi energy. In contrast, the electrons that are deep within the Fermi surface do not have enough energy to be excited to states above the Fermi energy. Hence, only a small fraction of order T/T_F of the N electrons have a reasonable probability of being excited, and the remainder of the electrons remain unaffected. This reasoning leads us to write the heat capacity of the electrons as $C_V \sim N_{\text{eff}} k$, where N_{eff} is the number of electrons that can be excited by their interaction with the heat bath. For a classical system, $N_{\text{eff}} = N$, but for a Fermi system at $T \ll T_F$, we have that $N_{\text{eff}} \sim N(T/T_F)$. Hence, we expect that the temperature dependence of the heat capacity is given by

$$C_V \sim Nk \frac{T}{T_F}. \qquad (T \ll T_F) \qquad (6.156)$$

From (6.156) we see that the contribution to the heat capacity from the electrons is much smaller than the prediction of the equipartition theorem and is linear in T as is found empirically. As an example, the measured specific heat of copper for $T < 1\,\text{K}$ is dominated by the contribution of the electrons and is given by $C_V/kN = 0.8 \times 10^{-4}\,T$.

Our qualitative argument for the low temperature behavior of C_V implicitly assumes that $\mu(T)$ is unchanged for $T \ll T_F$. We can understand why $\mu(T)$ remains unchanged as T is increased slightly from $T = 0$ by the following reasoning. The probability that a state is empty is

$$1 - \overline{n}(\epsilon) = 1 - \frac{1}{e^{\beta(\epsilon-\mu)} + 1} = \frac{1}{e^{\beta(\mu-\epsilon)} + 1}. \qquad (6.157)$$

We see from (6.157) that for a given distance from μ, the probability that a particle is lost from a previously occupied state below μ equals the probability that an previously empty state is occupied: $\overline{n}(\epsilon - \mu) = 1 - \overline{n}(\mu - \epsilon)$. This property implies that the area under the step function at $T = 0$ is nearly the same as the area under $\overline{n}(\epsilon)$ for $T \ll T_F$ (see Figure 6.4). That is, $\overline{n}(\epsilon)$ is symmetrical about $\epsilon = \mu$. If we make the additional assumption that the density of states changes very little in the region where $\overline{n}$ departs from a step function, we see that the mean number of particles *lost* from the previously occupied states just balances the mean number *gained* by the previously empty states. Hence, we conclude that for $T \ll T_F$, we still have the correct number of particles without any need to change the value of μ.

Similar reasoning implies that $\mu(T)$ must decrease slightly as T is increased from zero. Suppose that μ were to remain constant as T is increased. Because the density of states is an increasing function of ϵ, the number of electrons we would add at $\epsilon > \mu$ would be greater than the number we would lose from $\epsilon < \mu$. As a result, we would increase the number of electrons by increasing T. To prevent such an nonsensical increase, μ has to reduce slightly. In addition, we know that because $\mu \ll 0$ for high temperatures where the system behaves like an ideal classical gas, $\mu(T)$ must pass through zero. At what temperature would you estimate that $\mu(T) \approx 0$?

In Problem 6.33 we will determine $\mu(T)$ by evaluating the integral in (6.158) numerically. Then we will evaluate the integral analytically for $T \ll T_F$ and show that $\mu(T) - \mu(T = 0) \sim (T/T_F)^2$. Hence to first order in T/T_F, μ is unchanged.

Problem 6.33. Numerical evaluation of the chemical potential

To find the chemical potential for $T > 0$, we need to find the value of μ that yields the desired number of particles. We have

$$N = \int_0^\infty \overline{n}(\epsilon)g(\epsilon)d\epsilon = \frac{V(2m)^{3/2}}{2\pi^2\hbar^3}\int_0^\infty \frac{\epsilon^{1/2}d\epsilon}{e^{\beta(\epsilon-\mu)}+1}, \tag{6.158}$$

where we have used (6.102) for $g(\epsilon)$. It is convenient to let $\epsilon = x\epsilon_F$, $\mu = \mu^*\epsilon_F$, and $T^* = kT/\epsilon_F$ and rewrite (6.158) as

$$\rho = \frac{N}{V} = \frac{(2m)^{3/2}}{2\pi^2\hbar^3}\epsilon_F^{3/2}\int_0^\infty \frac{x^{1/2}\,dx}{e^{(x-\mu^*)/T^*}+1}, \tag{6.159}$$

or

$$1 = \frac{3}{2}\int_0^\infty \frac{x^{1/2}\,dx}{e^{(x-\mu^*)/T^*}+1}, \tag{6.160}$$

where we have substituted (6.147) for ϵ_F. To find the dependence of μ on T (or μ^* on T^*), use the application/applet at <stp.clarku.edu/simulations/idealgas/fermigas.html> to evaluate (6.160) numerically.

(a) Start with $T^* = 0.2$ and find μ^* such that (6.160) is satisfied. Does μ^* initially increase or decrease as T is increased from zero? What is the sign of μ^* for $T^* \gg 1$?

(b) At what value of T^* is $\mu^* \approx 0$?

(c) Given the value of $\mu(T^*)$, the program computes the corresponding numerical value of $C_V(T)$. Describe the qualitative T-dependence of C_V.

We now derive a quantitative expression for C valid for temperatures $T \ll T_F$.[9] The increase $\Delta E = E(T) - E(T=0)$ in the total energy is given by

$$\Delta E = \int_0^\infty \epsilon\,\overline{n}(\epsilon)g(\epsilon)\,d\epsilon - \int_0^{\epsilon_F} \epsilon\,g(\epsilon)\,d\epsilon, \tag{6.161a}$$

which we rewrite as

$$= \int_0^{\epsilon_F} \epsilon[\overline{n}(\epsilon)-1]g(\epsilon)\,d\epsilon + \int_{\epsilon_F}^\infty \epsilon\,\overline{n}(\epsilon)g(\epsilon)\,d\epsilon. \tag{6.161b}$$

We multiply the identity

$$N = \int_0^\infty \overline{n}(\epsilon)g(\epsilon)d\epsilon = \int_0^{\epsilon_F} g(\epsilon)\,d\epsilon \tag{6.162}$$

by ϵ_F and write the integral on the left-hand side as a sum of two contributions to obtain

$$\int_0^{\epsilon_F} \epsilon_F\,\overline{n}(e)g(\epsilon)\,d\epsilon + \int_{\epsilon_F}^\infty \epsilon_F\,\overline{n}(e)g(\epsilon)\,d\epsilon = \int_0^{\epsilon_F} \epsilon_F\,g(\epsilon)\,d\epsilon, \tag{6.163a}$$

or

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[9]The following derivation is adapted from Kittel.

$$\int_0^{\epsilon_F} \epsilon_F[\overline{n}(\epsilon) - 1]g(\epsilon)\, d\epsilon + \int_{\epsilon_F}^{\infty} \epsilon_F \overline{n}(\epsilon)g(\epsilon)\, d\epsilon = 0. \tag{6.163b}$$

We can use (6.163b) to rewrite as (6.161b) as

$$\Delta E = \int_{\epsilon_F}^{\infty} (\epsilon - \epsilon_F)\overline{n}(\epsilon)g(\epsilon)d\epsilon + \int_0^{\epsilon_F} (\epsilon_F - \epsilon)[1 - \overline{n}(\epsilon)]g(\epsilon)d\epsilon. \tag{6.164}$$

The heat capacity is found by differentiating ΔE with respect to T. The only temperature-dependent term in (6.164) is $\overline{n}(\epsilon)$. Hence, we can write C_V as

$$C_V = \int_0^{\infty} (\epsilon - \epsilon_F)\frac{d\overline{n}(\epsilon)}{dT}g(\epsilon)d\epsilon. \tag{6.165}$$

For $T \ll T_F$, the derivative $d\overline{n}/dT$ is large only for ϵ near ϵ_F. Hence it is a good approximation to evaluate the density of states $g(\epsilon)$ at $\epsilon = \epsilon_F$ and take it outside the integral:

$$C_V = g(\epsilon_F)\int_0^{\infty} (\epsilon - \epsilon_F)\frac{d\overline{n}}{dT}d\epsilon. \tag{6.166}$$

We can also ignore the temperature-dependence of μ in $\overline{n}(\epsilon)$ and replace μ by ϵ_F. With this approximation we have

$$\frac{d\overline{n}}{dT} = \frac{d\overline{n}}{d\beta}\frac{d\beta}{dT} = \frac{1}{kT^2}\frac{(\epsilon - \epsilon_F)e^{\beta(\epsilon - \epsilon_F)}}{[e^{\beta(\epsilon - \mu)} + 1]^2}. \tag{6.167}$$

We next let $x = (\epsilon - \epsilon_F)/kT$ and use (6.166) and (6.167) to write C_V as

$$C_V = k^2 T g(\epsilon_F)\int_{-\beta\epsilon_F}^{\infty} \frac{x^2 e^x}{(e^x + 1)^2}dx. \tag{6.168}$$

We can replace the lower limit by $-\infty$ because the factor e^x in the integrand is negligible at $x = -\beta\epsilon_F$ for low temperatures. If we use the integral

$$\int_{-\infty}^{\infty} \frac{x^2\, e^x}{(e^x + 1)^2}dx = \frac{\pi^2}{3}, \tag{6.169}$$

we can write the heat capacity of an ideal Fermi gas as

$$C = \frac{1}{3}\pi^2 g(\epsilon_F)k^2 T. \tag{6.170}$$

It is straightforward to show that

$$g(\epsilon_F) = \frac{3N}{2\epsilon_F} = \frac{3N}{2kT_F}, \tag{6.171}$$

and we finally arrive at our desired result

$$C_V = \frac{\pi^2}{2}Nk\frac{T}{T_F}. \qquad (T \ll T_F) \tag{6.172}$$

A more detailed discussion of the low temperature properties of an ideal Fermi gas is given in Section 6.13. For convenience, we summarize the main results here:

$$\Omega = -\frac{2}{3}\frac{2^{1/2}Vm^{3/2}}{\pi^2\hbar^3}\Big[\frac{2}{5}\mu^{5/2} + \frac{\pi^2}{4}(kT)^2\mu^{1/2}\Big]. \tag{6.173}$$

$$\overline{N} = -\frac{\partial\Omega}{\partial\mu} = \frac{V(2m)^{3/2}}{3\pi^2\hbar^3}\Big[\mu^{3/2} + \frac{\pi^2}{8}(kT)^2\mu^{-1/2}\Big]. \tag{6.174}$$

The results (6.173) and (6.174) are in the grand canonical ensemble in which the chemical potential is fixed. However, most experiments are done on a sample with a fixed number of electrons, and hence μ must change with T to keep $\overline{N}$ fixed. To find this dependence we rewrite (6.174) as

$$\frac{3\pi^2\hbar^3\rho}{(2m)^{3/2}} = \mu^{3/2}\Big[1 + \frac{\pi^2}{8}(kT)^2\mu^{-2}\Big], \tag{6.175}$$

where $\rho = \overline{N}/V$. If we raise both sides of (6.175) to the 2/3 power and use (6.147), we have

$$\mu = \frac{3^{2/3}\pi^{4/3}\hbar^2\rho^{2/3}}{2m}\Big[1 + \frac{\pi^2}{8}(kT)^2\mu^{-2}\Big]^{-2/3}, \tag{6.176a}$$

$$= \epsilon_F\Big[1 + \frac{\pi^2}{8}(kT)^2\mu^{-2}\Big]^{-2/3}. \tag{6.176b}$$

In the limit of $T \to 0$, $\mu = \epsilon_F$ as expected. From (6.176b) we see that the first correction for low temperatures is given by

$$\mu(T) = \epsilon_F\Big[1 - \frac{2}{3}\frac{\pi^2}{8}\frac{(kT)^2}{\mu^2}\Big] = \epsilon_F\Big[1 - \frac{\pi^2}{12}\Big(\frac{T}{T_F}\Big)^2\Big], \tag{6.177}$$

where we have made the expansion $(1 + x)^n \approx 1 + nx$ and replaced μ on the right-hand side by $\epsilon_F = kT_F$.

From (6.177) we see that the chemical potential decreases with temperature to keep N fixed, but the decrease is second order in T/T_F (rather than first order), consistent with our earlier qualitative considerations. The explanation for the decrease in $\mu(T)$ is that more particles move from energy states below the Fermi energy to energy states above the Fermi energy as the temperature increases. Because the density of states increases with energy, it is necessary to decrease the chemical potential to keep the number of particles constant. As we found in Problem 6.33 as the temperature becomes larger than the Fermi temperature, the chemical potential changes sign and becomes negative.

Problem 6.34. Low temperature behavior

(a) Fill in the missing steps in (6.161a)–(6.172).

(b) Use (6.173) and (6.177) to show that the mean pressure for $T \ll T_F$ is given by

$$P = \frac{2}{5}\rho\epsilon_F\Big[1 + \frac{5\pi^2}{12}\Big(\frac{T}{T_F}\Big)^2 + \dots\Big]. \tag{6.178}$$

(c) Use the general relation between E and PV to show that

$$E = \frac{3}{5}N\epsilon_F\left[1 + \frac{5\pi^2}{12}\left(\frac{T}{T_F}\right)^2 + \dots\right].$$

(6.179)

(d) For completeness, show that the low temperature behavior of the entropy is given by

$$S = \frac{\pi^2}{2}Nk\frac{T}{T_F}.$$

(6.180)

Why is it not possible to calculate S by using the relations $\Omega = -PV$ and $S = -\partial\Omega/\partial T$, with P given by (6.178)?

We see from (6.172) that the conduction electrons of a metal contribute a linear term to the heat capacity. In Section 6.11 we shall see that the contribution from lattice vibrations contributes a term proportional to T^3 to C_V at low T. Thus for sufficiently low temperature, the linear term dominates.

Problem 6.35. Effective electron mass

In Table 6.3 we found that $T_F = 8.5 \times 10^4\,$K for Copper. Use (6.172) to find the predicted value of C/NkT for Copper. How does this value compare with the experimental value $C/NkT = 8 \times 10^{-5}$? It is remarkable that the theoretical prediction agrees so well with the experimental result based on the free electron model. Show that the small discrepancy can be removed by defining an effective mass m^* of the conduction electrons equal to $\approx 1.3\,m_e$, where m_e is the mass of an electron. What factors might account for the effective mass being greater than m_e?

Problem 6.36. Consider a system of electrons restricted to a two-dimensional surface of area A. Show that the mean number of electrons can be written as

$$\overline{N} = \frac{mA}{\pi\hbar^2}\int_0^\infty \frac{d\epsilon}{e^{\beta(\epsilon-\mu)} + 1}.$$

(6.181)

The integral in (6.181) can be evaluated in closed form using

$$\int \frac{dx}{1 + ae^{bx}} = \frac{1}{b}\ln\frac{e^{bx}}{1 + ae^{bx}} + \text{constant}.$$

(6.182)

Show that

$$\mu(T) = kT\ln\left[e^{\rho\pi\hbar^2/mkT} - 1\right],$$

(6.183)

where $\rho = \overline{N}/A$. What is the value of the Fermi energy $\epsilon_F = \mu(T = 0)$? What is the value of μ for $T \gg T_F$? Plot μ versus T and discuss its qualitative dependence on T.

6.11   The Heat Capacity of a Crystalline Solid

The free electron model of a metal successfully explains the temperature dependence of the contribution to the heat capacity from the electrons. What about the contribution from the ions? In

a crystal each ion is localized about its lattice site and oscillates due to spring-like forces between nearest-neighbor atoms. Classically, we can regard each atom of the solid as having three degrees of freedom,[10] each of which contributes $\frac{1}{2}kT$ to the mean kinetic energy and $\frac{1}{2}kT$ to the mean potential energy. Hence, the heat capacity at constant volume of a homogeneous isotropic solid is given by $C_V = 3Nk$, independent of the nature of the solid. This behavior of C_V agrees with experiment remarkably well at high temperatures, where the meaning of high temperature will be defined later in terms of the parameters of the solid. At low temperatures, the classical behavior is an overestimate of the experimentally measured heat capacity, and C_V is found to be proportional to T^3. To understand this behavior, we first consider the Einstein model and then the more sophisticated Debye model of a solid.

6.11.1 The Einstein model

The reason why the heat capacity starts to decrease at low temperature is that the oscillations of the crystal must be treated quantum mechanically rather than classically. The simplest model of a solid, proposed by Einstein in 1906, is that each atom behaves like three independent harmonic oscillators each of frequency ω and possible energies $\epsilon = (n + \frac{1}{2})\hbar\omega$. Because the $3N$ identical oscillators are independent and are associated with distinguishable sites, we need only to find the thermodynamic functions of one of them. The partition function for one oscillator in one dimension is

$$Z_1 = e^{-\beta\hbar\omega/2} \sum_{n=0}^{\infty} \left[e^{-\beta\hbar\omega} \right]^n \tag{6.184a}$$

$$= \frac{e^{-\beta\hbar\omega/2}}{1 - e^{-\beta\hbar\omega}}. \tag{6.184b}$$

(We calculated Z_1 in Example 4.4.) Other thermodynamic properties of one oscillator are given by

$$f = -kT \ln Z_1 = \frac{\hbar\omega}{2} + kT \ln[1 - e^{-\beta\hbar\omega}] \tag{6.185}$$

$$s = -\frac{\partial f}{\partial T} = -k \ln[1 - e^{-\beta\hbar\omega}] + \beta\hbar\omega \frac{1}{e^{\beta\hbar\omega} - 1} \tag{6.186}$$

$$e = f + Ts = (\overline{n} + \frac{1}{2})\hbar\omega, \tag{6.187}$$

where

$$\overline{n} = \frac{1}{e^{\beta\hbar\omega} - 1}. \tag{6.188}$$

Note the form of $\overline{n}$. To obtain the extensive quantities such as F, S, and E, we multiply the single particle values by $3N$. For example, the heat capacity of an Einstein solid is given by

$$C_V = \left(\frac{\partial E}{\partial T} \right)_V = 3N \left(\frac{\partial e}{\partial T} \right)_V = 3Nk(\beta\hbar\omega)^2 \frac{e^{\beta\hbar\omega}}{[e^{\beta\hbar\omega} - 1]^2}. \tag{6.189}$$

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[10]Our use of the number of *degrees of freedom* is common, but other definitions of the number are also used.

It is convenient to introduce the Einstein temperature

$$kT_E = \hbar\omega, \tag{6.190}$$

and rewrite C_V as

$$C_V = 3Nk\Big(\frac{T_E}{T}\Big)^2 \frac{e^{T_E/T}}{[e^{T_E/T}-1]^2}. \tag{6.191}$$

The limiting behavior of C_V from (6.189) or (6.191) is

$$C_V \to 3Nk, \qquad (T \gg T_E) \tag{6.192a}$$

and

$$C_V \to 3Nk\Big(\frac{\hbar\omega}{kT}\Big)^2 e^{-\hbar\omega/kT}. \qquad (T \ll T_E) \tag{6.192b}$$

The calculated heat capacity is consistent with the third law of thermodynamics and is not very different from the heat capacity actually observed for insulating solids. However, it decreases too quickly at low temperatures and is not consistent with the observed low temperature behavior satisfied by all solids:

$$C_V \propto T^3. \tag{6.193}$$

Problem 6.37. Explain the form of $\bar{n}$ in (6.188). Why is the chemical potential zero in this case?

Problem 6.38. Derive the limiting behavior of C_V given in (6.192).

6.11.2 Debye theory

The Einstein model is based on the idea that each atom behaves like an harmonic oscillator whose motion is independent of the other atoms. A better approximation was made by Debye (1912) who observed that solids can carry sound waves. Because waves are inherently a collective phenomena and are not associated with the oscillations of a single atom, it is better to think of a crystalline solid in terms of the collective rather than the independent motions of the atoms. The collective or cooperative motions correspond to the normal modes of the system, each with its own frequency.

There are two independent transverse modes and one longitudinal mode corresponding to transverse and longitudinal sound waves with speeds, c_t and c_l, respectively. (Note that c_t and c_l are speeds of sound, not light.) Given that the density of states of each mode is given by (6.96), the density of states of the system is given by

$$g(\omega)d\omega = (2g_t + g_l)d\omega = \frac{V\omega^2 d\omega}{2\pi^2}\Big(\frac{2}{c_t^3} + \frac{1}{c_l^3}\Big). \tag{6.194}$$

It is convenient to define a mean speed of sound $\bar{c}$ by the relation

$$\frac{3}{\bar{c}^3} = \frac{2}{c_t^3} + \frac{1}{c_l^3}, \tag{6.195}$$

so that the density of states can be written as

$$g(\omega)\,d\omega = \frac{3V\omega^2 d\omega}{2\pi^2\bar{c}^3}. \tag{6.196}$$

The total energy is given by

$$E = \int \hbar\omega \, \overline{n}(\omega) g(\omega) \, d\omega, = \frac{3V\hbar}{2\pi^2 \overline{c}^3} \int \frac{\omega^3 \, d\omega}{e^{\beta\hbar\omega} - 1}. \tag{6.197}$$

Equation (6.197) does not take into account the higher frequency modes that do not satisfy the linear relation $\omega = kc$. However, we do not expect that the higher frequency modes will contribute much to the heat capacity. After all, we already know that the Einstein model gives the correct high temperature behavior. Because the low temperature heat capacity depends only on the low frequency modes, which we have treated correctly using (6.196), it follows that we can obtain a good approximation to the heat capacity by extending (6.196) beyond its range of validity up to a cutoff frequency chosen to give the correct number of modes. That is, we assume that $g(\omega) \propto \omega^2$ up to a maximum frequency ω_D such that

$$3N = \int_0^{\omega_D} g(\omega) \, d\omega. \tag{6.198}$$

If we substitute (6.196) into (6.198), we find that

$$\omega_D = 2\pi\overline{c} \left(\frac{3\rho}{4\pi}\right)^{1/3}. \tag{6.199}$$

It is convenient to relate the maximum frequency ω_D to a characteristic temperature, the Debye temperature T_D, by the relation

$$\hbar\omega_D = kT_D. \tag{6.200}$$

The thermal energy can now be expressed as

$$E = \frac{3V\hbar}{2\pi^2 c^3} \int_0^{kT_D/\hbar} \frac{\omega^3 \, d\omega}{e^{\beta\hbar\omega} - 1}, \tag{6.201a}$$

$$= 9NkT \left(\frac{T}{T_D}\right)^3 \int_0^{T_D/T} \frac{x^3 \, dx}{e^x - 1}. \tag{6.201b}$$

In the high temperature limit, $T_D/T \to 0$, and the important contribution to the integral in (6.201b) comes from small x. Because the integrand is proportional x^2 for small x, the integral is proportional to $(T/T_D)^{-3}$, and hence the energy is proportional to T. Thus in the high temperature limit, the heat capacity is independent of the temperature, consistent with the law of Dulong and Petit. In the low temperature limit $T_D/T \to \infty$, and the integral in (6.201b) is independent of temperature. Hence in the limit $T \to 0$, the energy is proportional to T^4 and the heat capacity is proportional to T^3, consistent with experimental results at low temperatures.

6.12 Ideal Bose Gas and Bose Condensation

The historical motivation for discussing the noninteracting Bose gas is that this idealized system exhibits Bose-Einstein condensation. The original prediction of Bose-Einstein condensation by Satyendra Nath Bose and Albert Einstein in 1924 was considered by some to be a mathematical artifact or even a mistake. In the 1930s Fritz London realized that superfluid liquid helium could

be understood in terms of Bose-Einstein condensation. However, the analysis of superfluid liquid helium is complicated by the fact that the helium atoms in a liquid strongly interact with one another. For many years scientists tried to create a Bose condensate in less complicated systems. In 1995 several groups used laser and magnetic traps to create a Bose-Einstein condensate of alkali atoms at approximately 10^{-6} K. In these systems the interaction between the atoms is very weak so that the ideal Bose gas is a good approximation and is no longer only a textbook example.[11]

Although the form of the Landau potential for the ideal Bose gas and the ideal Fermi gas differs only superficially (see (6.86)), the two systems behave very differently at low temperatures. The main reason is the difference in the ground states; that is, for a Bose system there is no limit to the number of particles in a single particle state.

The ground state of an ideal Bose gas is easy to construct. We can minimize the total energy by putting all the particles into the single particle state of lowest energy:

$$\epsilon_1 = \frac{\pi^2 \hbar^2}{2mL^2}(1^2 + 1^2 + 1^2) = \frac{3\pi^2 \hbar^2}{2mL^2}. \tag{6.202}$$

The energy of the ground state is given by $N\epsilon_1$. For convenience, we will choose the energy scale such that the ground state energy is zero. The behavior of the system cannot depend on the choice of the zero of energy.

The behavior of an ideal Bose gas can be understood by considering $\overline{N}(T, V, \mu)$:

$$\overline{N} = \sum_k \frac{1}{e^{\beta(\epsilon_k - \mu)} - 1} \rightarrow \int_0^\infty \overline{n}(\epsilon)g(\epsilon)d\epsilon \tag{6.203}$$

$$= \frac{V}{4\pi^2 \hbar^3}(2m)^{3/2} \int_0^\infty \frac{\epsilon^{1/2}\,d\epsilon}{e^{\beta(\epsilon - \mu)} - 1} = \overline{g}\,V \int_0^\infty \frac{\epsilon^{1/2}\,d\epsilon}{e^{\beta(\epsilon - \mu)} - 1}. \tag{6.204}$$

where $\overline{g} = (2m)^{3/2}/(4\pi^2 \hbar^3)$. For simplicity, we will assume that the gas of bosons has zero spin, the same value of the spin as the helium isotope ^{4}He.

To understand the nature of an ideal Bose gas at low temperatures, we will assume that the mean density of the system is fixed and consider the effect of lowering the temperature. The correct choice of μ gives the desired value of ρ when substituted into (6.205).

$$\rho = \frac{\overline{N}}{V} = \overline{g} \int_0^\infty \frac{\epsilon^{1/2}\,d\epsilon}{e^{\beta(\epsilon - \mu)} - 1}. \tag{6.205}$$

We study the behavior of μ as a function of the temperature in Problem 6.39.

Problem 6.39. Numerical evaluation of μ

We know that in the high temperature limit, the chemical potential μ is negative and large in magnitude. Let us investigate numerically how μ changes as we decrease the temperature. The application/applet at `<stp.clarku.edu/simulations/idealgas/bosegas.html>` evaluates the integral on the right-hand side of (6.205) for a given value of β and μ. The goal is to find the value of μ for a given value of T that yields the desired value of ρ.

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[11]The 2001 Nobel Prize for Physics was awarded to Eric Cornell, Wolfgang Ketterle, and Carl Wieman for achieving Bose-Einstein condensation in dilute gases of alkali atoms and for early fundamental studies of the properties of the condensate.

Let $\rho^* = \rho/\overline{g} = 1$ and begin with $T = 10$. First choose $\mu = -10$ and find the computed value of the right-hand side. Do you have to increase or decrease the value of μ to make the computed value of the integral closer to $\rho^* = 1$? By using trial and error, you should find that $\mu \approx -33.4$. Next choose $T = 5$ and find the value of μ needed to keep ρ^* fixed at $\rho^* = 1$. Does μ increase or decrease in magnitude? You can generate a plot of μ versus T by clicking on the `Accept parameters` button.

We found numerically in Problem 6.39 that as T is decreased at constant density, $|\mu|$ must decrease. We can understand this dependence by the following argument. We let $x = \beta\epsilon$, $\mu = -|\mu|$, and rewrite (6.205) as

$$\rho = \overline{g}\beta^{-3/2} \int_0^\infty \frac{x^{1/2} dx}{e^{x+|\mu|} - 1}. \tag{6.206}$$

As we decrease T we increase β, and because $\beta^{-3/2}$ becomes smaller, the integral in (6.206) has to increase to compensate. Hence $\beta|\mu|$ must become smaller, which implies that $|\mu|$ must become smaller.

Because μ is negative for Bose-Einstein statistics, this dependence implies that μ becomes less negative. However, this behavior implies that there would be a lower bound for the temperature at which $\mu = 0$ (the upper bound for μ for Bose systems). We can find the value of this temperature by solving (6.206) with $\mu = 0$:

$$\rho = \overline{g} \int_0^\infty \frac{\epsilon^{1/2} d\epsilon}{e^{\beta_c \epsilon} - 1} = \overline{g}(kT_c)^{3/2} \int_0^\infty \frac{x^{1/2} dx}{e^x - 1}, \tag{6.207}$$

where T_c is the value of T at which $\mu = 0$. The definite integral in (6.207) can be written in terms of known functions (see Appendix A) and has the value:

$$\int_0^\infty \frac{x^{1/2} dx}{e^x - 1} = 2.612 \frac{\pi^{1/2}}{2} = \kappa. \tag{6.208}$$

We have

$$kT_c = \left(\frac{\rho}{\overline{g}\kappa}\right)^{2/3} = 4\pi\hbar^2 \left(\frac{1}{2.612}\right)^{2/3} \frac{\hbar^2}{2ma^2}, \tag{6.209}$$

where $a = \rho^{-1/3}$ is the mean interparticle spacing. We thus obtain the temperature T_c that satisfies (6.207) for fixed density. The energy $\hbar^2/2ma^2$ in (6.209) can be interpreted as the zero-point energy associated with localizing a particle of mass m in a volume a^3.

Problem 6.40. Show that the maximum density for a given temperature is

$$\rho_c = \frac{2.612}{\lambda^3}, \tag{6.210}$$

where λ is given by (6.2).

Problem 6.41. Show that the thermal de Broglie wavelength is comparable to the interparticle spacing at $T = T_c$. What is the implication of this result?
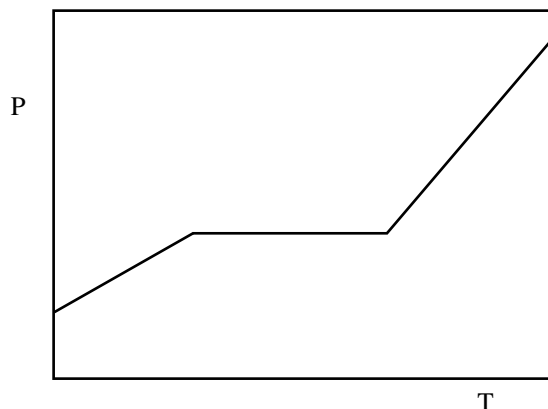
Figure 6.5: Sketch of the dependence of the pressure P on the temperature T for a typical gas and liquid.

Problem 6.42. Use `<stp.clarku.edu/simulations/idealgas/bosegas.html>` to find the numerical value of T at which $\mu = 0$ for $\rho^* = 1$. Confirm that your numerical value is consistent with (6.209).

Of course there is no physical reason why we cannot continue lowering the temperature at fixed density (or increasing the density at fixed temperature). Before discussing how we can resolve this difficulty, consider a familiar situation in which an analogous phenomena occurs. Suppose that we put Argon atoms into a container of fixed volume at a given temperature. If the temperature is high enough and the density is low enough, Argon will be a gas and obey the ideal gas equation of state which we write as $P = NkT/V$. If we now decrease the temperature, we expect that the pressure will decrease. However at some temperature, this dependence will abruptly break down, and P will stop changing as indicated in Figure 6.5. We will not study this behavior of P until Chapter 9, but you might recognize this behavior as a signature of the condensation of the vapor and the existence of a phase transition. That is, at a certain temperature for a fixed density, droplets of liquid Argon will begin to form in the container. As the temperature is lowered further, the liquid droplets will grow, but the pressure will remain constant because most of the extra particles will go into the denser liquid state.

We can describe the ideal Bose gas in the same terms, that is, in terms of a phase transition. That is, at a critical value of T, the chemical potential stops increasing and reaches its limit of $\mu = 0$. Beyond this point, the relation (6.204) is no longer able to keep track of all the particles.

The resolution of the problem lies with the behavior of the three-dimensional density of states $g(\epsilon)$, which is proportional to $\epsilon^{1/2}$ (see (6.101)). Because of this dependence on ϵ, $g(\epsilon = 0) = 0$, and hence our calculation of $\overline{N}$ has ignored all the particles in the ground state. For the classical and Fermi noninteracting gas, this neglect is of no consequence. In the classical case the mean number of particles in any state is much less than unity, while in the degenerate Fermi case there are only two electrons in the lowest kinetic energy state. However, for the noninteracting Bose gas, the mean number of particles in the ground state is given by

$$\overline{N}_0 = \frac{1}{e^{-\beta\mu} - 1}, \tag{6.211}$$

(Remember that we have set $\epsilon_0 = 0$.) When T is sufficiently low, N_0 will be very large. Hence, the denominator of (6.211) must be very small, which implies that $e^{-\beta\mu} \approx 1$ and the argument of the exponential $-\beta\mu$ must be very small. Therefore, we can approximate $e^{-\beta\mu}$ as $1 - \beta\mu$ and $\overline{N}_0 \gg 1$ becomes

$$\overline{N}_0 = -\frac{kT}{\mu}. \tag{6.212}$$

The chemical potential must be such that the number of particles in the ground state approaches its maximum value which is order N. Hence, if we were to use the integral (6.204) to calculate $\overline{N}$ for $T < T_c$, we would have ignored the particles in the ground state. We have resolved the problem – the missing particles are in the ground state. The phenomena we have described, *macroscopic occupation of the ground state*, is called *Bose-Einstein condensation*. That is for $T < T_c$, $\overline{N}_0/N$ is nonzero in the limit of $N \to \infty$.

Now that we know where to find the missing particles, we can calculate the thermodynamics of the ideal Bose gas. For $T < T_c$, the chemical potential is zero in the thermodynamic limit, and the number of particles *not* in the ground state is given by (6.204):

$$\overline{N}_\epsilon = \frac{V}{4\pi^2\hbar^3}(2m)^{3/2}\int_0^\infty \frac{\epsilon^{1/2}d\epsilon}{e^{\beta\epsilon}-1} = N\Big(\frac{T}{T_c}\Big)^{3/2}, \qquad (T < T_c) \tag{6.213}$$

where T_c is defined by (6.209). All of the remaining particles, which we denote as $\overline{N}_0$, are in the ground state, that is, have energy $\epsilon = 0$. Another way of understanding (6.213) is that for $T < T_c$, μ must be zero because the number of particles not in the ground state is determined by the temperature. Thus

$$\overline{N}_0 = N - \overline{N}_\epsilon = N\Big[1 - \Big(\frac{T}{T_c}\Big)^{3/2}\Big]. \qquad (T < T_c) \tag{6.214}$$

Note that for $T < T_c$, a finite fraction of the particles are in the ground state.

Because the energy of the gas is determined by the particles with $\epsilon > 0$, we have for $T < T_c$

$$E = \int_0^\infty \frac{\epsilon\, g(\epsilon)\, d\epsilon}{e^{\beta\epsilon}-1} = \frac{V(mkT)^{3/2}\, kT}{2^{1/2}\pi^2\hbar^3}\int_0^\infty \frac{x^{3/2}\, dx}{e^x - 1}. \tag{6.215}$$

The definite integral in (6.215) is given in Appendix A:

$$\int_0^\infty \frac{x^{3/2}\, dx}{e^x - 1} = 1.341\,\frac{3\pi^{1/2}}{4}. \tag{6.216}$$

If we substitute (6.216) into (6.215), we can write the energy as

$$E = 3\frac{1.341}{2^{5/2}\pi^{3/2}}\frac{V(mkT)^{3/2}kT}{\hbar^3} = 0.1277\, V\frac{m^{3/2}(kT)^{5/2}}{\hbar^3}. \tag{6.217}$$

Note that $E \propto T^{5/2}$ for $T < T_c$. The heat capacity at constant volume is

$$C_V = \frac{\partial E}{\partial T} = 3.2 V\frac{(mkT)^{3/2}k}{\hbar^3}, \tag{6.218a}$$

or

$$C_V = 1.9N_\epsilon k. \tag{6.218b}$$

Note that the heat capacity has a form similar to an ideal classical gas for which $C_V = 1.5Nk$.

The pressure of the Bose gas for $T < T_c$ can be obtained easily from the general relation $PV = 2E/3$ for a nonrelativistic ideal gas. From (6.217) we obtain

$$P = \frac{1.341}{2^{3/2}\pi^{3/2}} \frac{m^{3/2}(kT)^{5/2}}{\hbar^3} = 0.085 \frac{m^{3/2}(kT)^{5/2}}{\hbar^3}. \tag{6.219}$$

Note that the pressure is proportional to $T^{5/2}$ and is independent of the density. This independence is a consequence of the fact that the particles in the ground state do not contribute to the pressure. If additional particles are added to the system at $T < T_c$, the number of particles in the state $\epsilon = 0$ increases, but the pressure does not increase.

What is remarkable about the phase transition in an ideal Bose gas is that it occurs at all. That is, unlike all other known transitions, its occurrence has nothing to do with the interactions between the particles and has everything to do with the nature of the statistics. Depending on which variables are being held constant, the transition in an ideal Bose gas is either first-order or continuous. We postpone a discussion of the nature of first-order and continuous phase transitions until Chapter 9 where we will discuss phase transitions in more detail. It is sufficient to mention here that the order parameter in the ideal Bose gas can be taken to be the fraction of particles in the ground state, and this fraction goes continuously to zero as $T \to T_c$ from below at fixed density.

Another interesting feature of the Bose condensate is that for $T < T_c$, a finite fraction of the atoms are described by the same quantum wavefunction, which gives the condensate many unusual properties. In particular, Bose condensates have been used to produce atom lasers – laser-like beams in which photons are replaced by atoms – and to study fundamental processes such as superfluidity.

Problem 6.43. Temperature dependence of the pressure

(a) Start from the classical pressure equation of state, $PV = NkT$, replace N by Neff for an ideal Bose gas, and give a qualitative argument why $P \propto T^{5/2}$ at low temperatures.

(b) Show that the ground state contribution to the pressure is given by

$$P_0 = \frac{kT}{V} \ln(\overline{N}_0 + 1). \tag{6.220}$$

Explain why P_0 can be regarded as zero and why the pressure of an Bose gas for $T < T_c$ is independent of the volume.

Problem 6.44. Estimate of Bose condensation temperature

What is the approximate value of T_c for a noninteracting Bose gas at a density of $\rho = 0.14\,\mathrm{gm\,cm}^{-3}$, the density of liquid ${}^4\mathrm{He}$? Take $m = 6.65 \times 10^{-27}\,\mathrm{kg}$.

6.13 *Low Temperature Expansion of an Ideal Fermi Gas

We derive the low temperature expansion of the thermodynamic properties of an ideal Fermi gas. For convenience, we first give the formal expressions for the thermodynamic properties of a ideal Fermi gas at temperature T. The mean number of particles is given by

$$\overline{N} = \frac{2^{1/2}Vm^{3/2}}{\pi^2\hbar^3}\int_0^\infty \frac{\epsilon^{1/2}\,d\epsilon}{e^{\beta(\epsilon-\mu)}+1}. \tag{6.221}$$

After an integration by parts, the Landau potential Ω is given by (see (6.105))

$$\Omega = -\frac{2}{3}\frac{2^{1/2}Vm^{3/2}}{\pi^2\hbar^3}\int_0^\infty \frac{\epsilon^{3/2}\,d\epsilon}{e^{\beta(\epsilon-\mu)}+1}. \tag{6.222}$$

The integrals in (6.221) and (6.222) cannot be expressed in terms of familiar functions for all T. However, in the limit $T \ll T_F$ (as is the case for almost all metals), it is sufficient to approximate the integrals. To understand the approximations, we express the integrals (6.221) and (6.222) in the form

$$I = \int_0^\infty \frac{f(\epsilon)\,d\epsilon}{e^{\beta(\epsilon-\mu)}+1}, \tag{6.223}$$

where $f(\epsilon) = \epsilon^{1/2}$ and $e^{3/2}$, respectively.

The expansion procedure is based on the fact that the Fermi-Dirac distribution function $\overline{n}(\epsilon)$ differs from its $T = 0$ form only in a small range of width kT about μ. We let $\epsilon - \mu = kTx$ and write I as

$$I = kT\int_{-\beta\mu}^\infty \frac{f(\mu+kTx)}{e^x+1}\,dx \tag{6.224a}$$

$$= kT\int_{-\beta\mu}^0 \frac{f(\mu+kTx)}{e^x+1}\,dx + kT\int_0^\infty \frac{f(\mu+kTx)}{e^x+1}\,dx. \tag{6.224b}$$

In the first integrand in (6.224b) we let $x \to -x$ so that

$$I = kT\int_0^{\beta\mu} \frac{f(\mu-kTx)}{e^{-x}+1}\,dx + kT\int_0^\infty \frac{f(\mu+kTx)}{e^x+1}\,dx. \tag{6.224c}$$

We next write $1/(e^{-x}+1) = 1 - 1/(e^x+1)$ in the first integrand in (6.224c) and obtain

$$I = kT\int_0^{\beta\mu}f(\mu-kTx)\,dx - kT\int_0^{\beta\mu} \frac{f(\mu-kTx)}{e^x+1}\,dx + kT\int_0^\infty \frac{f(\mu+kTx)}{e^x+1}\,dx. \tag{6.225}$$

Equation (6.225) is still exact.

Because we are interested in the limit $T \ll T_F$ or $\beta\mu \gg 1$, we can replace the upper limit in the second integral by infinity. Then after making a change of variables in the first integrand, we find

$$I = \int_0^\mu f(\epsilon)\,d\epsilon + kT\int_0^\infty \frac{f(\mu+kTx)-f(\mu-kTx)}{e^x+1}\,dx. \tag{6.226}$$

The values of x that contribute to the integrand in the second term in (6.226) are order unity, and hence it is reasonable to expand $f(\mu \pm kTx)$ in a power series in kTx and integrate term by term. The result is

$$I = \int_0^\mu f(\epsilon)\,d\epsilon + 2(kT)^2 f'(\mu)\int_0^\infty \frac{x\,dx}{e^x+1}\,dx + \frac{1}{3}(kT)^4 f'''(\mu)\int_0^\infty \frac{x^3 dx}{e^x+1}\,dx + \dots \tag{6.227}$$

The definite integrals in (6.227) can be evaluated using analytical methods (see Appendix A). The results are

$$\int_0^\infty \frac{x\,dx}{e^x+1} = \frac{\pi^2}{12} \tag{6.228}$$

$$\int_0^\infty \frac{x^3\,dx}{e^x+1} = \frac{7\pi^4}{120} \tag{6.229}$$

If we substitute (6.228) and (6.229) into (6.227), we obtain the desired result

$$I = \int_0^\mu f(\epsilon)\,d\epsilon + \frac{\pi^2}{6}(kT)^2 f'(\mu) + \frac{7\pi^4}{360}(kT)^4 f''' + \dots \tag{6.230}$$

Note that although we expanded $f(\mu - kTx)$ in a power series in kTx, the expansion of I in (6.230) is not a power series expansion in $(kT)^2$. Instead (6.230) represents an asymptotic series that is a good approximation to I if only the first several terms are retained.

To find Ω in the limit of low temperatures, we let $f(\epsilon) = \epsilon^{3/2}$ in (6.230). From (6.222) and (6.230) we find that in the limit of low temperatures

$$\Omega = -\frac{2}{3}\frac{2^{1/2}Vm^{3/2}}{\pi^2\hbar^3}\Big[\frac{2}{5}\mu^{5/2} + \frac{\pi^2}{4}(kT)^2\mu^{1/2}\Big]. \tag{6.231}$$

$$\overline{N} = -\frac{\partial\Omega}{\partial\mu} = \frac{V(2m)^{3/2}}{3\pi^2\hbar^3}\Big[\mu^{3/2} + \frac{\pi^2}{8}(kT)^2\mu^{-1/2}\Big]. \tag{6.232}$$

We we mentioned, the expansions in (6.231) and (6.232) are asymptotic and provide good approximations only if the first few terms are kept. A more careful derivation of the low temperature behavior of an ideal Fermi gas has been given by Weinstock.

Vocabulary

thermal de Broglie wavelength, λ

equipartition theorem

Maxwell velocity and speed distribution

occupation numbers, spin and statistics, bosons and fermions

Bose-Einstein distribution, Fermi-Dirac distribution, Maxwell-Boltzmann distribution

single particle density of states, $g(\epsilon)$

Fermi energy ϵ_F, temperature T_F, and momentum p_F

macroscopic occupation, Bose-Einstein condensation

Einstein and Debye theories of a crystalline solid, law of Dulong and Petit

Additional problems

Listing of inline problems.

Problem 6.45. Suppose that two systems are initially in thermal and mechanical equilibrium, but not in chemical equilibrium, that is, $T_1 = T_2$, $P_1 = P_2$, but $\mu_1 \neq \mu_2$. Use reasoning similar to that used in Section 2.12 to show that particles will move from the system with higher density to the system at lower density.

Problem 6.46. Explain in simple terms why the mean kinetic energy of a classical particle in equilibrium with a heat bath at temperature T is $\frac{1}{2}kT$ per quadratic contribution to the kinetic energy, independent of the mass of the particle.

Problem 6.47. Linear rigid rotator

The atoms we discussed in Section 6.3 were treated as symmetrical, rigid structures capable of only undergoing translation motion, that is, their internal motion was ignored. Real molecules are

neither spherical nor rigid, and rotate about two or three axes and vibrate with many different frequencies. For simplicity, consider a linear rigid rotator with two degrees of freedom. The rotational energy levels are given by

$$\epsilon(j) = j(j+1)\frac{\hbar^2}{2I}, \tag{6.233}$$

where I is the moment of inertia and $j = 0, 1, 2, \ldots$ The degeneracy of each rotational level is $(2j+1)$.

(a) Find the partition function Z_{rot} for the rotational states of one molecule.

(b) For $T \gg T_r = \hbar^2/(2kI)$, the spectrum of the rotational states may be approximated by a continuum and the sum over j can be replaced by an integral. Show that the rotational heat capacity is given by $C_{V,\mathrm{rot}} = Nk$ in the high temperature limit. Compare this result with the prediction of the equipartition theorem.

(c) A more accurate evaluation of the sum for Z_{rot} can be made using the Euler-Maclaurin formula (see Appendix A)

$$\sum_{i=0}^{\infty} f(x) = \int_0^{\infty} f(x)\,dx + \frac{1}{2}f(0) - \frac{1}{12}f'(0) + \frac{1}{720}f'''(0) + \ldots \tag{6.234}$$

Show that the corresponding result for $C_{V,\mathrm{rot}}$ is

$$C_{V,\mathrm{rot}} = Nk\left[1 + \frac{1}{45}\left(\frac{T_r}{T}\right)^2 + \ldots\right]. \tag{6.235}$$

(d) Show that the leading contribution to $C_{V,\,\mathrm{rot}}$ for $T \ll T_r$ s is

$$C_{V,\mathrm{rot}} = 12Nk\left(\frac{T_r}{T}\right)^2 e^{-2T_r/T} + \ldots \tag{6.236}$$

Problem 6.48. Diatomic gas

In Section 6.3 we found the specific heat of monatomic gases using the equipartition theorem. In this problem we consider the specific heat of a diatomic gas. A monatomic gas is described by three independent coordinates and is said to have three degrees of freedom per particle. The total energy of a diatomic gas is a sum of three terms, a translational, rotational, and vibrational part, and hence the total specific heat of the gas can be written as

$$c_v = c_{\mathrm{tr}} + c_{\mathrm{rot}} + c_{\mathrm{vib}}. \tag{6.237}$$

The last two terms in (6.237) arise from the internal degrees of freedom, two for rotation and one for vibration. (Some textbooks state that there are two vibrational degrees of freedom because the vibrational energy is part kinetic and part potential.) What is the high temperature limit of c_v for a diatomic gas? The values of $\hbar^2/2kI$ and $\hbar\omega/k$ for H_2 are 85.5 K and 6140 K, respectively, where ω is the vibrational frequency. What do you expect the value of c_v to be at room temperature? Sketch the T-dependence of c_v in the range $10\,\mathrm{K} \le T \le 10000\,\mathrm{K}$.
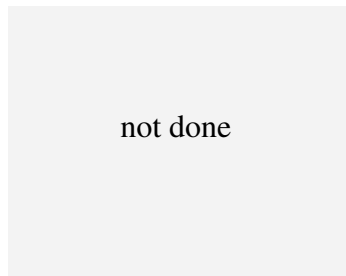
Figure 6.6: A schematic representation of a diatomic molecule.

Problem 6.49. What is the probability that a classical nonrelativistic particle has kinetic energy in the range ϵ to $\epsilon + d\epsilon$?

Problem 6.50. Consider an ideal classical gas in equilibrium at temperature T in the presence of an uniform gravitational field. Find the probability $P(z)dz$ that an atom is at a height between z and $z + dz$ above the earth's surface. How do the density and the pressure depend on z?

Problem 6.51. We can write the total energy of a system of N particles in the form

$$E = \sum_{i=1}^{N} \frac{p_i^2}{2m} + \sum_{i=j+1}^{N} \sum_{j=1}^{N} u_{ij} \tag{6.238}$$

where $u_{ij} = u(|\mathbf{r}_i - \mathbf{r}_j|)$ is the interaction energy between particles i and j. Discuss why the partition function of a classical system of N particles can be written in the form

$$Z_N = \frac{1}{N!\,h^{3N}} \int d^{3N}\mathbf{p}\, d^{3N}\mathbf{r}\, e^{-\beta \sum_i p_i^2/2m}\, e^{-\beta \sum_{i<j} u_{ij}}. \tag{6.239}$$

Problem 6.52. Granular systems

A system of glass beads or steel balls is an example of a *granular* system. In such system the beads are macroscopic objects and the collisions between the beads is inelastic. Because the collisions in such a system are inelastic, a gas-like steady state is achieved only by inputting energy, usually by shaking or vibrating the walls of the container. Suppose that the velocities of the particles are measured in a direction perpendicular to the direction of shaking. Do you expect the distribution of the velocities to be given by a Gaussian distribution as in (6.58)? See for example, the experiments by Daniel L. Blair and Arshad Kudrolli, "Velocity correlations in dense granular gases," Phys. Rev. E **64**, 050301(R) (2001) and the theoretical arguments by J. S. van Zon and F. C. MacKintosh, "Velocity distributions in dissipative granular gases," Phys. Rev. Lett. **93**, 038001 (2004).

****Problem 6.53.** In one of his experiments on gravitational sedimentation, Perrin observed the number of particles in water at $T = 293\,\mathrm{K}$ and found that when the microscope was raised by $100\,\mu\mathrm{m}$, the mean number of particles in the field of view decreased from 203 to 91. Assume that the particles have a mean volume of $9.78 \times 10^{-21}\,\mathrm{m}^3$ and a mass density of $1351\,\mathrm{kg/m}^3$. The density of water is $1000\,\mathrm{kg/m}^3$. Use this information to estimate the magnitude of Boltzmann's constant.

Problem 6.54. Maxwell velocity distribution

(a) What is the most probable kinetic energy of an atom in a classical system in equilibrium with a heat bath at temperature T? Is it equal to $\frac{1}{2}m\tilde{v}^2$, where $\tilde{v}$ is the most probable speed?

(b) Find the following mean values for the same system: $\overline{v}_x$, $\overline{v_x^2}$, $\overline{v_x^2 v_y^2}$, and $\overline{v_x v_y^2}$. No calculations are necessary.

Problem 6.55. Mean energy of a nonlinear oscillator

Consider a classical one-dimensional nonlinear oscillator whose energy is given by

$$\epsilon = \frac{p^2}{2m} + ax^4, \tag{6.240}$$

where x, p, and m have their usual meanings; the parameter a is a constant.

(a) If the oscillator is in equilibrium with a heat bath at temperature T, calculate its mean kinetic energy, mean potential energy, and the mean total energy.

(b) Consider a classical one-dimensional oscillator whose energy is given by

$$\epsilon = \frac{p^2}{2m} + \frac{1}{2}kx^2 + ax^4. \tag{6.241}$$

In this case the anharmonic contribution ax^4 is very small. What is the leading contribution of this term to the mean potential energy?

Problem 6.56. Consider a system consisting of two noninteracting particles connected to a heat bath at temperature T. Each particle can be in one of three states with energies 0, ϵ_1, and ϵ_2. Find the partition function for the following cases:

(a) The particles obey Maxwell-Boltzmann statistics and can be considered distinguishable.

(b) The particles obey Fermi-Dirac statistics.

(c) The particles obey Bose-Einstein statistics.

(d) Find the probability in each case that the ground state is occupied by one particle.

(e) What is the probability that the ground state is occupied by two particles?

(f) Estimate the probabilities in (d) and (e) for $kT = \epsilon_2 = 2\epsilon_1$.

Problem 6.57. Show that the grand partition function $\mathcal{Z}$ can be expressed as

$$\mathcal{Z} = \sum_{N=0}^{\infty} e^{\beta\mu N} Z_N \tag{6.242}$$

where Z_N is the partition function for a system of N particles. Consider a system of noninteracting (spinless) fermions such that each particle can be a single particle state with energy 0, Δ, and 2Δ. Find an expression for $\mathcal{Z}$. Show how the mean number of particles depends on μ for $T = 0$, $kT = \Delta/2$, and $kT = \Delta$.

*__Problem 6.58.__ Assume periodic boundary conditions so that the wave function ψ satisfies the condition (in one dimension)

$$\psi(x) = \psi(x + L). \tag{6.243}$$

The form of the one particle eigenfunction consistent with (6.243) is given by

$$\psi(x) \propto e^{ik_x x}. \tag{6.244}$$

What are the allowed values of k_x? How do they compare with the allowed values of k_x for a particle in a one-dimensional box? Generalize the form (6.244) to a cube and determine the allowed values of $\mathbf{k}$. Find the form of the density of states and show that the same result (6.93) is obtained.

__Problem 6.59.__ A system contains N identical noninteracting fermions with $2N$ distinct single particle states. Suppose that $2N/3$ of these states have energy zero, $2N/3$ have energy Δ, and $2N/3$ have energy 2Δ. Show that μ is independent of T. Calculate and sketch the T-dependence of the energy and heat capacity.

__Problem 6.60.__ Find general expressions for N, Ω, and E for a highly relativistic ideal gas and find a general relation between PV and E.

__Problem 6.61.__ Calculate the chemical potential $\mu(T)$ of a noninteracting Fermi gas at low temperatures $T \ll T_F$ for a one-dimensional ideal Fermi gas. Use the result for $\mu(T)$ found for the two-dimensional case in Problem 6.36 and compare the qualitative behavior of $\mu(T)$ in one, two, and three dimensions.

__Problem 6.62.__ Discuss the meaning of the Fermi temperature T_F and why most metals can be treated as if they are effectively at low temperatures, even at room temperatures.

__Problem 6.63.__ High temperature limit of the ideal Fermi gas

If $T \gg T_F$ at fixed density, quantum effects can be neglected and the thermal properties of an ideal Fermi gas reduces to the ideal classical gas.

(a) Does the pressure increase or decrease when the temperature is lowered (at constant density)? That is, what is the first quantum correction to the classical equation of state? The pressure is given by (see (6.105))

$$P = \frac{(2m)^{3/2}}{3\pi^2\hbar^3} \int_0^\infty \frac{\epsilon^{3/2}\,d\epsilon}{e^{\beta(x-\mu)}+1}. \tag{6.245}$$

In the high temperature limit, $e^{\beta\mu} \ll 1$, and we can make the expansion

$$\frac{1}{e^{\beta(\epsilon-\mu)}+1} = e^{\beta(\mu-\epsilon)}\frac{1}{1+e^{-\beta(\epsilon-\mu)}} \tag{6.246a}$$

$$\approx e^{\beta(\mu-\epsilon)}[1 - e^{-\beta(\epsilon-\mu)}]. \tag{6.246b}$$

If we use (6.246b), we obtain

$$e^{\beta\mu} \int_0^\infty x^{3/2} e^{-x} (1 - e^{\beta\mu}e^{-x})\, dx = \frac{3}{4}\pi^{1/2}e^{\beta\mu}[1 - \frac{1}{2^{5/2}}e^{\beta\mu}]. \qquad (6.247)$$

Use (6.247) to show that P is given by

$$P = \frac{m^{3/2}(kT)^{5/2}}{2^{1/2}\,\pi^{3/2}\hbar^3}\, e^{\beta\mu}\Big[1 - \frac{1}{2^{5/2}}e^{\beta\mu}\Big]. \qquad (6.248)$$

(b) Derive a expression for N similar to (6.248). Eliminate μ and show that the leading order correction to the equation of state is given by

$$PV = NkT\Big[1 + \frac{\pi^{3/2}}{4}\frac{\rho\hbar^3}{(mkT)^{3/2}}\Big], \qquad (6.249a)$$

$$= NkT\Big[1 + \frac{1}{2^{7/2}}\rho\lambda^3\Big]. \qquad (6.249b)$$

(c) What is the condition for the correction term in (6.249b) to be small? Note that as the temperature is lowered at constant density, the pressure increases. This dependence implies that quantum effects due to Fermi statistics lead to an effective "repulsion" between the particles. What do you think would be the effect of Bose statistics in this context (see Problem 6.66)?

Mullin and Blaylock have emphasized that it is misleading to interpret the sign of the correction term in (6.249b) in terms of an effective repulsive exchange "force," and stress that the positive sign is a consequence of the symmetrization requirement for same spin fermions.

Problem 6.64. In the text we gave a simple argument based on the assumption that $C_V \sim N_{\text{eff}}k$ to obtain the qualitative T-dependence of C_V at low temperatures for an ideal Bose and Fermi gas. Use a similar argument based on the assumption that $PV = N_{\text{eff}}kT$ to obtain the T-dependence of the pressure at low temperatures.

*__Problem 6.65.__ Consider a system of N noninteracting fermions with single particle energies given by $\epsilon_n = n\Delta$, where $n = 1, 2, 3, \ldots$ Find the mean energy and heat capacity of the system. Although this problem can be treated exactly, it is not likely that you will be able to solve the problem by thinking about the case of general N. The exact partition function for general N has been found by several authors including Peter Borrmann and Gert Franke, "Recursion formulas for quantum statistical partition functions," J. Chem. Phys. **98**, 2484–2485 (1993) and K. Schönhammer, "Thermodynamics and occupation numbers of a Fermi gas in the canonical ensemble," Am. J. Phys. **68**, 1032–1037 (2000).

Problem 6.66. High temperature limit of ideal Bose gas

If $T \gg T_c$ at fixed density, quantum effects can be neglected and the thermal properties of an ideal Bose gas reduces to the ideal classical gas. Does the pressure increase or decrease when the

temperature is lowered (at constant density)? That is, what is the first quantum correction to the classical equation of state? The pressure is given by (see (6.105))

$$P = \frac{2^{1/2} m^{3/2} (kT)^{5/2}}{3\pi^2 \hbar^3} \int_0^\infty \frac{x^{3/2} \, dx}{e^{x - \beta\mu} - 1}. \tag{6.250}$$

Follow the same procedure as in Problem 6.63 and show that

$$PV = NkT \left[1 - \frac{\pi^{3/2}}{2} \frac{\rho \hbar^3}{(mkT)^{3/2}} \right]. \tag{6.251}$$

We see that as the temperature is lowered at constant density, the pressure becomes less than its classical value.

Problem 6.67. Does Bose condensation occur for a one and two-dimensional ideal Bose gas? If so, find the transition temperature. If not, explain.

Problem 6.68. Discuss why Bose condensation does not occur in a gas of photons in thermal equilibrium (blackbody radiation).

****Problem 6.69.** Effect of boundary conditions

(a) Assume that N noninteracting bosons are enclosed in a cube of edge length L with rigid walls. What is the ground state wave function? How does the density of the condensate vary in space?

(b) Assume instead the existence of periodic boundary conditions. What is the spatial dependence of the ground state wave function on this case?

(c) Do the boundary conditions matter in this case? If so, why?

****Problem 6.70.** Bose-Einstein condensation in low-dimensional traps

As we found in Problem 6.67, Bose-Einstein condensation does not occur in ideal one and two-dimensional systems. However, this result holds only if the system is confined by rigid walls. In the following, we will show that Bose-Einstein condensation can occur if a system is confined by a spatially varying potential. For simplicity, we will treat the system semiclassically

Let us assume that the confining potential has the form

$$V(r) \sim r^n. \tag{6.252}$$

Then the region accessible to a particle with energy ϵ has a radius $L \sim \epsilon^{1/n}$. Show that the corresponding density of states behaves as

$$g(\epsilon) \sim L^d \epsilon^{\frac{1}{2}d - 1} \sim \epsilon^{d/n} \epsilon^{\frac{1}{2}d - 1} \sim \epsilon^\alpha, \tag{6.253}$$

where

$$\alpha = \frac{d}{n} + \frac{d}{2} - 1 \tag{6.254}$$

What is the range of values of n for which $T_c > 0$ for $d = 1$ and 2? More information about experiments on Bose-Einstein condensation can be found in the references.

Problem 6.71. More on the Debye model

(a) Show that if the volume of the crystal is Na^3, where a is the equilibrium distance between atoms, then the Debye wave number, $k_D = \omega_D/\bar{c}$, is about π/a.

(b) Evaluate the integral in (6.201b) numerically and plot the heat capacity versus T/T_D over the entire temperature range.

*__Problem 6.72.__ Show that the probability $P(N)$ of finding a system in the T, V, μ ensemble with exactly N particles, regardless of their positions and momenta, is given by

$$P(N) = \frac{1}{\mathcal{Z}} e^{\beta N \mu} Z_N(V, T). \tag{6.255}$$

Use (6.255) to show that

$$\overline{N} = \sum_{N=0}^{\infty} N P(N) = \frac{z}{\mathcal{Z}} \frac{\partial \mathcal{Z}}{\partial z} = \frac{\partial \ln \mathcal{Z}}{\partial \beta \mu}, \tag{6.256}$$

where the *activity* z is defined as

$$z = e^{\beta \mu}. \tag{6.257}$$

Also show that the variance of the number of particles is given by

$$\overline{N^2} - \overline{N}^2 = kT \frac{\partial \overline{N}}{\mu}. \tag{6.258}$$

*__Problem 6.73.__ Number fluctuations in a noninteracting classical gas

Show that the grand partition function of a noninteracting classical gas can be expressed as

$$\mathcal{Z} = \sum_{N=0}^{\infty} \frac{(z Z_1)^N}{N!} = e^{z Z_1}. \tag{6.259}$$

Show that the mean value of N is given by

$$\overline{N} = z Z_1, \tag{6.260}$$

and that the probability that there are N particles in the system is given by a Poisson distribution:

$$P_N = \frac{z^N Z_N}{\mathcal{Z}} = \frac{(z Z_1)^N}{N! \mathcal{Z}} = \frac{\overline{N}^N}{N!} e^{-\overline{N}}. \tag{6.261}$$

What is the variance, $\overline{(N - \overline{N})^2}$, and the N-dependence of the relative root mean square deviation, $[\langle N^2 \rangle - \overline{N}^2]^{1/2}/\overline{N}$?

*__Problem 6.74.__ Number fluctuations in a degenerate noninteracting Fermi gas

Use the relation

$$\overline{(N - \overline{N})^2} = kT \frac{\partial N}{\partial \mu} \tag{6.262}$$

to find the number fluctuations in the noninteracting Fermi gas for fixed T, V and μ. Show that

$$\overline{(N - \overline{N})^2} = \frac{kT}{2} \frac{V(2m)^{3/2}}{2\pi^2\hbar^3} \int_0^\infty \frac{\epsilon^{-1/2}\, d\epsilon}{e^{\beta(\epsilon-\mu)} + 1}, \tag{6.263a}$$

$$\to \frac{3\overline{N}T}{2T_F}. \qquad (T \ll T_F) \tag{6.263b}$$

Explain why the fluctuations in a degenerate Fermi system are much less than in the corresponding classical system.

***Problem 6.75.** Absence of classical magnetism

As mentioned in Chapter 5, van Leeuwen's theorem states that the phenomena of diamagnetism does not exist in classical physics. Hence, magnetism is an intrinsically quantum mechanical phenomena. Prove van Leeuwen's theorem using the following hints.

The proof of this theorem requires the use of classical Hamiltonian mechanics for which the regular momentum $\mathbf{p}$ is replaced by the canonical momentum $\mathbf{p} - \mathbf{A}/c$, where the magnetic field enters through the vector potential, $\mathbf{A}$. Then make a change of variables that eliminates $\mathbf{A}$, and thus the electric and magnetic fields from the Hamiltonian. Because the local magnetic fields are proportional to the velocity, they too will vanish when the integral over momenta is done in the partition function.

***Problem 6.76.** The Fermi-Pasta-Ulam (FPU) problem

The same considerations that make the Debye theory of solids possible also suggest that a molecular dynamics simulation of a solid at low temperatures will fail. As we noted in Section 6.11, a system of masses linked by Hooke's law springs can be represented by independent normal modes. The implication is that a molecular dynamics simulation of a system of particles interacting via the Lennard-Jones potential will fail at low temperatures because the simulation will not be ergodic. The reason is that at low energies, the particles will undergo small oscillations, and hence the system can be represented by a system of masses interacting via Hooke's law springs. A initial set of positions and velocities would correspond to a set of normal modes. Because the system would remain in this particular set of modes indefinitely, a molecular dynamics simulation would not sample the various modes and the simulation would not be ergodic.

In 1955 Fermi, Pasta, and Ulam did a simulation of a one-dimensional chain of springs connected by springs. If the force between the springs is not linear, for example, $V(x) = kx^2/2 + \kappa x^4/4$, the normal modes will not be an exact representation of the system for $\kappa > 0$. Would a molecular dynamics simulation be ergodic for any value of $\kappa > 0$? The answer to this question is nontrivial and is of continuing interested to physicists and mathematicians. A good place to start is the book by Weissert.

Suggestions for further reading

More information about Bose-Einstein condensation can be found at `<jilawww.colorado.edu/bec/>`, `<bec.nist.gov/>`, and `<cua.mit.edu/ketterle_group/>`.

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David L. Goodstein, *States of Matter*, Prentice Hall (1975). An excellent text whose emphasis is on the applications of statistical mechanics to gases, liquids and solids. Chapter 3 on solids is particularly relevant to this chapter.

J. D. Gunton and M. J. Buckingham, "Condensation of ideal Bose gas as cooperative transition," Phys. Rev. **166**, 152 (1968).

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Charles Kittel, *Introduction to Solid State Physics*, seventh edition, John Wiley & Sons (1996). See Chapters 5 and 6 for a discussion of the Debye model and the free electron gas.

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Chapter 7

Using Thermodynamics

7.1 Understanding the chemical potential

Most of our discussion thus far has been concerned with the behavior of systems composed of one type of particle. However, in many cases we have more than one type of particle interacting with each other or we have the same type of particle in two or more different phases that are in contact with each other. An example would be an ice cube in a glass of water. We now discuss the chemical potential more deeply so that we can more fully appreciate the behavior of these *multi-species* systems.

Just as temperature measures the ability of a system to transfer energy to another system and pressure is a measure of the ability of a system to transfer volume, the chemical potential is a measure of the ability of a system to transfer particles. Two systems in thermal and particle equilibrium will not only come to the same temperature, but also will come to the same chemical potential.

We now discuss some techniques for calculating the chemical potential in computer simulations as a way of obtaining more insight into the meaning of the chemical potential. Using (2.155) and (4.101) the chemical potential can be written as

$$\mu = \left(\frac{\partial F}{\partial N}\right)_{T,V} = F_{N+1} - F_N = -kT \ln Z_{N+1} + kT \ln Z_N = -kT \ln Z_{N+1}/Z_N \qquad (7.1)$$

in the limit $N \to \infty$. To understand how we might compute the chemical potential in a standard Monte Carlo simulation in the canonical ensemble, we need to write μ in terms of an appropriate average of an N particle system. The probability that the N particle system is in the ith microstate is $P_i = e^{-\beta E_i}/Z_N$. Z_{N+1} can be written as $\sum_i \sum_j e^{-\beta E_i} e^{-\beta \Delta E_{ij}}$, where the sum over i is over all microstates of the N particle system, and the sum over j is over all possible dynamical variables that characterize the state of the $(N+1)$st particle. The energy difference ΔE_{ij} is the difference in

energy between the ith state with N particles and the ith state with N particles plus an additional particle in state j. Thus (7.1) can be written as

$$\mu = -kT \ln \sum_i \sum_j P_i e^{-\beta \Delta E_{ij}}. \tag{7.2}$$

Equation (7.2) states that the ratio Z_{N+1}/Z_N is the average of $e^{-\beta \Delta E}$ over all possible states of an added particle with added energy ΔE. Because a Monte Carlo simulation generates configurations with probability P_i, we can compute the chemical potential by periodically calculating the change in the energy ΔE that would occur if an imaginary particle were added to an N particle system at random locations. The added particle is removed once ΔE is calculated. Thus, the chemical potential is given by

$$\mu = -kT \ln \langle e^{-\beta \Delta E} \rangle, \tag{7.3}$$

where the average $\langle \ldots \rangle$ is over many insertions into many different configurations that are generated by the Monte Carlo algorithm, and which are thus distributed according to the Boltzmann distribution P_i. This method of computing the chemical potential is called the Widom insertion method.

For an ideal classical gas only the momentum degrees of freedom are relevant. Equation (7.3) with

$$\langle e^{-\beta \Delta E} \rangle = V \int e^{-\beta p^2/2m} d^3 p / h^3 \tag{7.4}$$

plus a factor of $1/N$ to account for indistinguishability leads to the usual classical ideal gas expression for μ given in (6.31). Because the momentum degrees of freedom yield the same result independent of the inter-particle potential, Monte Carlo simulations only need to include the position degrees of freedom, and the chemical potential in (7.3) is interpreted as the excess chemical potential beyond the ideal gas contribution.

We can use (7.3) to understand the behavior of the chemical potential as we change the density of a fluid. Consider a fluid for which the inter-particle potential consists of a Lennard-Jones type potential made up of a hard core positive potential at small inter-particle separations and a negative potential well which vanishes at large inter-particle separations. At very low densities an added particle will likely land in a region where the inter-particle potential is small and negative and thus this added particle will contribute a very small negative energy ($\Delta E < 0$) to the system. Thus from (7.3), $-\beta \Delta E$ will be small and positive, the exponential will be greater than unity, and thus the excess chemical potential will be negative. As the density is increased, an added particle is more likely to land in the potential well and thus ΔE is more likely to be more negative. Thus the excess chemical potential will decrease (become larger in magnitude, but more negative). As the density is further increased the added particles will land on the steeply rising positive part of the potential, and thus more often ΔE will be large and positive, leading to $-\beta \Delta E < 0$, an exponential less than unity, and thus a positive excess chemical potential. Thus, as a function of density we would expect a minimum in the excess chemical potential.

One of the reasons that understanding thermodynamic quantities such as the chemical potential is difficult is that there is no measurement device that directly measures such quantities. For example, the measurement of temperature is rather complicated and subtle. It relies on finding a relation between temperature and some physically measurable quantity such as the volume of mercury in a tube. Then we havene quantify the relation. As discussed in Chapter 2, we rely

on the ideal gas law to determine the temperature from mechanical measurements on enclosed gases. Thus, the measurement of temperature does not usually provide much insight into the role of temperature in nature. In Section 4.9 we discussed the demon algorithm, which is helpful in understanding how temperature controls the flow of energy between two systems. We can allow the demon to exchange particles as well as energy and then obtain some further insight into the chemical potential.

A demon which can exchange both energy and particles will follow the Gibbs distribution (4.141):

$$P(N_d, E_d) = \frac{1}{\mathcal{Z}} e^{-\beta(E_d - \mu N_d)}, \qquad \text{(Gibbs distribution)} \qquad (7.5)$$

which tells us the probability of the demon having energy E_d and N_d particles. Here $\mathcal{Z}$ is the grand canonical partition function. We can think of the demon as a system in equilibrium with our system of interest that acts as a heat path. We can measure both temperature and chemical potential by plotting the natural log of $P(N_d, E_d)$ versus E_d at fixed N_d and versus N_d at fixed E_d. In a simulation particles are transferred to and from the demon. When a particle is transferred the energy of the system we are simulating may change. If that happens, then the transfer is only accepted if the energy is decreased (the lost energy is given to the demon) or the energy is increased and the demon has enough energy to supply this increased energy. As the simulation is run the demon and system come to equilibrium and the demon's energy and particle number distribution follows (7.5). The applet/application at `<stp.clarku.edu/simulations/latticedemon.html>` implements this algorithm, which is described in an article in the American Journal of Physics.

To understand how the demon algorithm helps us understand the chemical potential, consider how the algorithm with only energy exchange helps us understand temperature. Imagine a demon distribution such that energy flows into and out of the demon very easily. Under what circumstances would this happen? What can you say about the slope of $\ln P(E_d)$ versus E_d? The answer to the latter question is that the slope would be relatively shallow or small and negative, because many demon energies would have nearly the same probability for occurring as energy can easily come into and out of the demon. The answer to the first question is that the system would be at a high temperature if energy easily flows into and out of the system, because we associate high temperature with large energy fluctuations (the specific heat is proportional to the energy fluctuations, and specific heat increases with temperature), and thus the system energy can fluctuate easily by giving and taking energy from the demon. If the system is at a low temperature, then a similar argument shows that we would expect a steep negative slope for $\ln P(E_d)$ versus E_d. This behavior is independent of the system size because the exchange of energy is a local event between the demon and a small piece of the system for most materials. This independence of system size explains why temperature is an intensive quantity.

Now consider the situation for particle transfers. From (7.5) we see that for particle transfers μ/kT plays the role of $1/kT$ for energy. Because μ/kT depends on two thermodynamic variables, it is more subtle to discuss how the chemical potential behaves independent of temperature. We will assume in what follows that the total energy of the system plus the demon is adjusted so that the temperature is the same for any two situations we compare, and that the difference in total energy does not effect our conclusions. These assumptions have been shown to be valid by actually doing the simulations.

For ease of understanding consider one of the simplest systems, a one-dimensional ideal gas,

which has a two-dimensional phase space, one dimension for location and one for momentum. Further assume that phase space is divided into cells of area of the order of Planck's constant. This is the standard assumption we used in Chapter 6. Begin with a dilute system and let us see what we can infer by thinking about the behavior of the demon. We know that the chemical potential should be negative, which would mean a negative slope for $\ln P(N_d)$ versus N_d, which means that the probability of the demon having N_d particles decreases as N_d increases. Why is this? Imagine phase space in this system. Particles move in and out of the two-dimensional phase space. Because the total energy is fixed, the particles will be restricted between some upper positive momentum and an equivalent negative momentum. Imagine we begin with the particles randomly placed in phase space so that the total energy ($\sum_i p_i^2/2m$) is some fixed specified value. If the system is dilute, then there are many cells in phase space near zero momentum to place particles. As soon as any particle from one of the higher momentum states comes into the demon, it will give the demon lots of energy which can then be used to move particles back to the system at a lower momentum. Once this happens, it will become very difficult for the demon to ever move a particle back to a high momentum state. Thus, the demon will tend to always have enough energy to move particles to the system as soon as it gets them. Thus, the probability of the demon having N_d particles will decrease with N_d and the chemical potential will be negative. This argument is a concrete illustration of how entropy (which depends on the vast number of spots in phase space to place particles) is controlling the situation.

In analytical calculations we add a factor of $1/N!$ in the partition function to account for indistinguishability. This factor tells us that the state with particle i in one cell and particle j in another cell in phase space is the same as swapping the particles and thus should not be counted twice. However, the factor of $1/N!$ counts states where both particles are in the same spot in phase space, which is not allowed in the simulation we just described. How should the analytically calculated chemical potential compare with the computed one which does not allow multiple occupancy? In very large dilute systems the difference is negligible, which is why we don't need to be more careful in the analytical calculation. However, in a simulation the system can be small enough for such finite size effects to be detectable. Because multiple occupancy is not allowed, we expect that occasionally the demon will try to move a particle to the system and fail because there is already a particle there. The demon will tend to have more particles than it would have if it simulated exactly the analytically approach. Thus, in the simulation we will obtain a larger chemical potential (less negative) than that found analytically, and that is what is found. We can change the simulation to allow multiple occupancy. This would then make it easier for the demon to add particles to the system and we would expect the chemical potential to decrease (become more negative), and that is what happens.

A system which excludes multiple occupancy in phase space is a simulation of a system of fermions. At very low densities this restriction has little effect, and fermions and bosons behave similarly at low densities. Once the density becomes high enough that the restriction to single occupancy in phase space becomes important, then the fermion chemical potential will increase relative to the boson chemical potential. For the small systems that we can simulate, at high enough densities the demon will eventually start taking in more and more particles so that $\ln P(N_d)$ versus N_d is no longer linear and the initial slope becomes positive indicating a positive chemical potential, which is what we expect for dense Fermi systems.

Let us return to dilute systems and discuss the effects of adding an inter-particle potential. First, let's simply add a hard core repulsion so that particles can not be in the same cell in phase

space as before, but also no two particles can have the same location. This clearly makes it more difficult for the demon to return particles to the system and we would expect the chemical potential to increase (become less negative) compared to the non-interacting system. If we add an attractive square well for two particles that are next to each other, then for some particle additions this lowers the energy of the system giving the demon more energy making it easier to find other places in phase space to add particles. The result is a lowering of the chemical potential compared to the hard core system. These trends can be observed in the simulations.

The discussion so far provides some intuition about the behavior of the chemical potential. The conclusions are sometimes similar to the naive idea that one simply looks at whether an added particle adds or subtracts energy to determine if the chemical potential is positive or negative, respectively. Our discussion shows that the situation is more subtle, and it is better to discuss changes in the chemical potential as the system characteristics are changed, and that thinking about how easy it is for one system such as the demon to exchange particles with another system is what is important. Just as temperature is not a measurement of energy, but rather a measurement of the ability to transfer energy, chemical potential is not a measurement of an additional particle's energy but rather a measure of the ease of transferring particles.

7.2 Equilibrium Between Phases

Every substance can exist in qualitatively different forms, called *phases*. For example, most substances exist in the form of a gas, liquid, or a solid. The most familiar substance of this type is water which exists in the form of water vapor, liquid water, and ice.[1] The existence of different phases depends on the pressure and temperature and the transition of one phase to another occurs at particular temperatures and pressures. For example, water is a liquid at room temperature and atmospheric pressure, but if it is cooled below 273.15 K, it eventually solidifies , and if heated above 373.15 K it vaporizes.[2] At each of these temperatures, water undergoes dramatic changes in its properties, and we say that a *phase transition* occurs. The existence of distinct phases must be the result of the intermolecular interactions, yet these interactions are identical microscopically in all phases. Why is the effect of the interactions so different macroscopically? The answer is the existence of *cooperative effects*, which we discussed briefly in Section 5.5.1 and will discuss in more detail in Chapter 8.

7.2.1 Equilibrium conditions

Before we discuss the role of intermolecular interactions, we obtain the conditions for equilibrium between two phases of a substance consisting of a single type of molecule. We discuss mixtures of more than one substance in Section 7.4. For example, the phases might be a solid and a liquid or a liquid and a gas. We know that for any two bodies in thermodynamic equilibrium, the temperatures T_1 and T_2 of the two phases must be equal:

$$T_1 = T_2. \tag{7.6}$$

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[1] All of the natural ice on earth is hexagonal, as manifested in six-cornered snow flakes. At lower temperatures and at pressures above about 10^8 Pa, many other ice phases with different crystalline structures exist.

[2] If you were to place a thermometer in a perfectly pure boiling water, the thermometer would not read $100°$ C. A few degrees of superheating is almost inevitable. Superheating and supercooling are discussed in Section xx.

We also know that the pressure of the two phases must be equal,

$$P_1 = P_2, \tag{7.7}$$

because the forces exerted by the two phases on each other at their surface of contact must be equal and opposite.

We show in the following that because the number of particles N_1 and N_2 of each species can vary, the chemical potentials of the two phases must be equal:

$$\mu_1 = \mu_2. \tag{7.8}$$

Because the temperatures and pressures are uniform, we can write (7.8) as

$$\mu_1(T, P) = \mu_2(T, P). \tag{7.9}$$

Note that because $\mu(T, P) = g(T, P)$, where g is the Gibbs free energy per particle, we can equivalently write the equilibrium condition (7.9) as

$$g_1(T, P) = g_2(T, P). \tag{7.10}$$

We now derive the equilibrium condition (7.10) for the chemical potential. Because T and P are well defined quantities for a system of two phases, the natural thermodynamic potential is the Gibbs free energy $G = E - TS + PV$. Let N_i be the number of particles in phase i and $g_i(T, P)$ be the Gibbs free energy per particle in phase i. Then G can be written as

$$G = N_1 g_1 + N_2 g_2. \tag{7.11}$$

Conservation of matter implies that the total number of particles remains constant:

$$N = N_1 + N_2 = \text{constant}. \tag{7.12}$$

Suppose we let N_1 vary. Because G is a minimum in equilibrium, we have

$$dG = 0 = g_1 dN_1 + g_2 dN_2 = (g_1 - g_2)dN_1, \tag{7.13}$$

with $dN_2 = -dN_1$. Hence, we find that a necessary condition for equilibrium is

$$g_1(T, P) = g_2(T, P). \tag{7.14}$$

7.2.2 Clausius-Clapeyron equation

Usually, the thermodynamics of a simple substance depends on two variables, for example, T and P. However, if two phases of a substance are to coexist in equilibrium, then only one variable can be chosen freely. For example, the pressure and temperature of a given amount of liquid water may be chosen at will, but if liquid water is in equilibrium with its vapor, then the pressure of the water equals the vapor pressure, which is a unique function of the temperature. If the pressure is increased above the vapor pressure, the vapor will condense. If the pressure is decreased below the vapor pressure, the liquid will evaporate.
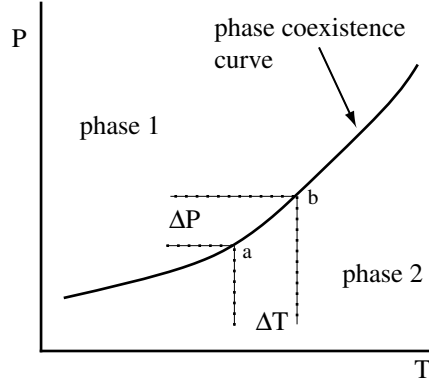
Figure 7.1: Derivation of the Clausius-Clapeyron equation.

In general, g_i is a well-defined function that is characteristic of the particular phase i. If T and P are such that $g_1 < g_2$, then the minimum value of G corresponds to all N particles in phase 1 and $G = Ng_1$. If T and P are such that $g_1 > g_2$, then the minimum value of G corresponds to all N particles in phase 2 so that $G = Ng_2$. If T and P are such that $g_1 = g_2$, then any number N_1 of particles in phase 1 can coexist in equilibrium with $N_2 = N - N_1$ of particles in phase 2. The locus of points (T, P) such that $g_1 = g_2$ is called the *phase coexistence curve*.

We now show that the equilibrium condition (7.10) leads to a differential equation for the slope of the phase coexistence curve. Consider two points on the phase coexistence curve, for example, point a at T, P and nearby point b at $T + \Delta T$ and $P + \Delta P$ (see Figure 7.1). The equilibrium condition (7.10) implies that $g_1(T, P) = g_2(T, P)$ and $g_1(T + \Delta T, P + \Delta P) = g_2(T + \Delta T, P + \Delta P)$. If we write $g(T + \Delta T, P + \Delta P) = g(T, P) + \Delta g$, we have

$$\Delta g_1 = \Delta g_2, \tag{7.15}$$

or using (2.158)

$$- s_1 \Delta T + v_1 \Delta P = -s_2 \Delta T + v_2 \Delta P. \tag{7.16}$$

Therefore,

$$\frac{\Delta P}{\Delta T} = \frac{s_2 - s_1}{v_2 - v_1} = \frac{\Delta s}{\Delta v}. \qquad \text{(Clausius-Clapeyron equation)} \tag{7.17}$$

The relation (7.17) is called the *Clausius-Clapeyron equation*. It relates the slope of the phase coexistence curve at the point T, P to the entropy change Δs per particle and the volume change Δv per particle when the curve is crossed at this point. For N particles we have $\Delta S = N\Delta s$ and $\Delta V = N\Delta v$, and hence (7.17) can be expressed as

$$\frac{dP}{dT} = \frac{\Delta S}{\Delta V}. \tag{7.18}$$

From the relation (2.200), we can write

$$T\frac{\partial S}{\partial V} = \frac{\partial E}{\partial V} + P. \tag{7.19}$$

At the phase coexistence curve for a given T and P, we can write

$$T\frac{S_2 - S_1}{V_2 - V_1} = \frac{E_2 - E_1}{V_2 - V_1} + P, \tag{7.20}$$

or

$$T(S_2 - S_1) = (E_2 - E_1) + P(V_2 - V_1). \tag{7.21}$$

Because the enthalpy $H = U + PV$, it follows that

$$L_{2\to1} \equiv T(S_2 - S_1) = H_2 - H_1. \tag{7.22}$$

The energy L required to melt a given amount of a solid is called the *enthalpy of fusion*.[3] The enthalpy of fusion is related to the difference in entropies of the liquid and the solid phase and is given by

$$L_{\text{fusion}} = H_{\text{liquid}} - H_{\text{solid}} = T(S_{\text{liquid}} - S_{\text{solid}}), \tag{7.23}$$

where T is the melting temperature at the given pressure. Similarly, the equilibrium of a vapor and liquid leads to the enthalpy of vaporization

$$\ell_{\text{vaporization}} = h_{\text{vapor}} - h_{\text{liquid}}. \tag{7.24}$$

where h is the specific enthalpy. The enthalpy of sublimation associated with the equilibrium of vapor and solid is given by

$$\ell_{\text{sublimation}} = h_{\text{vapor}} - h_{\text{solid}}. \tag{7.25}$$

We say that if there is a discontinuity in the entropy and the volume at the transition, the transition is *discontinuous* or *first-order* and $L = \Delta H = T\Delta S$. Thus the Clausius-Clapeyron equation can be expressed in the form

$$\frac{dP}{dT} = \frac{L}{T\Delta V} = \frac{\ell}{T\Delta v}. \tag{7.26}$$

7.2.3 Simple phase diagrams

A typical phase diagram for a simple substance is shown in Figure 7.2(a). The lines represent the phase coexistence curves between the solid and liquid phases, the solid and vapor phases, and the liquid and vapor phases. The condition $g_1 = g_2 = g_3$ for the coexistence of all three phases leads to a unique temperature and pressure that defines the *triple point*. This unique property of the triple point makes the triple point of water a good choice for a readily reproducible temperature reference point. If we move along the liquid-gas coexistence curve toward higher temperatures, the two phases become more and more alike. At the *critical point*, the liquid-gas coexistence curve ends, and the volume change ΔV between a given amount of liquid and gas has approached zero. Beyond the critical point there is no distinction between a gas and a liquid, and there exists only a dense fluid phase. Note that a system can cross the phase boundary from its solid phase

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[3]The more familiar name is *latent heat of fusion*. As we discussed in Chapter 2, latent heat is an archaic term and is a relic from the time it was thought that there were two kinds of heat: sensible heat, the kind you can feel, and latent heat, the kind you cannot.

directly to its vapor without passing through a liquid, a transformation known as *sublimination.* An important commercial process that exploits this transformation is called freeze drying.

For most substances the slope of the solid-liquid coexistence curve is positive. The Clausius-Clapeyron equation shows that this positive slope is due to the fact that most substances expand on melting and therefore have $\Delta V > 0$. Water is an important exception and contracts when it melts. Hence, for water the slope of the melting curve is negative (see Figure 7.2)b)).

(a)
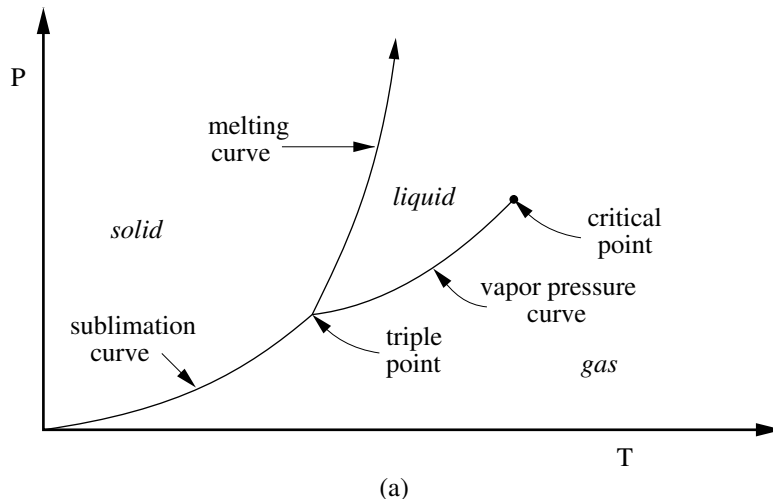
Figure 7.2: (a) Typical phase diagram of simple substances, for example, carbon dioxide. The triple point of CO_2 is at illustrates the more common forward slope of the melting point line. Notice that the triple point of carbon dioxide is well above one atmosphere. Notice also that at 1 atm carbon dioxide can only be the solid or the gas. Liquid carbon dioxide does not exist at 1 atm. Dry ice (solid carbon dioxide) has a temperature of $-78.5°$ at room pressure which is why you can get a serious burn (actually frostbite) from holding it in your hands. (b) Phase diagram of water which expands on freezing. [xx not done xx]

Example 7.1. Why is the triple-point temperature of water, $T_{\text{tp}} = 273.16\,\text{K}$ higher than the ice-point temperature, $T_{\text{ice}} = 273.15\,K$, especially given that at both temperatures ice and water are in equilibrium?

Solution. The triple-point temperature T_3 is the temperature at which water vapor, liquid water, and ice are in equilibrium. At $T = T_3$, the vapor pressure of water equals the sublimation pressure of ice which is equal to $P_3 = 611\,\text{Pa}$. The ice point is defined as the temperature at which pure ice and air-saturated liquid water are in equilibrium under a total pressure of $1\,\text{atm} = 1.013 \times 10^5\,\text{Pa}$. Hence, the triple-point temperature and the ice point temperature differ for two reasons – the total pressure is different and the liquid phase is not pure water.

Let us find the equilibrium temperature of ice and pure water when the pressure is increased

from the triple point to a pressure of 1 atm. From (7.26), we have for liquid-solid equilibrium

$$\Delta T = \frac{T(v_{\text{solid}} - v_{\text{liquid}})}{\ell_{\text{fusion}}} \Delta P. \tag{7.27}$$

Because the changes in T and P are very small, we can assume that all the terms in the coefficient of ΔP are very small. Let T_{ice} be the equilibrium temperature of ice and pure water. If we integrate the left-hand side of (7.27) from T_3 to T_{ice} and the right side from P_3 to atmospheric pressure P, we obtain

$$T_{\text{ice}} - T_3 = \frac{T(v_{\text{solid}} - v_{\text{liquid}})}{l_{\text{fusion}}} (P - P_3). \tag{7.28}$$

To three significant figures, $T = 273\,\text{K}$, $P - P_3 = 1.01 \times 10^5\,\text{Pa}$, $v_{\text{solid}} = 1.09 \times 10^{-3}\,\text{m}^3/\text{kg}$, $v_{\text{liquid}} = 1.00 \times 10^{-3}\,\text{m}^3/\text{kg}$, and $\ell_{\text{fusion}} = 3.34 \times 10^5\,\text{J/kg}$. If we substitute these values into (7.28), we find $T_{\text{ice}} - T_3 = -0.0075\,\text{K}$. That is, the ice point temperature of pure water is $0.0075\,\text{K}$ below the temperature of the triple point. Hence, the effect of the dissolved air is to lower the temperature by $0.0023\,\text{K}$ at which the liquid phase is in equilibrium with pure ice at atmospheric pressure below the equilibrium temperature for pure water.

7.2.4 Pressure dependence of the melting point

We consider the equilibrium between ice and water as an example of the pressure dependence of the melting point. The enthalpy of fusion of water at $0°C$ is

$$\ell_{\text{fusion}} = 3.35 \times 10^5\,\text{J/kg}. \tag{7.29}$$

The specific volumes in the solid and liquid phase are

$$v_{\text{solid}} = 1.09070 \times 10^{-3}\,\text{m}^3/\text{kg}, \text{and} \quad v_{\text{liquid}} = 1.00013 \times 10^{-3}\,\text{m}^3/\text{kg}, \tag{7.30}$$

so that $\Delta v = v_{\text{liquid}} - v_{\text{solid}} = -0.0906 \times 10^{-3}\,\text{m}^3/\text{kg}$. If we substitutes these values of ℓ and Δv in (7.26), we find

$$\frac{dP}{dT} = -\frac{3.35 \times 10^5}{273.2 \times 9.06 \times 10^{-5}} = -1.35 \times 10^7\,\text{Pa/K}. \tag{7.31}$$

From (7.31) we see that an increase in pressure of $1.35 \times 10^7\,\text{Pa}$ or 133 atmospheres lowers the melting point by $1°C$.

The lowering of the melting point of ice under pressure is responsible for the motion of glaciers. The deeper parts of a glacier melt under the weight of ice on top allowing the bottom of a glacier to flow. The bottom freezes again when the pressure decreases.

Some textbooks state that ice skaters are able to skate freely because the pressure of the ice skates lowers the melting point of the ice and allows ice skaters to skate on a thin film of water between the blade and the ice. As soon as the pressure is released, the water refreezes. From the above example we see that if the ice is at $-1°C$, then the pressure due to the skates must be 135 atmospheres for bulk melting to occur. However, even for extremely narrow skates and a large person, the skates do not exert enough pressure to cause this phenomenon. As an example, we

take the contact area of the blades to be $10^{-4}\,\text{m}^2$ and the mass of the skater to be 100 kg. Then the pressure is given by

$$P = \frac{F}{A} = \frac{mg}{A} \approx 10^7\,\text{Pa} \approx 100\,\text{atm}. \tag{7.32}$$

Given that on many winter days, the temperature is lower than a fraction of a degree below freezing, there must be a mechanism different than pressure-induced melting that is responsible for ice skating. And how do we explain the slide of a hockey puck, which has a large surface area and a small weight? The answer appears to be the existence of surface melting, that is, the existence of a layer of liquid water on the surface of ice that exists independently of the pressure of an ice skate (see the references).

7.2.5   Pressure dependence of the boiling point

Because Δv is always positive for the transformation of liquid to gas, increasing the pressure on a liquid always increases the boiling point. For water the enthalpy of vaporization is

$$\ell_{\text{vaporization}} = 2.257 \times 10^6\,\text{J/kg}. \tag{7.33}$$

The specific volumes in the liquid and gas phase at $T = 373.15\,\text{K}$ and $P = 1\,\text{atm}$ are

$$v_{\text{liquid}} = 1.043 \times 10^{-3}\,\text{m}^3/\text{kg} \text{ and } v_{\text{gas}} = 1.673\,\text{m}^3/\text{kg}. \tag{7.34}$$

Hence from (7.26) we have

$$\frac{dP}{dT} = \frac{2.257 \times 10^6}{373.15 \times 1.672} = 3.62 \times 10^3\,\text{Pa/K}. \tag{7.35}$$

7.2.6   The vapor pressure curve

The Clausius-Clapeyron equation for the vapor pressure curve can be approximated by neglecting the specific volume of the liquid in comparison to the gas, $\Delta v = v_{\text{gas}} - v_{\text{liquid}} \approx v_{\text{gas}}$. From (7.34) we see that for water at its normal boiling point, this approximation introduces an error of less than 0.1 per cent. If we assume that the vapor behaves like an ideal gas, we have that $v_{\text{gas}} = RT/P$ for one mole of the gas. With these approximations, the Clausius-Clapeyron equation can be written as

$$\frac{dP}{P} = \ell\frac{dT}{RT^2}. \tag{7.36}$$

If we also assume that ℓ is approximately temperature independent, we can integrate (7.36) to find

$$\ln P(T) = -\frac{\ell}{RT} + \text{constant} \tag{7.37}$$

or

$$P(T) \approx P_0 e^{-\ell/RT}, \tag{7.38}$$

where P_0 is a constant.

Example 7.2. In the vicinity of the triple point the liquid-vapor coexistence curve of liquid ammonia can be represented by $\ln P = 24.38 - 3063/T$, where the pressure is given in Pascals. The vapor pressure of solid ammonia is $\ln P = 27.92 - 3754/T$. What are the temperature and pressure at the triple point? What are the enthalpies of sublimation and vaporization? What is the enthalpy of fusion at the triple point?

Solution. At the triple point, $P_{\text{solid}} = P_{\text{liquid}}$ or $24.38 - 3063/T = 27.92 - 3754/T$. The solution is $T = 691/3.54 = 195.2\,\text{K}$. The corresponding pressure is $8.7\,\text{Pa}$. The relation (7.37), $\ln P = -\ell/RT + \text{constant}$, can be used to find the enthalpy of sublimation and vaporization of ammonia at the triple point. We have $\ell_{\text{sublimation}} = 3754R = 3.12 \times 10^4\,\text{J/mol}$ and $\ell_{\text{vaporization}} = 3063R = 2.55 \times 10^4\,\text{J/mol}$. The enthalpy of melting satisfies the relation $\ell_{\text{sublimation}} = \ell_{\text{vaporization}} + \ell_{\text{fusion}}$. Hence, $\ell_{\text{fusion}} = (3.12 - 2.55) \times 10^4 = 5.74 \times 10^3\,\text{J/mol}$.

7.3   The van der Waals Equation

To expand our understanding of phase equilibrium we consider an explicit model. Within the context of thermodynamics such a model takes the form of equations of state. Here we explore some of the qualitative features of the van der Waals equations of state, which we repeat here for convenience:

$$P = \frac{NkT}{V - Nb} - \frac{aN^2}{V^2}, \tag{7.39}$$

$$E = \frac{3}{2}NkT - \frac{aN^2}{V}. \tag{7.40}$$

As we have mentioned, the quantity b represents the effective volume of a given particle and the term $a(N/V)^2 = a\rho^2$ accounts for the attractive forces between particles. The parameters a and b depend on the nature of the molecule. For small molecules such as N_2 and H_2O, a reasonable value of b is about $6 \times 10^{-20}\,\text{m}^3 \approx (4\,\text{Å})^3$. For N_2 $a \approx 3 \times 10^{-49}\,\text{Jm}^3$.

Figure 7.3 shows a series of isotherms (curves for P versus V for fixed T) with temperature increasing as you move up the figure. Notice that at low temperatures there is a local minimum and a local maximum, but at high temperatures these local extrema disappear. This structure is characteristic of a system which has two phases at low temperature, but only one phase at high temperatures. The transition between the two phase region and the one phase region occurs at a specific temperature and can be identified with the critical temperature, T_c. At this temperature there is an inflection point at a specific value of the pressure and volume, which we call the critical pressure P_c and critical volume V_c. At this inflection point the first and second derivatives of P with respect to V vanish. Calculating the derivatives the critical values in terms of the parameters a and b in the van der Waals model are found to be

$$V_c/N = 3b, \tag{7.41}$$

$$P_c = \frac{a}{27b^2} \tag{7.42}$$

$$kT_c = \frac{8a}{27b} \tag{7.43}$$

$$E_c/N = \frac{a}{9b}. \tag{7.44}$$

Problem 7.1. Derive (7.41) through (7.44).

One of the features of this model is that it predicts the *law of corresponding states*, which states that the equations of state of all fluids are identical if the equations of state are written in terms of the ratio of each thermodynamic variable and its value at the critical point. This "law" is only approximately true in reality, but it is exactly true in the van der Waals model. To see this replace T, P, V and E in (7.39) and (7.40) with the reduced variables $t = T/T_c$, $p = P/P_c$, $v = V/V_c$ and $e = E/E_c$, and use (7.41)–(7.44). The results of these calculations are

$$p = \frac{8t}{3v - 1} - \frac{3}{v^2},\tag{7.45}$$

$$e = 4t - \frac{3}{v}..\tag{7.46}$$

Note that in (7.45) and (7.46) there is no reference to the material parameters a and b, and thus these equations are consistent with the law of corresponding states.

Problem 7.2. Derive (7.45) and (7.46).

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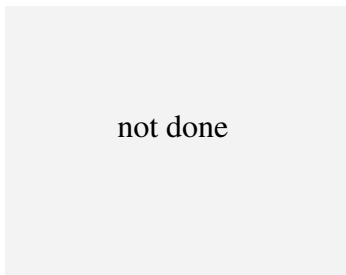
Figure 7.3: Isotherms for a van der Waals fluid.

How can we understand the different nature of the $P - V$ diagram curves above and below T_c. Above T_c there is a unique value of the volume for each value of pressure. This indicates that a substance at constant temperature can pass from a gas to a liquid and vice versa without passing through a phase transition where there would be a dramatic change in some thermodynamic property such as the compressibility. The van der Waals equation (7.45) at fixed p and t is a cubic equation in v. Above T_c two of the solutions are complex and thus unphysical, and there is only one physically relevant value of the volume which you can read off from Fig. 7.3. Below T_c there are three real valued solutions to the cubic, and thus a more sophisticated analysis is needed. What happens experimentally? Imagine that we are below T_c and at a low pressure such that the system is a gas. As we increase the pressure the volume will decrease, and then eventually droplets of liquid will appear. If there is gravity present then the liquid will condense out of the gas and fall to the bottom of the container. The liquid and gas will coexist in a closed container. This is called two-phase coexistence. The volume of the gas and the volume of the liquid are two points on the isotherm at the same pressure. How do we determine the pressure when the two phase coexistence begins?

Consider the isotherm for a temperature below T_c ($t < 1$) shown in Fig. 7.4. We want to find the value of p_1. To do this we consider the Gibb's free energy. We know that when a system has a choice between two different phases, it will be found in the phase with the lowest Gibb's free energy. For $p < p_1$ this will be the gas phase and for $p > p_1$ it will be a liquid. At p_1 the Gibb's free energy for the gas and liquid phases will be equal. Thus, we start with a general expression for the reduced Gibb's free energy integrated along an isotherm between two pressures p_1 and p_2:

$$g(p_2, t) = g(p_1, t) + \int_{p_1}^{p_2} \left(\frac{\partial g}{\partial p} \right)_t dp. \tag{7.47}$$

Because $(\frac{\partial g}{\partial p})_t = v$ we have

$$g(p_2, t) = g(p_1, t) + \int_{p_1}^{p_2} v \, dp. \tag{7.48}$$

At two phase coexistence the pressures p_1 and p_2 represent the pressures of the liquid and gas phases, respectively. They must be equal so that the two phases are in mechanical equilibrium. Also, the Gibb's free energies $g(p_2, t)$ and $g(p_1, t)$ must be equal for diffusive equilibrium. Thus, (7.48) becomes

$$0 = \int_{p_1}^{p_2} v \, dp. \tag{7.49}$$

To understand (7.49) turn Fig. 7.4 90° counter-clockwise so that the pressure axis is horizontal. Then the integral in (7.49) has a negative contribution from p_1 to the minimum value of p, a larger in magnitude positive contribution from the minimum p back to p_1. These two contributions give a positive value whose magnitude is the area of the bottom shaded region. Continuing the integral along the isotherm, the contribution from p_1 to the maximum value of p is positive, and the rest of the integral to $p_2 = p_1$ has a negative value of larger magnitude. These last two contributions give a negative value whose magnitude is the area of the top shaded region. The sum of the positive and negative values must be equal to zero, and thus the two areas must be equal. This construction is called the *Maxwell equal area construction*. These computations of the areas can be carried out numerically.

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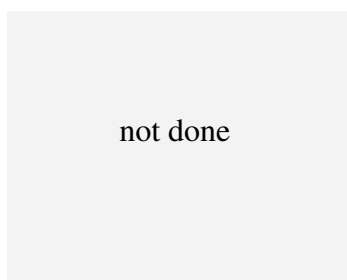
Figure 7.4: Maxwell equal area construction. The pressure P_1 where the two phase coexistence begins is determined so that the areas above and below the horizontal line in the figure are equal.

The Maxwell equal area construction is equivalent to integrating over v from v_1 to v_2 and

subtracting the area under the dashed line in Fig. 7.4:

$$\int_{v_1}^{v_2} pdv - p_1(v_2 - v_1) = 0. \tag{7.50}$$

Replacing p by the expression in (7.39) we have

$$\int_{v_1}^{v_2} \left(\frac{8t}{3v - 1} - \frac{3}{v^2} \right) dv - p_1(v_2 - v_1) = 0. \tag{7.51}$$

Carrying out the integral we have

$$\frac{8t}{3} \ln (3v_2 - 1) + \frac{3}{v_2} - \frac{8t}{3} \ln (3v_1 - 1) - \frac{3}{v_1} - p_1(v_2 - v_1) = 0, \tag{7.52}$$

or rearranging:

$$-\frac{8t}{3} \ln (3v_1 - 1) - \frac{3}{v_1} + p_1 v_1 = -\frac{8t}{3} \ln (3v_2 - 1) - \frac{3}{v_2} + p_2 v_2, \tag{7.53}$$

where we have replaced p_1 by p_2 on the right-hand side so that all quantities on the right-hand side are labeled by point 2 and all on the right by point 1. The expression on the left-hand side is the Gibbs free energy of the liquid up to a function of temperature, and the expression on the right-hand side is the Gibbs free energy of the gas up to the same function of temperature. The Gibb's free energy is a function of temperature and pressure. To convert the right or left-hand side of (7.53) to the proper functional form, we would need to solve (7.39) for v, however the result would be three possible solutions and a very messy formula that is not worth writing down. Instead we show plots of v versus p and g versus p for two temperatures in Fig. 7.5. Note that for $t < 1$ there is an interval for p where there are three values of v and g. At low pressure the system is a gas, as the pressure increases the volume decreases until it reaches point A on the graph of g or the last stable gas point A_g on the graph of v. At this point the system can do one of two things. It could remain a gas until point B. This corresponds to a supercooled gas, which is a metastable state. Such a state does not have the lowest free energy, but it is not unstable. The system can not be in the region from point B to point C because this is unstable. As can be seen from Fig. 7.5 in this region $\frac{\partial v}{\partial p} > 0$, which would mean the system would expand with an increase in pressure, which is clearly unphysical. Thus, an increase in pressure at point B would cause the system to immediately jump out of the metastable supercooled state into the stable liquid state. A similar process occurs as the pressure is lowered from a high pressure liquid. At point A_l the system could continue into the metastable superheated liquid until point C, at which point the system would jump up to the stable gas phase at higher volume. In actual experiments special precautions are needed to achieve the metastable states. Usually, one needs very pure substances and the pressure changes must be made very slowly. For temperatures above the critical temperature, the system can continuously change from a gas to a liquid with no phase transition as shown by the plots in Fig. 7.5 for $t = 1.1$. This is accomplished by increasing the pressure while maintaining a constant temperature.

Because $G = F + pV$, we have that the Helmholtz free energy in reduced units $f(v, t)$ is:

$$f(v, t) = c(T) - NkT(\ln (V - Nb) - \frac{aN^2}{V}, \tag{7.54}$$

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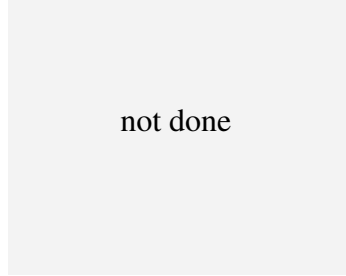
Figure 7.5: (a) Reduced volume and (b) reduced Gibbs free energy for two different temperatures of the van der Waals model.

where $c(T)$ is a function of temperature, which we can determine by using the fact that $e = \partial \beta f / \partial \beta$, where for the van der Waals model e is given by (7.46). We have

$$\beta F(V,T) = \beta f(T) - N \ln (V - Nb) - \beta \frac{aN^2}{V},, \tag{7.55}$$

and thus

$$E = \frac{\partial \beta F(V,T)}{\partial \beta} = \frac{\partial \beta f(T)}{\partial \beta} - \frac{aN^2}{V} = \frac{3}{2} NkT - \frac{aN^2}{V},, \tag{7.56}$$

or

$$\frac{\partial \beta f(T)}{\partial \beta} = \frac{3}{2} NkT,. \tag{7.57}$$

Integrating we obtain up to a constant, which we can set to zero:

$$f(T) = \frac{3}{2} NkT \ln kT. \tag{7.58}$$

Equations (7.54) and (7.58) lead to our final result for the Helmholtz free energy:

$$F(V,T) = \frac{3}{2} NkT \ln kT - NkT \ln (V - Nb) - \frac{aN^2}{V}. \tag{7.59}$$

which is at the end of the phase transition curve in a P-T diagram as shown in Fig. 7.2.

7.4   Mixtures and Chemical Reactions

So far we have considered systems with a single component, that is, all the particles were of the same species. What happens if we have a mixture of two or more types of particles? Consider a mixture of two species which do not chemically interact such as a binary alloy or binary fluid with a fixed number of particles N. Assume that the fraction of species A is $x_A = N_A/N$ and of B is $x_B = N_B/N = 1 - x_A$.

Figure 7.6 shows the chemical potential computed using (7.3)in a Monte Carlo simulation of a binary lattice gas. Notice that the chemical potential of A decreases as the fraction of A particles

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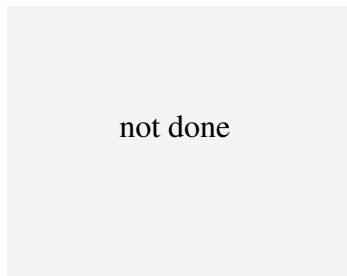
Figure 7.6: Chemical potential of A and B particles from a Monte Carlo simualtion on a 32×32 lattice with 800 particles such that neighboring like particles have an inter-particle energy of -1 in reduced units and neighboring unlike particles have an energy of $+1$. The temperature in reduced units is $T = 4$.

increases. This makes physical sense because as you increase the fraction of A particles you are more likely to encounter a neighboring A particle when inserting another A particle, which contributes negative energy. Similar reasoning explains why the chemical potential of the B particles increases as the fraction of A particles increases. Note at $x_A = 0.5$ the two chemical potentials are identical which must be the case because of the symmetry between A and B particles.

7.4.1 Chemical Reactions

Consider the a chemical reaction such as the production of water from hydrogen and oxygen:

$$2H_2 + O_2 \rightleftharpoons 2H_2O, \tag{7.60}$$
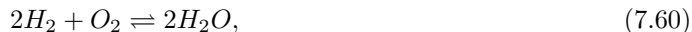
where the symbol $\rightleftharpoons$ indicates that the reaction can go either way depending on the circumstances. Equation (7.60) says that it takes two molecules of hydrogen and one molecule of oxygen to make two molecules of water. We rewrite (7.60) in the following general notation

$$-\nu_1 N_1 - \nu_2 N_2 \rightleftharpoons \nu_3 N_3, \tag{7.61}$$

where N_1 is the number of hydrogen molecules, N_2 the number of oxygen molecules and N_3 the number of water molecules. The *stoichiometric* coefficients are $\nu_1 = -2$, $\nu_2 = -1$ and $\nu_3 = 2$. The negative sign for ν_1 and ν_2 means that these molecules are on the left-hand side of the equation. Another way of saying this is that ν_i is positive for products and negative for reactants.

Now imagine we place some hydrogen, oxygen and water in a container and start the reaction, perhaps by supplying a spark. Think of the Hindenburg disaster. Some of the hydrogen and oxygen will be converted to water, such that the number of hydrogen molecules reduced will be twice that of oxygen, and the number of water molecules produced will be the same as the reduction of hydrogen molecules. Using our notation we have:

$$-\nu_1 dN_1 - \nu_2 dN_2 = \nu_3 dN_3. \tag{7.62}$$

We can also write:

$$\frac{dN_1}{\nu_1} = \frac{dN_2}{\nu_2} = \frac{dN_3}{\nu_3} \equiv d\xi, \tag{7.63}$$

where ξ is called the *extent of the reaction*, and we now see that the use of positive and negative values for the ν_i leads to all terms in (7.63) having the same form. If we define $\xi = 0$ at the initial time, then the solutions to the equations in (7.63) are

$$N_i(\xi) = N_i(0) + \nu_i \xi. \tag{7.64}$$

If we know how much of each substance we have initially and we measure how much we have of one substance at some later time, we can use (7.64) to determine ξ and then determine how much we have of all the other substances.

We can now determine the equilibrium conditions. We begin with (2.158) generalized to many components:

$$dG = -SdT + VdP + \sum_i \mu_i dN_i. \tag{7.65}$$

Using (7.63) we have

$$dG = -SdT + VdP + d\xi \sum_i \mu_i \nu_i. \tag{7.66}$$

At constant pressure and temperature and using the equilibrium condition $dG = 0$, we have

$$\sum_i \mu_i \nu_i = 0. \tag{7.67}$$

If the system is not in chemical equilibrium then the sum in (7.67) will not vanish. If the sum is negative then the reaction proceeds spontaneously toward the products(those molecules on the right hand side of the reaction equation) and if it is positive the reaction proceeds towards the reactants.

At this point we need to know something about how the chemical potential of a mixture of chemicals varies with the concentrations of the materials. For an *ideal* solution this variation is given by

$$\mu_i(T, p, N_i) = \mu_i^0(T, p) + kT \ln n_i, \tag{7.68}$$

where $\mu_i^0(T, p)$ is the chemical potential for a pure system made up of molecules labeled by the index i, and n_i is the fraction of molecules that are of the ith species. Note that the chemical potential only depends on the fraction of the ith species, and not on the individual fractions of the other molecules. This is in general not true. Ideal behavior occurs when the compounds that are mixed are chemically similar, in dilute solutions that do not involve electrolytes or in mixtures of gases at low pressure or high temperature. Combining (7.67) and (7.68) we obtain the *law of mass action*

$$\Delta G^0(T, p) \equiv \sum_i \mu_i^0(T, p)\nu_i = -kT \ln K, \tag{7.69}$$

where the equilibrium constant K is defined by

$$K \equiv \prod_i (n_i)^{\nu_i}. \tag{7.70}$$

For example, assuming ideal behavior , K for our example reaction would be

$$K \equiv \frac{(n_{H_2O})^2}{(n_{H_2})^2 n_{O_2}}. \tag{7.71}$$

If the mixture of compounds is not ideal then the n_i are replaced by compound *activities* a_i, which in general must be measured for each reaction.

What do we learn from this discussion? First, if K is much less than unity then at equilibrium the products will be present in correspondingly small amounts. One needs to know the chemical potentials $\mu_i^0(T, p)$ and even more empirical data for non-ideal reactions to determine the equilibrium constant, and thus predict equilibrium concentrations. Chemists accumulate data on the Gibbs free energy of formation of various molecular species under standard conditions from their elemental constituents. One can use this Gibbs free energy data instead of the chemical potentials, because these two sets of quantities differ only by the same constant reference energy.

How does the equilibrium constant depend on temperature? To determine this we need to find out how the chemical potentials of the pure substances change with temperature. Begin with the fact that the chemical potential is the Gibbs free energy per particle, which is related to the enthalpy by

$$g = \mu = h - Ts, \tag{7.72}$$

where the lower case quantities indicate intensive quantities. From the Gibbs-Duhem relation (2.162) we have that $-s = (\partial \mu / \partial T)_p$, and thus (7.72) becomes

$$\mu = h + T \left(\frac{\partial \mu}{\partial T} \right)_p, \tag{7.73}$$

or rearranging and dividing by T^2 gives

$$-\frac{\mu}{T^2} + \frac{1}{T} \left(\frac{\partial \mu}{\partial T} \right)_p = -\frac{h}{T^2}, \tag{7.74}$$

which can be re-written as

$$\frac{\partial}{\partial T} \left(\frac{\mu}{T} \right)_p = -\frac{h}{T^2}, \tag{7.75}$$

You can check (7.75) by taking the derivatives to obtain (7.74).

Dividing the law of mass action (7.69) by T, taking the temperature derivative and using (7.75) gives:

$$\left(\frac{\partial \ln K}{\partial T} \right)_{p, \{n_i\}} = \frac{1}{kT^2} \sum_i \nu_i h_i^0, \tag{7.76}$$

where h_i^0 is the specific enthalpy of the pure ith substance. Similar calculations lead to

$$\left(\frac{\partial \ln K}{\partial p} \right)_{T, \{n_i\}} = -\frac{1}{kT} \sum_i \nu_i v_i^0, \tag{7.77}$$

which gives us the change in K with pressure in terms of the specific volumes v_i^0. If one has sufficient empirical data for the enthalpies and volumes, one can determine K at any temperature and pressure.

Note that from (7.76) that if the right-hand side is positive we call this an endothermic reaction, which means that the reaction consumes thermal energy to produce the products. If we add energy to the system by heating, (7.76) indicates that $\ln K$ and thus K will increase, which in turn will consume at least some of the added energy, which in turn will cool the system down. Similar reasoning says that if the reaction is exothermic (gives off energy when producing products) then increasing the temperature will decrease the amount of the products and again energy will be absorbed. Cooling the system will result in energy being produced by the reactions so as to oppose the cooling. In all cases the system's behavior after a change in temperature is to oppose the change. Analogous behavior occurs for pressure changes. If we increase the pressure and the right-hand side of (7.77) is positive, this means the reactants have more volume than the products (recall that ν_i is negative for reactants and positive for products), and K increases. An increase in K leads to more products, which in turn lowers the volume thus decreasing the pressure. In all cases the system opposes changes. This general rule is called Le Chatelier's principle. It works just like Lenz's Law in magnetism.

Problem 7.3. Consider the exothermic reaction to produce ammonia:

$$N_2 + 3H_2 \rightleftharpoons 2NH_3. \tag{7.78}$$

To speed this reaction a chemist might increase the temperature. Use Le Chatelier's principle to determine whether this will tend to increase or decrease the amount of ammonia

Problem 7.4. Consider the same exothermic reaction in (7.78) and assume that the reactants and products are gases. Use Le Chatelier's principle to determine whether increasing the pressure will produce more or less ammonia.

7.5   Vocabulary

Maxwell relations
free expansion, Joule-Thomson process
phase coexistence curve, phase diagram
triple point, critical point
Clausius-Clapeyron equation
enthalpy of fusion, vaporization, and sublimation

Additional Problems

Problems	page
7.1 and 7.2	342
7.3 and 7.4	349

Table 7.1: Listing of inline problems.

Problem 7.5. Show that the three enthalpy (differences) are not independent, but are related by

$$\ell_{\text{fusion}} + \ell_{\text{vaporization}} = \ell_{\text{sublimation}}. \tag{7.79}$$

Interpret this relation in physical terms.

Problem 7.6. Show that

$$+\left(\frac{\partial C_P}{\partial P}\right)_T = -T\left(\frac{\partial^2 V}{\partial T^2}\right)_P, \tag{7.80}$$

and

$$\left(\frac{\partial C_V}{\partial V}\right)_T = T\left(\frac{\partial^2 P}{\partial T^2}\right)_V. \tag{7.81}$$

Problem 7.7. Show that

$$\frac{K_T}{K_S} = \frac{C_P}{C_V}, \tag{7.82}$$

where

$$K_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T \tag{7.83a}$$

$$K_S = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_S. \tag{7.83b}$$

K_S is the adiabatic compressibility. Use (7.83b) and (2.209) to obtain the relation

$$K_T - K_S = \frac{TV}{C_P}\alpha^2. \tag{7.84}$$

Problem 7.8. The inversion temperature for the Joule-Thomson effect is determined by the relation $(\partial T/\partial V)_P = T/V$ (see (??))). In Section **??** we showed that for low densities and high temperatures (low pressures) the inversion temperature is given by $kT_{\text{inv}} = 2a/b$. Show that at high pressures, T_{inv} is given by

$$kT_{\text{inv}} = \frac{2a}{9b}(2 \pm \sqrt{1 - 3b^2 P/a})^2. \tag{7.85}$$

Show that as $P \to 0$, $kT_{\text{inv}} = 2a/b$. For $P < a/3b^2$, there are two inversion points between which the derivative $(\partial T/\partial P)_H$ is positive. Outside this temperature interval the derivative is negative. For $P > a/3b^2$ there are no inversion points and $(\partial T/\partial P)_H < 0$ is negative everywhere. Find the pressure dependence of the inversion temperature for the Joule-Thomson effect.

Problem 7.9. Use the result (7.35) to estimate the boiling temperature of water at the height of the highest mountain in your geographical region.

Problem 7.10. A particular liquid boils at 127°C at a pressure of 1.06×10^5 Pa. Its enthalpy of vaporization is 5000 J/mol. At what temperature will it boil if the pressure is raised to 1.08×10^5 Pa?

Problem 7.11. A particular liquid boils at a temperature of 105°C at the bottom of a hill and at 95°C at the top of the hill. The enthalpy of vaporization is 1000 J/mol. What is the approximate height of the hill?

Suggestions for Further Reading

Daan Frenkel and Berend Smit, *Understanding Molecular Simulation*, Academic Press, San Diego (1996). This monograph discusses the Widom insertion method as well as many other useful algorithms.

Horia Metiu, *Physical Chemistry: Thermodynamics*, Taylor & Francis (2006). This text has a very clear and easy to follow discussion of the thermodynamics of chemical reactions, and provides many examples of how to explicitly use chemical data and the results presented in this chapter to draw further conclusions.

David Lind and Scott P. Sanders, *The Physics of Skiing: Skiing at the Triple Point*, Springer (2004). See Technote 1 for a discussion of the thermodynamics of phase changes.

Jan Tobochnik, Harvey Gould, and Jonathan Machta, "Understanding temperature and chemical potential using computer simulations," Am. J. Phys. **73** (8), 708–716 (2005).

James D. White, "The role of surface melting in ice skating," Phys. Teacher **30**, 495 (1992).

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