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Chapter 1

From Microscopic to Macroscopic Behavior

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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, 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 *microscopic* systems. An example of a question about a microscopic system is “What is the shape of the trajectory of the Earth in the solar system?” 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 might 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 iron lose its magnetism above a certain temperature?
8. 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?
9. How fast does a river current have to be before its flow changes from laminar to turbulent?
10. 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 4–8 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 9 and 10 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 1–8.

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 limit¹ 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

¹Of course, the efficiency cannot exceed 100%.

equivalent to the raising of a weight (see Problem 1.18). 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

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

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. 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 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

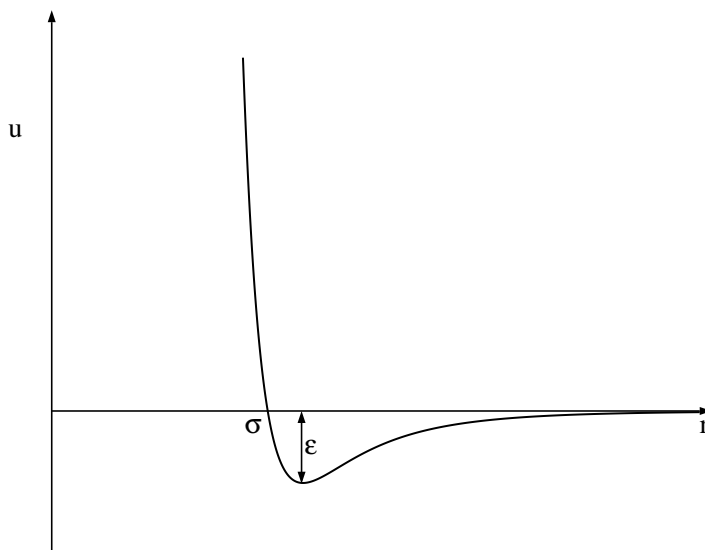


Figure 1.1: Plot of the Lennard-Jones potential $u(r)$, where r is the distance between the particles. Note that the potential is characterized by a length σ and an energy ϵ .

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*.²

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/choose.html. 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 a box is divided into three equal parts and N particles are placed at random in the middle third of the box.³ 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

²The nature of molecular dynamics is discussed in Chapter 8 of Gould, Tobochnik, and Christian.

³We 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 in the middle third of the box 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. The initial density $\rho = N/A$ is $\rho = 0.2$.

three parts and 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/approach.html implements this simulation. Give your answers to the following questions before you do the simulation.

- (a) Start the simulation with $N = 27$, $n_1 = 0$, $n_2 = N$, 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 ?
- (b) Suppose that we made a video of the motion of the particles considered in Problem 1.1a. Would you be able to tell if the video were played forward or backward for the various values of N ? Would you be willing to make an even bet about the direction of time? Does your conclusion about the direction of time become more certain as N increases?
- (c) After n_1 , n_2 , and n_3 become approximately equal for $N = 270$, reverse the time and continue the simulation. Reversing the time is equivalent to letting $t \rightarrow -t$ and changing the signs of all the velocities. Do the particles return to the middle third of the box? Do the simulation again, but let the particles move for a longer time before the time is reversed. What happens now?
- (d) From watching the motion of the particles, describe the nature of the boundary conditions that are used in the simulation.

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 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 particles do not interact with one another so that 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:

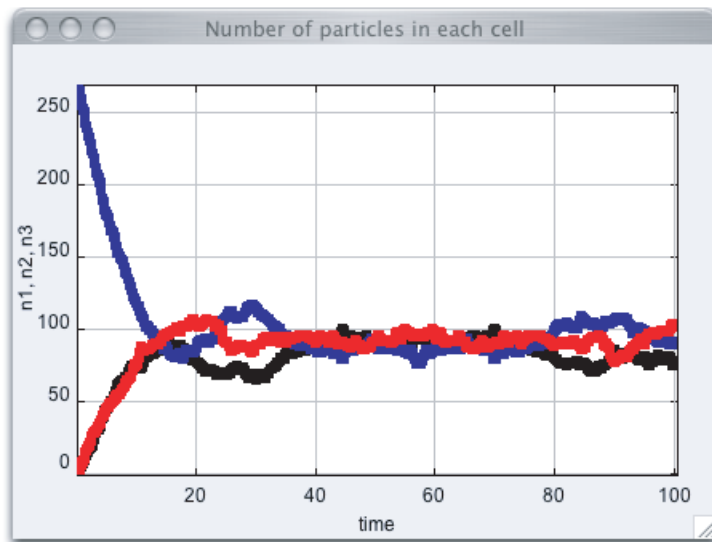


Figure 1.2: Evolution of the number of particles in each third of the box for $N = 270$. The particles were initially restricted to the middle third of the box. Toroidal boundary conditions are used in both directions. The initial velocities were assigned at random from a distribution corresponding to temperature $T = 5$. The time was reversed at $t \approx 59$. Does the system exhibit a direction of time?

1. Generate a random number r from a uniformly distributed set of random numbers in the unit interval $0 \leq r < 1$.
2. If $r \leq n/N$, move a particle from left to right, that is, let $n \rightarrow n - 1$; otherwise, move a particle from right to left, $n \rightarrow n + 1$.
3. Increase the “time” by 1.

Problem 1.2. Particles in a box

- (a) The applet at stp.clarku.edu/simulations/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 ever return to its initial state?

- (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 $\sigma^2 = \overline{(n - \bar{n})^2}$. What does σ measure? What would be its value if n were constant? How does σ depend on N ? How does the ratio σ/\bar{n} depend on N ? In what sense is equilibrium better defined as N increases?

From Problems 1.1 and 1.2 we see that after a system reaches equilibrium, the macroscopic quantities of interest become independent of time on the average, but 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.

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. 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*. 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	1	2
R L		
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 $n = 2$.

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	4	4/16
L	R	L	L	3		
L	L	R	L	3		
L	L	L	R	3		
R	R	L	L	2	6	6/16
R	L	R	L	2		
R	L	L	R	2		
L	R	R	L	2		
L	R	L	R	2		
L	L	R	R	2		
R	R	R	L	1	4	4/16
R	R	L	R	1		
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

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

We 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. We also observed

that 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.

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 earlier discussion, we 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 done 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 \bar{n} does not. If N is large, fluctuations corresponding to a very nonuniform distribution of the particles almost never occur, and the relative fluctuations, σ/\bar{n} become smaller as N is increased.

History independence. The properties of *equilibrium systems are independent of their history*. For example, \bar{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. However, 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.

Equal a priori probabilities. In our analysis of the probability of each macrostate in Problem 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 fascinating 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.

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.⁴ 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 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 cube of volume V and linear dimension L . The center of mass momentum of the particles is zero. Imagine a planar surface of area $A = L^2$ placed in the system and oriented perpendicular to the x -axis as shown in Figure 1.3. The pressure P can be defined as the force per unit area acting normal to the surface:

$$P = \frac{F_x}{A}. \quad (1.2)$$

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 (1.2) as

$$P = \frac{1}{A} \frac{d(mv_x)}{dt}. \quad (1.3)$$

From (1.3) we see that the pressure is the amount of momentum that crosses a unit area of the surface per unit time. We could use (1.3) to determine the pressure, but this relation uses information only from the fraction of particles that are crossing an arbitrary surface at a given time. Instead, our simulations will use the relation of the pressure to the *virial*, a quantity that involves all the particles in the system.⁵

⁴We 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.

⁵See Gould, Tobochnik, and Christian, Chapter 8. The relation of the pressure to the virial is usually considered in graduate courses in mechanics.

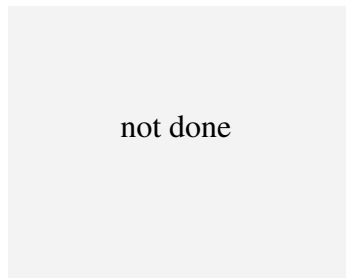


Figure 1.3: Imaginary plane perpendicular to the x -axis across which the momentum flux is evaluated.

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.

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.⁶ 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

Describe some of the simple thermometers with which you are familiar. On what physical principles do these thermometers operate? What requirements must a thermometer have?

Now let's 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, $E_d \rightarrow E_d + |\Delta E|$, 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, $E_d \rightarrow E_d - \Delta E$, and the trial configuration is accepted. Otherwise, the trial configuration is rejected and the configuration is not changed.

⁶In 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.

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.html 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 \bar{E}_d and the mean energy of the system \bar{E} . Why is $\bar{E} \neq E_0$?
- (b) What is \bar{e} , the mean energy per particle of the system? How do \bar{e} and \bar{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 \bar{e} and \bar{E}_d . What conclusion, if any, can you make?⁷
- (d) Run the simulation for several other values of the initial total energy E_0 and determine how \bar{e} depends on \bar{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 \bar{e} and \bar{E}_d for fixed 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 \bar{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 \bar{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?

⁷There are finite size effects that are order $1/N$.

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 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. 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 say “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.

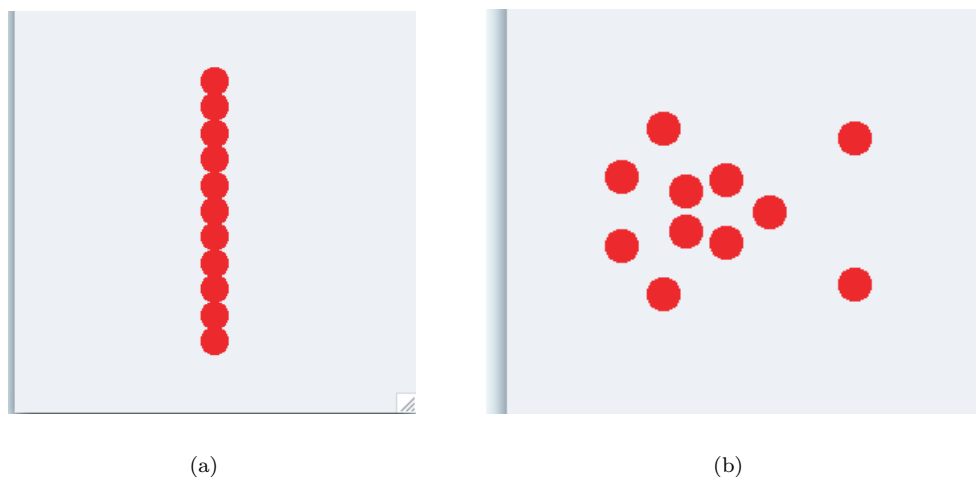


Figure 1.4: (a) A special initial condition for $N = 11$ particles such that their motion remains parallel indefinitely. (b) The positions of the particles at time $t = 8.0$ after the change in $v_x(6)$. The only change in the initial condition from part (a) is that $v_x(6)$ was changed from 1 to 1.000001.

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 $i = 1, \dots, 11$ (see Fig. 1.4(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. 1.4(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 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 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 physically 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 the interaction between the individual particles is very small. 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 black-body radiation (Section 6.9), electrons in metals (Section 6.10), the low temperature behavior of crystalline solids (Section 6.12), and a simple model of superfluidity (Section 6.11).

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 potential⁸ given in (1.1). This potential has a weak attractive tail at large r , reaches a minimum at $r = 2^{1/6}\sigma \approx 1.122\sigma$, 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. Nevertheless, 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

$$V(r) = \begin{cases} \infty & (r \leq \sigma) \\ 0 & (r > \sigma) \end{cases} \quad (1.4)$$

A system of particles interacting via (1.4) 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 (1.4) 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.

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?

⁸This potential is named after John Lennard-Jones, 1894–1954, a theoretical chemist and physicist at Cambridge University.

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*.⁹ 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 Schrodinger'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.

⁹Robert Fulghum, *All I Really Need to Know I Learned in Kindergarten*, Ballantine Books (2004).

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 in *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.

Vocabulary

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

Problems

Problems	page
1.1	7
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1.8	17
1.9	19

Table 1.3: Listing of inline problems.

Problem 1.10. (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 1.11. 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 1.12. In what contexts can we treat water as a fluid? In what context can water not be treated as a fluid?

Problem 1.13. How do you know that two objects are at the same temperature? How do you know that two bodies are at different temperatures?

Problem 1.14. Summarize your understanding of the properties of macroscopic systems.

Problem 1.15. Ask some of your friends why a ball falls when released above the Earth's surface. Explain why the answer "gravity" is not really an explanation.

Problem 1.16. 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 1.17. 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 1.18. Write a brief paragraph on the meaning 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 1.19. A box of glass beads is also an example of macroscopic systems if the number of beads is sufficiently large. In what ways such a system different than the macroscopic systems that we have discussed in this chapter?

Problem 1.20. 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.)

Appendix 1A: Mathematics Refresher

As discussed in Sec. 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 adopt one mathematical tool. Appendix 2B 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 1.21. 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 1.22. Calculate the following integrals:

$$\int_1^2 \frac{dx}{2x^2} \quad (1.5a)$$

$$\int_1^2 \frac{dx}{4x} \quad (1.5b)$$

$$\int_1^2 e^{3x} dx \quad (1.5c)$$

Problem 1.23. Calculate the partial derivative of $x^2 + xy + 3y^2$ with respect to x and y .

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 $a \approx 3/2$. What is the explanation for this power law behavior? 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).
- F. Reif, *Statistical Physics*, Volume 5 of the Berkeley Physics Series, McGraw-Hill (1967). This text was 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*, Bantam Books (1980). Although this popular book raises some important issues, it, like many other popular books/articles, 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/.

Chapter 2

Thermodynamic Concepts and Processes

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The study of temperature, energy, work, heating, entropy, and related macroscopic concepts comprise the field known as thermodynamics.

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.

¹A. Einstein, *Autobiographical Notes*, Open Court Publishing Company (1991).

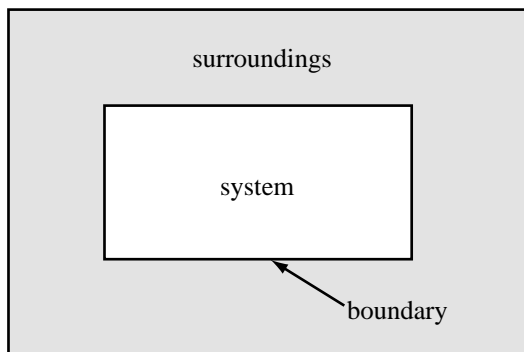


Figure 2.1: Schematic of a thermodynamic system.

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*. The boundary may be real or imaginary and may or may not be fixed in shape or volume. 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 a volume defined by an imaginary fixed boundary within a flowing liquid.

The remainder of the universe is called the *surroundings* (see Figure 2.1). 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 we can usually 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, it might be more relevant to take 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.

As in Chapter 1 the *macrostate* of a system refers to its macroscopic 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 at every point in the coffee to fully specify its state. 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 state through an infinity of possible ways. The final state 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 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 the 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 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. (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*.² 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. Of course, 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.

Now 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 enclosed in a glass tube. (That is, 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. Now 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

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.

²An insulating wall is sometimes called an *adiabatic wall*.

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

To use different thermometers quantitatively, 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

$$T(P) = aP + b, \quad (2.1)$$

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

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

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 $P \rightarrow 0$. 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.

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 pressure³) 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).

The *centigrade* temperature scale is defined as

$$T_{\text{centigrade}} = (T - T_{\text{ice}}) \times \frac{100}{T_{\text{steam}} - T_{\text{ice}}}, \quad (2.3)$$

³Standard atmospheric pressure is the pressure of the earth's atmosphere under normal conditions at sea level and is defined to be $1.013 \times 10^5 \text{ N/m}^2$. The SI unit of pressure is N/m^2 ; this unit has been given the name *pascal* (Pa).

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.

where T_{ice} and T_{steam} are the ice and steam points of water. By definition, there is 100 centigrade units between the ice and steam points. Because the centigrade unit defined in (2.3) is slightly smaller than the kelvin, it is convenient to define the *Celsius* scale:

$$T_{\text{Celsius}} = T - 273.15, \quad (2.4)$$

where T is the ideal gas temperature. Note that Celsius is not a new name for centigrade and 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 ($^{\circ}\text{C}$), but no degree sign is used with K for kelvin.

Problem 2.4. (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 normal 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 ?

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

2.5 Pressure Equation of State

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

$$P = f(T, \rho), \quad (2.5)$$

which 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:

$$P \propto \frac{1}{V}. \quad (\text{fixed temperature}) \quad (2.6)$$

or

$$PV = \text{constant}. \quad (2.7)$$

The relation (2.7) is sometimes called Boyle's law and was published by Robert Boyle in 1660. Note that the relation (2.7) is not a law of physics, but an empirical relation. An equation such as (2.7), which relates different states of a system all at the same temperature, is called an *isotherm*.

We also have the empirical relation

$$V \propto T. \quad (\text{fixed pressure}) \quad (2.8)$$

Some textbooks refer to (2.8) as Charles's law, but it should be called the *law of Gay-Lussac*.

We can express the two empirical relations, (2.7) and (2.8), 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

$$PV = NkT, \quad (\text{ideal gas pressure equation of state}) \quad (2.9)$$

where the constant of proportionality k in (2.9) is found experimentally to have the same value for all gases in the limit $P \rightarrow 0$. The value of k is

$$k = 1.38 \times 10^{-23} \text{ J/K}, \quad (\text{Boltzmann's constant}) \quad (2.10)$$

and is called *Boltzmann's constant*. The relation (2.9) will be derived using statistical mechanics in Section 4.5.

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 mole of gas. A (gram) mole of any substance consists of Avogadro's number, $N_A = 6.022 \times 10^{23}$, of that substance. Avogadro's number is defined so that 12.0 g of ^{12}C atoms contain exactly one mole of these atoms. If there are ν moles, then $N = \nu N_A$, and the ideal gas equation of state can be written as

$$PV = \nu N_A kT = \nu RT, \quad (2.11)$$

where

$$R = N_A k = 8.314 \text{ J/K mole} \quad (2.12)$$

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 phenomenological⁴ equation of state of a real gas with an interparticle interaction similar to the Lennard-Jones potential (see Figure 1.1). The

⁴Phenomenological is a word that we will use often. It means a description of the phenomena; such a description is not derived from fundamental considerations.

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

$$(P + \frac{N^2}{V^2}a)(V - Nb) = NkT, \quad (\text{van der Waals equation of state}) \quad (2.13)$$

where a and b are empirical constants characteristic of the 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 state of the system to another is called a thermodynamic *process*. Thermodynamics cannot determine how much time such a process will take, and the final state is independent of the amount of time it takes to reach equilibrium. It is convenient to consider thermodynamic processes where a system is taken from an initial to a final state by a continuous succession of intermediate states. 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 of the thermodynamic variables is changing. However, 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.

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 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 milk 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 state of the system is unchanged. In this case we can say that this process is reversible. Of course, 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? The process 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.

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. The piston is girded by rings so that no gas or liquid can escape (see Figure 2.2). 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 by⁵

$$dW = -(PA) dx = -P(Adx) = -PdV. \quad (2.15)$$

The negative sign in (2.15) 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 a 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

$$W_{1 \rightarrow 2} = - \int_{V_1}^{V_2} P(T, V) dV. \quad (\text{quasistatic process}) \quad (2.16)$$

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 is given by

$$\begin{aligned} W_{1 \rightarrow 2} &= -NkT \int_{V_1}^{V_2} \frac{dV}{V} \\ &= -NkT \ln \frac{V_2}{V_1}. \end{aligned} \quad (\text{ideal gas at constant temperature}) \quad (2.17)$$

⁵Equation (2.15) can be written as

$$\frac{dW}{dt} = -P \frac{dV}{dt}, \quad (2.14)$$

if the reader does not like the use of differentials. See Appendix 2B.

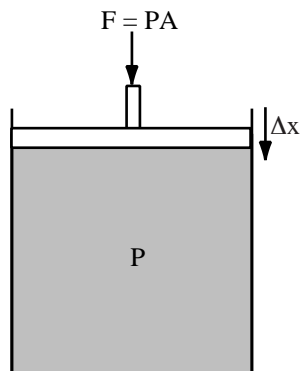


Figure 2.2: Example of work done on a fluid enclosed within a cylinder fitted with a piston when the latter moves a distance Δx .

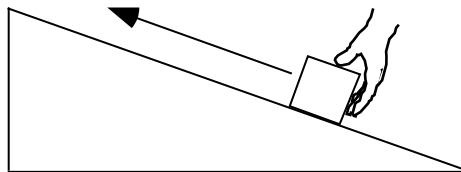


Figure 2.3: A block on an frictionless incline. The figure is taken from Loverude et al.

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 than PA . This difference is necessary if the piston is to move downward 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 downward 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 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. To refresh your understanding of work in the context of mechanics, look at Fig. 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

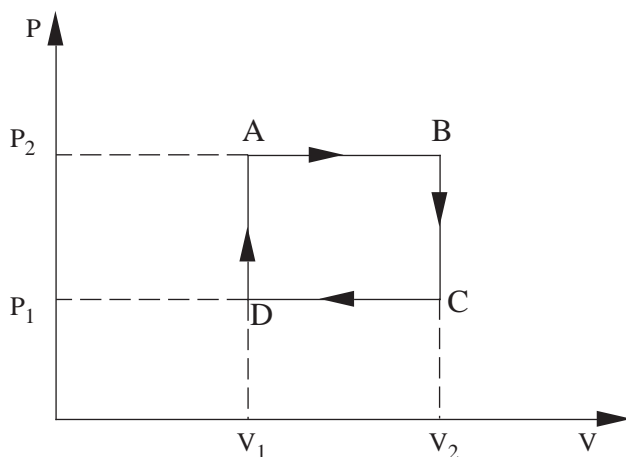


Figure 2.4: A simple cyclic process. What is the net work done on the gas?

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 $A \rightarrow B$, the work done on the gas is

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

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

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

The net work done on the gas is then

$$\begin{aligned} W_{\text{net}} &= W_{AB} + W_{CD} = -P_2(V_2 - V_1) - P_1(V_1 - V_2) \\ &= -(P_2 - P_1)(V_2 - V_1) < 0. \end{aligned} \quad (2.20)$$

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 ?

2.8 The First Law of Thermodynamics

If we think of a macroscopic system as consisting of a large number of 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.⁶

Consider a system enclosed by insulating walls – walls that prevent the system from being heated by the environment. Such a system is *thermally isolated*. A process in which the state of the system is changed only by work done on the system is called *adiabatic*. We know from overwhelming empirical evidence that the amount of work needed to change the state 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 state 1 to state 2, the work done on a thermally isolated system equals the change in E :

$$W = E_2 - E_1 = \Delta E. \quad (\text{adiabatic process}) \quad (2.21)$$

The quantity E is called the (internal) energy of the system.⁷ The internal energy in (2.21) is measured with respect to the center of mass.⁸ 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.

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

If we choose a convenient reference state as the zero of energy, then E has a unique value for each state 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.) In general, 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

$$\Delta E = W + Q. \quad (\text{first law of thermodynamics}) \quad (2.22)$$

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 (2.22) 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.

⁶These experiments were done by Joseph Black (1728–1799), Benjamin Thompson (Count Rumford) (1753–1814), especially Robert Mayer (1814–1878), and James Joule (1818–1889). Mayer and Joule are now recognized as the co-discoverers of the first law of thermodynamics, but Mayer received little recognition at the time of his work.

⁷Another common notation for the internal energy is U .

⁸Microscopically, 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.

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.

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 state of the system. These latter quantities depend on the thermodynamic process by which the system changed from one state to another.

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, electric field, magnetic field, etc). 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.⁹ 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.¹⁰ Take a small plastic container and add just enough water to it so that its temperature can be conveniently measured. Then 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 uncaps 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

⁹See page 20.

¹⁰See page 25.

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.

2.9 Energy Equation of State

In (2.9) we gave the pressure equation of state for an ideal gas. Now that we know that the internal energy also determines the state of a system of particles, we need to know how E depends on two of the three variables, T and P or V . 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

$$E = \frac{3}{2}NkT. \quad (\text{ideal gas energy equation of state}) \quad (2.23)$$

Note that the energy of an ideal gas is independent of its volume.

Similarly, the approximate thermal equation of state of a real gas corresponding to the pressure equation of state (2.13) is given by

$$E = \frac{3}{2}NkT - N\frac{N}{V}a. \quad (\text{van der Waals energy equation of state}) \quad (2.24)$$

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

Example 2.2. Work is done on an ideal gas at constant temperature. (a) What is the change in the energy¹¹ of the gas?

Solution.

Because the energy of an ideal gas depends only on the temperature (see (2.23)), there is no change in its internal energy for an *isothermal* (constant temperature) process. Hence, $\Delta E = 0 = Q + W$, and

$$Q = -W = NkT \ln \frac{V_2}{V_1}. \quad (\text{isothermal process for an ideal gas}) \quad (2.25)$$

¹¹We actually mean the internal energy, but the meaning should be clear from the context.

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 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.¹² The magnitude of the increase in temperature depends on the nature of the 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 that 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 due to heating Q , then the average heat capacity is given by the ratio

$$\text{average heat capacity} = \frac{Q}{T_2 - T_1}. \quad (2.26)$$

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

$$C_V = \left(\frac{\partial E}{\partial T} \right)_V. \quad (2.27)$$

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 (2.27) is at constant volume, and we will write $C_V = \partial E / \partial T$ if there is no ambiguity.¹³ (See Appendix 2B for a discussion of the mathematics of thermodynamics.)

Equation (2.27) together with (2.23) can be used to obtain the heat capacity at constant volume of a monatomic ideal gas:

$$C_V = \frac{3}{2}Nk. \quad (\text{monatomic ideal gas}) \quad (2.28)$$

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

¹²Can you think of a counterexample?

¹³Although the number of particles also is held constant, we will omit the subscript N in (2.27) and in other partial derivatives to reduce the number of subscripts.

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

$$H = E + PV. \quad (\text{enthalpy}) \quad (2.29)$$

We can use (2.29) to find a simple expression for C_P , the heat capacity at constant pressure. From (2.15) and (2.22), 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

$$C_P = \frac{\partial H}{\partial T}, \quad (2.30)$$

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.

Problem 2.12. (a) Give some of examples of materials that have a relatively low and relatively high 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 kg of water. How much energy is required to raise the water temperature from 18 °C to 50 °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 °C is

$$\begin{aligned} Q &= mc(T_2 - T_1) = 150 \text{ kg} \times (4184 \text{ J/kg K}) \times (50^\circ\text{C} - 18^\circ\text{C}) \\ &= 2 \times 10^7 \text{ J}. \end{aligned}$$

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 kg glass brick is heated to 180 °C and then plunged into a cold bath containing 10 kg of water at 20 °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 J/kg K.

Solution. Conservation of energy implies that

$$\Delta E_{\text{glass}} + \Delta E_{\text{water}} = 0,$$

or

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

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

$$\begin{aligned} T &= \frac{m_{\text{glass}}c_{\text{glass}}T_{\text{glass}} + m_{\text{water}}c_{\text{water}}T_{\text{water}}}{m_{\text{glass}}c_{\text{glass}} + m_{\text{water}}c_{\text{water}}} \\ &= \frac{(1.5 \text{ kg})(750 \text{ J/kg K})(180^\circ\text{C}) + (10 \text{ kg})(4184 \text{ J/kg K})(20^\circ\text{C})}{(1.5 \text{ kg})(750 \text{ J/kg K}) + (10 \text{ kg})(4184 \text{ J/kg K})} \\ &= 24.2^\circ\text{C}. \end{aligned}$$

Example 2.5. The temperature of one mole of helium gas is increased from 20°C to 40°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 (2.28) and (2.12), 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

$$\Delta E = Q = \int C_V dT = \nu c_V \int dT = 1 \text{ mole} \times 12.5 \frac{\text{J}}{\text{mole K}} \times 20 \text{ K} = 250 \text{ J}.$$

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 6.12, we 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:

$$Q = \int_{T_1}^{T_2} C(T) dT. \quad (2.31)$$

In this case we have

$$Q = A \int_{T_1}^{T_2} T^3 dT = \frac{A}{4}(T_2^4 - T_1^4). \quad (2.32)$$

General relation between C_P and C_V . The first law can be used to find the general relation (2.36) 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 (2.29) and (2.30), we have

$$C_P = \left(\frac{\partial H}{\partial T} \right)_P = \left(\frac{\partial E}{\partial T} \right)_P + P \left(\frac{\partial V}{\partial T} \right)_P. \quad (2.33)$$

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

$$dE = \left(\frac{\partial E}{\partial T}\right)_V dT + \left(\frac{\partial E}{\partial V}\right)_T dV, \quad (2.34)$$

and hence (by dividing by ΔT and taking the limit $\Delta T \rightarrow 0$ at constant P)

$$\left(\frac{\partial E}{\partial T}\right)_P = C_V + \left(\frac{\partial E}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P. \quad (2.35)$$

If we eliminate $(\partial E/\partial T)_P$ in (2.33) by using (2.35), we obtain our desired result:

$$C_P = C_V + \frac{\partial E}{\partial V} \frac{\partial V}{\partial T} + P \frac{\partial V}{\partial T}. \quad (\text{general result}) \quad (2.36)$$

Equation (2.36) 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 7.3.2.

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

$$C_P = C_V + Nk \quad (\text{ideal gas}) \quad (2.37)$$

Note that C_P is bigger than C_V , a general result for any macroscopic body. Note that we used the two equations of state for an ideal gas, (2.9) and (2.23), 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.

The result (2.37) for C_P for an ideal gas illustrates the power of thermodynamics. We used a general principle, the first law, and one equation of state to determine C_P , a quantity that we did not know directly. In Chapter 7 we will derive the general relation $C_P > C_V$ for any thermodynamic system.

2.11 Adiabatic Processes

So far we have considered processes at constant temperature, constant volume, and constant pressure.¹⁴ 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.

¹⁴These processes are called *isothermal*, *isochoric*, and *isobaric*, respectively.

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

$$dE = dW. \quad (\text{adiabatic process}) \quad (2.38)$$

For an ideal gas we have $\partial E/\partial V = 0$, and hence (2.34) reduces to

$$dE = C_V dT = -PdV, \quad (\text{ideal gas only}) \quad (2.39)$$

where we have used (2.38). The easiest way to proceed is to eliminate P in (2.39) using the ideal gas law $PV = NkT$:

$$C_V dT = -NkT \frac{dV}{V} \quad (2.40)$$

We next eliminate Nk in (2.40) in terms of $C_P - C_V$ and express (2.40) as

$$\frac{C_V}{C_P - C_V} \frac{dT}{T} = \frac{1}{\gamma - 1} \frac{dT}{T} = -\frac{dV}{V}, \quad (2.41)$$

where the symbol γ is the ratio of the heat capacities:

$$\gamma = \frac{C_P}{C_V}. \quad (2.42)$$

For an ideal gas C_V and C_P and hence γ are independent of temperature, and we can integrate (2.41) to obtain

$$TV^{\gamma-1} = \text{constant}. \quad (\text{quasistatic adiabatic process}) \quad (2.43)$$

For an ideal monatomic gas, we have from (2.28) and (2.37) that $C_V = 3Nk/2$ and $C_P = 5Nk/2$, and hence

$$\gamma = 5/3. \quad (\text{ideal monatomic gas}) \quad (2.44)$$

Problem 2.14. Use (2.43) and the ideal gas pressure equation of state in (2.9) to show that in a quasistatic adiabatic processes P and V are related as

$$PV^\gamma = \text{constant}. \quad (2.45)$$

Also show that T and P are related as

$$TP^{(1-\gamma)/\gamma} = \text{constant}. \quad (2.46)$$

The relations (2.43)–(2.46) hold for a quasistatic adiabatic process of an ideal gas; the relation (2.45) is the easiest relation to remember. Because $\gamma > 1$, the relation (2.45) 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 the 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.

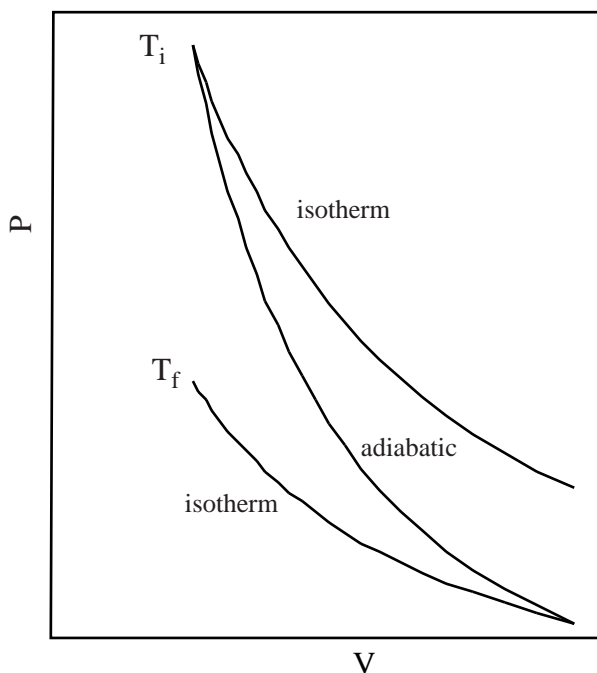


Figure 2.5: A P - V diagram for adiabatic and isothermal processes. The two processes begin at the same initial temperature, but the adiabatic process has a steeper slope and ends at a higher temperature.

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 (2.45) we see that the slope of an adiabatic curve for an ideal gas is

$$\left(\frac{\partial P}{\partial V}\right)_{\text{adiabatic}} = -\gamma \frac{P}{V}, \quad (2.47)$$

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

$$\left(\frac{\partial P}{\partial V}\right)_T = -\frac{P}{V}. \quad (2.48)$$

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 ($Q = 0$) and isothermal (no temperature change). During an adiabatic process, the temperature of an ideal gas must change.

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 $T = 300$ K and $P = 2.0 \times 10^5$ 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

$$V_1 = \frac{\nu RT_1}{P_1} = \frac{0.060 \text{ mole} \times 8.3 \text{ J/(K mole)} \times 300 \text{ K}}{2.0 \times 10^5 \text{ Pa}} = 7.5 \times 10^{-4} \text{ m}^3.$$

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 K.

For adiabatic compression we have

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

or

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

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 $T_2 = 250$ K.

Problem 2.16. Air initially at 20°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

$$W = C_V(T_2 - T_1). \quad (\text{quasistatic adiabatic process for an ideal gas}) \quad (2.49)$$

We leave it to Problem 2.17 to show that (2.49) can be expressed in terms of the pressure and volume as

$$W = \frac{P_2 V_2 - P_1 V_1}{\gamma - 1}. \quad (2.50)$$

Problem 2.17. Another way to derive (2.50), the work done in a quasistatic adiabatic process, is to use the relation (2.45). 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°C is required for ignition, what is the compression ratio? Assume that $\gamma = 1.4$ for air and the temperature is 20°C before compression.

Solution. Equation (2.43) 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 (2.45) becomes

$$T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1}. \quad (2.51)$$

Hence the compression ratio V_1/V_2 is

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

Of course it is only an approximation to assume that the compression is quasistatic.

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.)

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*.¹⁵

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 relationship 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:

No process is possible whose sole result is the complete conversion of energy transferred by heating into work (Kelvin statement).

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).

¹⁵This thermodynamic variable was named by Rudolf Clausius, who wrote in 1850 that he formed the word *entropy* (from the Greek word for transformation) so as to be as similar as possible to the word energy.

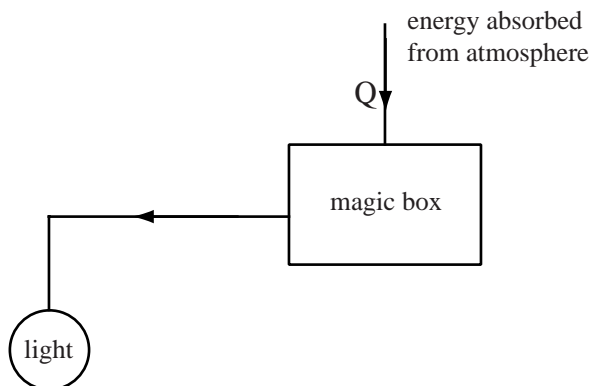


Figure 2.6: A machine that converts energy transferred by heating into work with 100% efficiency violates the Kelvin statement of the second law of thermodynamics.

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

$$\Delta E = Q + W = 0. \quad (2.52)$$

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 statement because the state of the gas is different at the end than at the beginning. 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 (see Appendix 2A).

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. 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). In general, the system of interest can exchange energy with its surroundings. In many cases the surroundings may be idealized as 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

$$\Delta S_{\text{composite}} \geq 0, \quad (2.53)$$

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

$$\Delta S_{\text{composite}} = 0. \quad (\text{reversible process}) \quad (2.54)$$

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 be 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. So the possibility of work and the absence of equilibrium are related.

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

$$E = E_A + E_B = \text{constant}, \quad (2.55)$$

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

$$S(E_A, V_A, N_A, E_B, V_B, N_B) = S_A(E_A, V_A, N_A) + S_B(E_B, V_B, N_B). \quad (2.56)$$

Most divisions of 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 relaxed 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 (2.56), we calculate

$$dS = \left(\frac{\partial S_A}{\partial E_A} \right)_{V_A, N_A} dE_A + \left(\frac{\partial S_B}{\partial E_B} \right)_{V_B, N_B} dE_B. \quad (2.57)$$

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

$$dS = \left[\left(\frac{\partial S_A}{\partial E_A} \right)_{V_A, N_A} - \left(\frac{\partial S_B}{\partial E_B} \right)_{V_B, N_B} \right] dE_A. \quad (2.58)$$

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

$$\left(\frac{\partial S_A}{\partial E_A} \right)_{V_A, N_A} = \left(\frac{\partial S_B}{\partial E_B} \right)_{V_B, N_B}. \quad (2.59)$$

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

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E} \right)_{V, N}, \quad (\text{thermodynamic definition of temperature}) \quad (2.60)$$

which implies that the condition for thermal equilibrium is

$$\frac{1}{T_A} = \frac{1}{T_B}. \quad (2.61)$$

Of course we can rewrite (2.61) 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 (2.58) we can write the change in entropy as

$$\Delta S \approx \left[\frac{1}{T_A} - \frac{1}{T_B} \right] \Delta E_A > 0, \quad (2.62)$$

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 (2.62) to be satisfied. Hence, we conclude that the definition (2.60) 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 (2.62) as: *No process exists in which a cold body cools off while a hotter body heats up and the constraints on the bodies and the state of its surroundings are left unchanged.* We recognize this statement as the Clausius statement of the second law.

The definition (2.60) 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 (2.60) 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. We also will sometimes use the term *thermal bath*. 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

$$dS = \left(\frac{\partial S}{\partial E} \right)_{V,N} dE. \quad (2.63)$$

In this case $dE = dQ$ because no work is done. If we express the partial derivative in (2.63) in terms of T , we can rewrite (2.63) as

$$dS = \frac{dQ}{T}. \quad (\text{pure heating}) \quad (2.64)$$

We emphasize that the relation (2.64) holds only for quasistatic changes. Note that (2.64) implies that the entropy does not change in a quasistatic, adiabatic process.

We now use (2.64) 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 (2.64), 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 one 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

$$W = Q_{\text{high}} - Q_{\text{low}}, \quad (2.65)$$

where in this context Q_{high} and Q_{low} are positive quantities. From the second law we have that

$$\Delta S_{\text{total}} = \Delta S_{\text{high}} + \Delta S_{\text{low}} = -\frac{Q_{\text{high}}}{T_{\text{high}}} + \frac{Q_{\text{low}}}{T_{\text{low}}} \geq 0. \quad (2.66)$$

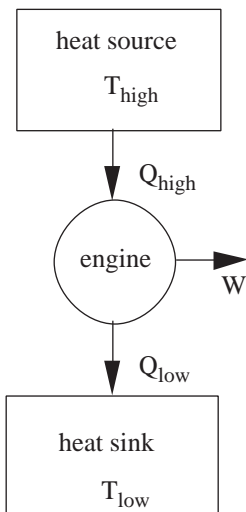


Figure 2.7: Schematic energy transfer diagram for an ideal heat engine. By convention, the quantities Q_{high} , Q_{low} , and W are taken to be positive.

We rewrite (2.66) as

$$\frac{Q_{\text{low}}}{Q_{\text{high}}} \geq \frac{T_{\text{low}}}{T_{\text{high}}}. \quad (2.67)$$

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

$$\eta = \frac{\text{what you obtain}}{\text{what you pay for}} \quad (2.68)$$

$$= \frac{W}{Q_{\text{high}}} = \frac{Q_{\text{high}} - Q_{\text{low}}}{Q_{\text{high}}} = 1 - \frac{Q_{\text{low}}}{Q_{\text{high}}}. \quad (2.69)$$

From (2.69) we see that the engine is most efficient when the ratio $Q_{\text{low}}/Q_{\text{high}}$ is as small as possible. Equation (2.67) shows that $Q_{\text{low}}/Q_{\text{high}}$ is a minimum when the cycle is reversible so that

$$\Delta S_{\text{total}} = 0, \quad (2.70)$$

and

$$\frac{Q_{\text{low}}}{Q_{\text{high}}} = \frac{T_{\text{low}}}{T_{\text{high}}}. \quad (2.71)$$

For these conditions we find that the maximum thermal efficiency is

$$\eta = 1 - \frac{T_{\text{low}}}{T_{\text{high}}}. \quad (\text{maximum thermal efficiency}) \quad (2.72)$$

Note that the temperature in (2.72) is the thermodynamic temperature.

The result (2.72) 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*. That is, 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.

Of course, 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 during each 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

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

We can use this result for η and the general relation (2.72) 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 work with 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:

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

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

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

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 (2.72). 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.

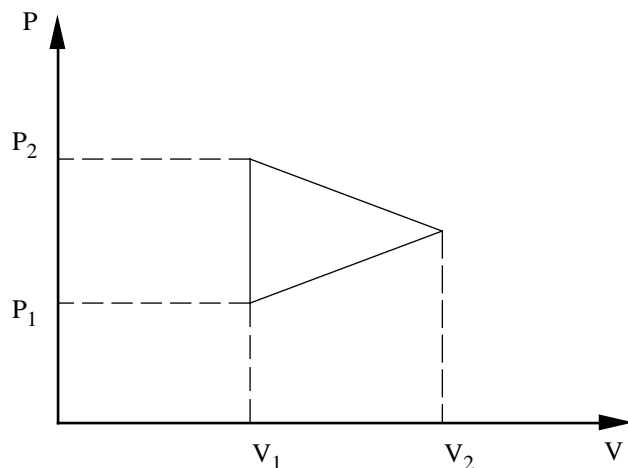


Figure 2.8: The cycle of the hypothetical engine considered in Example 2.10.

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 fall. 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

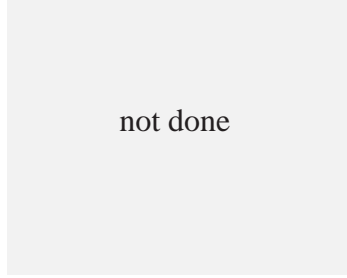


Figure 2.9: The four steps of the Carnot cycle.

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 our 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. Work out 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 $\eta = 1 - T_2/T_1$.

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,

$$Q_{\text{high}} = -W_{A \rightarrow B} = NkT_{\text{high}} \ln \frac{V_B}{V_A}, \quad (2.73)$$

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

$$Q_{\text{low}} = -NkT_{\text{low}} \ln \frac{V_D}{V_C}. \quad (2.74)$$

(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

$$T_{\text{high}}V_B^{\gamma-1} = T_{\text{low}}V_C^{\gamma-1} \quad (2.75a)$$

$$T_{\text{low}}V_D^{\gamma-1} = T_{\text{high}}V_A^{\gamma-1}, \quad (2.75b)$$

which implies that

$$\frac{V_B}{V_A} = \frac{V_C}{V_D}. \quad (2.76)$$

The net work is given by

$$W_{\text{net}} = Q_{\text{high}} - Q_{\text{low}} = Nk(T_{\text{high}} - T_{\text{low}}) \ln \frac{V_B}{V_C}. \quad (2.77)$$

The efficiency is given by

$$\eta = \frac{W_{\text{net}}}{Q_{\text{high}}} = \frac{T_{\text{high}} - T_{\text{low}}}{T_{\text{high}}}, \quad (2.78)$$

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. A solid with 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

$$S_2 - S_1 = \int_{T_1}^{T_2} \frac{dQ}{T} = \int_{T_1}^{T_2} C(T) \frac{dT}{T}. \quad (2.79)$$

Because the heat capacity C is a constant, we find

$$\Delta S = S_2 - S_1 = C \int_{T_1}^{T_2} \frac{dT}{T} = C \ln \frac{T_2}{T_1}. \quad (2.80)$$

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

How can we measure 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 (2.79). In practice, such an integral can be done numerically. Note that such a determination gives only an 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

$$T = \frac{C_A T_A + C_B T_B}{C_A + C_B}. \quad (2.81)$$

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 (2.80) which yields $\Delta S_A = C_A \ln T/T_A$. The total change in the entropy of the system is given by

$$\Delta S = \Delta S_A + \Delta S_B = C_A \ln \frac{T}{T_A} + C_B \ln \frac{T}{T_B}, \quad (2.82)$$

where T is given by (2.81). Substitute real numbers for T_A , T_B , and C 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 changes

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

$$\Delta S_{H_2O} = C \ln \frac{T_2}{T_1} = 4184 \ln \frac{273 + 50}{273 + 0} = 703.67 \text{ J/K}. \quad (2.83)$$

Why does the factor of 273 enter in (2.83)? The amount of energy transferred to the water from the heat bath is

$$Q = C(T_2 - T_1) = 4184 \times 50 = 209,200 \text{ J}. \quad (2.84)$$

The change in entropy of the heat bath is

$$\Delta S_B = \frac{-Q}{T_2} = -\frac{209200}{323} = -647.68 \text{ J/K}. \quad (2.85)$$

Hence the total change in the entropy is

$$\Delta S = \Delta S_{H_2O} + \Delta S_B = 703.67 - 647.68 = 56 \text{ J/K}. \quad (2.86)$$

Problem 2.18. 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?

Example 2.14. 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 the melting temperature $T = 273.15$ K, the effect is to melt the ice rather than to raise the 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 $0.02 \text{ kg} \times 334 \text{ kJ/kg} = 6680 \text{ J}$ from a heat bath at 273.15 K, the ice-water mixture being in equilibrium at atmospheric pressure. Hence, the entropy increase is given by $\Delta S = 6680/273.15 = 24.46 \text{ J/K}$.

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?

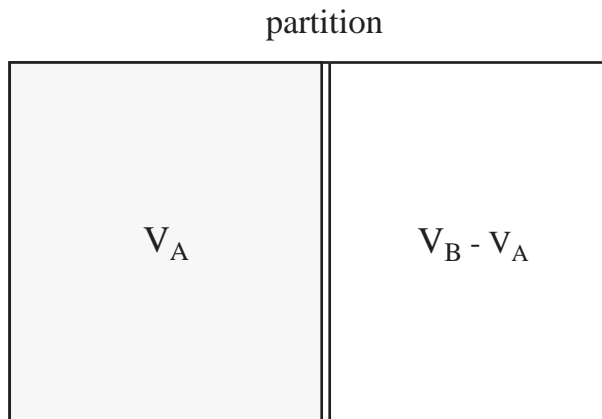


Figure 2.10: The free expansion of an isolated ideal gas. The second chamber is initially a vacuum and the total volume of the two chambers is V_B .

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.

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 between the same two states. 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 ,

$$Q = NkT \ln \frac{V_B}{V_A}, \quad (2.87)$$

where we have used (2.25). Hence, from (2.79), the entropy change is given by

$$\Delta S = \frac{Q}{T} = Nk \ln \frac{V_B}{V_A}. \quad (2.88)$$

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 state is given by

$$W = - \int_{V_B}^{V_A} P dV = NkT \ln \frac{V_B}{V_A}, \quad (2.89)$$

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. One is that 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 (2.87) is the energy transferred in an isothermal process. Of course, 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.

Because the process is assumed to be reversible, we have

$$\Delta S = \Delta S_A + \Delta S_B = 0, \quad (2.90)$$

from which it follows using (2.79) that

$$C_A \ln \frac{T}{T_A} + C_B \ln \frac{T}{T_B} = 0. \quad (2.91)$$

If we solve (2.91) for T , we find that

$$T = T_A^{C_A/(C_A+C_B)} T_B^{C_B/(C_A+C_B)}. \quad (2.92)$$

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 $T_1 = 256$ K and $T_B = 144$ K. What are the relative values of the final temperatures in (2.81) and (2.92) 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

$$W = \Delta E = C_A(T - T_A) + C_B(T - T_B). \quad (2.93)$$

Are all forms of energy equivalent? If you were offered 100 J of energy, would you choose to have it delivered as compressed gas at room temperature or as a hot brick at 400 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 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 deterioration 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 (2.25)):

$$W = NkT \ln \frac{V_B}{V_A}. \quad (2.94)$$

After the adiabatic free expansion, the gas can no longer do this work, even though its energy is unchanged. If we compare (2.94) with (2.88), we see that the energy that becomes unavailable to do work in an adiabatic free expansion is

$$E_{\text{unavailable}} = T \Delta S. \quad (2.95)$$

Equation (2.95) 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 (2.60). We now show that the two temperatures are proportional and can be made equal if we choose the units of S appropriately.

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

$$\theta = PV/Nk. \quad (2.96)$$

That is, θ is proportional to the pressure of a gas at a fixed low density and is equal to 273.16 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

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

or

$$\frac{dQ}{\theta} = \frac{dE}{\theta} + Nk \frac{dV}{V}. \quad (2.97)$$

The first term on the right-hand side of (2.97) depends only on θ and the second term depends only on the volume. If we integrate (2.97) around one cycle, both θ and V return to their starting values, and hence the loop integral of the right-hand side of (2.97) is zero. We conclude that

$$\oint \frac{dQ}{\theta} = \frac{Q_{\text{cold}}}{\theta_{\text{cold}}} - \frac{Q_{\text{hot}}}{\theta_{\text{hot}}} = 0. \quad (2.98)$$

In Section 2.14 we showed that $Q_{\text{cold}}/Q_{\text{hot}} = T_{\text{cold}}/T_{\text{hot}}$ for a Carnot engine (see (2.71)). If we combine this result with (2.98), we find that

$$\frac{T_{\text{cold}}}{T_{\text{hot}}} = \frac{\theta_{\text{cold}}}{\theta_{\text{hot}}}. \quad (2.99)$$

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

$$dS_{\text{total}} = \frac{\partial S_A}{\partial V_A} dV_A + \frac{\partial S_B}{\partial V_B} dV_B = 0. \quad (2.100)$$

Because $dV_A = -dV_B$, we can use (2.100) to write the condition for *mechanical equilibrium* as

$$\frac{\partial S_A}{\partial V_A} = \frac{\partial S_B}{\partial V_B}. \quad (2.101)$$

We define the thermodynamic pressure P as

$$\frac{P}{T} = \left(\frac{\partial S}{\partial V} \right)_{E,N}. \quad (\text{thermodynamic definition of the pressure}) \quad (2.102)$$

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

$$\frac{\mu}{T} = - \left(\frac{\partial S}{\partial N} \right)_{E,V}. \quad (\text{thermodynamic definition of the chemical potential}) \quad (2.103)$$

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 (2.21):

$$\Delta E = Q + W. \quad (\text{any process}) \quad (2.104)$$

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

$$dW = -PdV, \quad (\text{quasistatic process}) \quad (2.105)$$

and

$$dQ = TdS. \quad (\text{quasistatic process}) \quad (2.106)$$

Thus, for an infinitesimal change in energy, we obtain

$$dE = TdS - PdV. \quad (2.107)$$

There are two ways of thinking about (2.107). As our derivation suggests this equation tells us the relationship between changes in energy, entropy, and volume in a quasistatic process. However, because S , V , and E are functions of state, we can view (2.107) as the differential form (for fixed N) of the fundamental equation $E = E(S, V, N)$ which describes the relationship between E , S , V , and N for all equilibrium states. We can also understand (2.107) by considering S as a function of E , V , and N , and writing dS as

$$dS = \frac{\partial S}{\partial E} dE + \frac{\partial S}{\partial V} dV + \frac{\partial S}{\partial N} dN. \quad (2.108)$$

If we use the definitions (2.60), (2.102), and (2.103) of the various partial derivatives of $S(E, V, N)$, we can write

$$dS = \frac{1}{T}dE + \frac{P}{T}dV - \frac{\mu}{T}dN, \quad (2.109)$$

which is equivalent to (2.107) for a fixed number of particles.

If we know the entropy S as a function of E, V and N , we can immediately 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 (2.109) as

$$dE = TdS - PdV + \mu dN. \quad (\text{fundamental thermodynamic relation}) \quad (2.110)$$

Equation (2.110) is a mathematical statement of the combined first and second laws of thermodynamics. Although there are few equations in physics that are necessary to memorize, (2.110) is one of the few equations of thermodynamics that you should know without thinking.

Many useful thermodynamic relations can be derived using (2.110). For example, if we regard E as a function of S, V , and N , we can write

$$dE = \frac{\partial E}{\partial S} dS + \frac{\partial E}{\partial V} dV + \frac{\partial E}{\partial N} dN. \quad (2.111)$$

If we compare (2.110) and (2.111), we see that

$$T = \left(\frac{\partial E}{\partial S} \right)_{V,N} \quad P = - \left(\frac{\partial E}{\partial V} \right)_{S,N} \quad \mu = \left(\frac{\partial E}{\partial N} \right)_{S,V}. \quad (2.112)$$

Note that $E(S, V, N)$ also can be interpreted as a thermodynamic potential. Or we can start with (2.110) and easily obtain (2.109) and the thermodynamics 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, (2.9) and (2.23), 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 (2.109), we obtain

$$dS = \frac{3}{2}Nk \frac{dE}{E} + Nk \frac{dV}{V}. \quad (2.113)$$

We can integrate (2.113) to obtain the change in the entropy from state E_1, V_1 to state E_2, V_2 :

$$\Delta S = \frac{3}{2}Nk \ln \frac{E_2}{E_1} + Nk \ln \frac{V_2}{V_1}. \quad (2.114)$$

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 (2.114) and obtain

$$\Delta S = \frac{3}{2}Nk \ln \frac{T_2}{T_1} + Nk \ln \frac{V_2}{V_1}. \quad (2.115)$$

Problem 2.20. (a) Find $\Delta S(T, P)$ for an ideal gas. (b) Use (2.115) to derive the relation (2.45) 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

$$\lim_{T \rightarrow 0} S = 0. \quad (\text{third law of thermodynamics}) \quad (2.116)$$

A statement equivalent to (2.116) was first proposed by Nernst in 1906 on the basis of empirical observations.¹⁶ 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

$$S(T_2, V) - S(T_1, V) = \int_{T_1}^{T_2} \frac{C_V(T)}{T} dT. \quad (2.117)$$

The condition (2.116) implies that in the limit $T_1 \rightarrow 0$, the integral in (2.117) must go to a finite limit, and hence we require that $C_V(T) \rightarrow 0$ as $T \rightarrow 0$. Similarly, we can argue that $C_P \rightarrow 0$ as $T \rightarrow 0$. 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 2.15. 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 (2.79)):

$$S(T) = \int_0^T \frac{C_V(T)}{T} dT, \quad (2.118)$$

¹⁶Walther Nernst (1864–1943) was awarded the 1920 Nobel prize in chemistry for his discovery of the third law and related work.

where we have used the fact that $S(T = 0) = 0$. We can integrate the right-hand side of (2.118) from $T = 0$ to the desired value of T to find the absolute value of S . The result in this case is $S = AT^3/3$.

Problem 2.21. Is the expression (2.115) applicable at very low temperatures? Explain.

2.21 Free Energies

We have seen that the entropy of an isolated system can never decrease. However, an isolated system is not of much experimental interest, and we wish to consider the more typical case where the system of interest is connected to a much larger system whose properties do not change significantly. As we have discussed on page 51, this larger system is called 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. Because the entropy is additive, we have¹⁷

$$S_{\text{composite}} = S + S_{\text{bath}}, \quad (2.119)$$

and

$$\Delta S_{\text{composite}} = \Delta S + \Delta S_{\text{bath}} \geq 0, \quad (2.120)$$

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

$$\Delta S_{\text{bath}} = \frac{-Q}{T_{\text{bath}}}, \quad (2.121)$$

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 (2.121) and the fundamental thermodynamic relation, (2.110), we can rewrite (2.120) as

$$\Delta S_{\text{composite}} = \Delta S - \frac{Q}{T_{\text{bath}}}. \quad (2.122)$$

The application of the first law to the system gives

$$\Delta E = Q + W, \quad (2.123)$$

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

$$\Delta S_{\text{composite}} = \Delta S - \frac{\Delta E - W}{T_{\text{bath}}} = \Delta S - \frac{\Delta E + P_{\text{bath}}\Delta V}{T_{\text{bath}}} \geq 0. \quad (2.124)$$

¹⁷The following discussion is adapted from Mandl, pp. 89–92.

A little algebra leads to

$$\Delta E + P_{\text{bath}}\Delta V - T_{\text{bath}}\Delta S \leq 0. \quad (2.125)$$

This result suggests that we define the *availability* by

$$A = E + P_{\text{bath}}V - T_{\text{bath}}S, \quad (2.126)$$

so that (2.125) becomes

$$\Delta A = \Delta E + P_{\text{bath}}\Delta V - T_{\text{bath}}\Delta S \leq 0. \quad (2.127)$$

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

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, $T_{\text{bath}} = T$ and $\Delta V = 0$. In this case we have

$$\Delta A = \Delta E - T\Delta S \equiv \Delta F \leq 0, \quad (2.128)$$

where we have defined the *Helmholtz free energy* as

$$F = E - TS. \quad (2.129)$$

The inequality in (2.128) 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 (2.128) 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).

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 (2.129) and using (2.110). The result is

$$dF = dE - SdT - TdS \quad (2.130a)$$

$$= (TdS - PdV + \mu dN) - SdT - TdS \quad (2.130b)$$

$$= -SdT - PdV + \mu dN. \quad (2.130c)$$

We substituted $dE = TdS - PdV + \mu dN$ to go from (2.130a) to (2.130b).

From (2.130c) 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,

$$S = -\left(\frac{\partial F}{\partial T}\right)_{V,N}, \quad (2.131)$$

and

$$P = -\left(\frac{\partial F}{\partial V}\right)_{T,N} \quad (2.132)$$

Hence, we conclude that the Helmholtz free energy is a minimum for a given T , V , and N .

The Helmholtz free energy is only one example of a free energy or thermodynamic potential. 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 using fluids where the pressure is fixed at atmospheric pressure. We write $P_{\text{bath}} = P$ and express (2.125) as

$$\Delta A = \Delta E + P\Delta V - T\Delta S \equiv \Delta G \leq 0, \quad (2.133)$$

where we have defined the Gibbs free energy as

$$G = E - TS + PV = F + PV. \quad (2.134)$$

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

$$\begin{aligned} dG &= dE - SdT - TdS + PdV + VdP \\ &= (TdS - PdV + \mu dN) - SdT - TdS + PdV + VdP \\ &= -SdT + VdP + \mu dN. \end{aligned} \quad (2.135)$$

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 :

$$G = Ng(T, P), \quad (2.136)$$

where $g(T, P)$ is the Gibbs free energy per particle. This function must be the chemical potential because $\partial G/\partial N = g(T, P)$ from (2.136) and $\partial G/\partial N = \mu$ from (2.135). Thus, the chemical potential is the Gibbs free energy per particle:

$$\mu(T, P) = \frac{G}{N} = g(T, P). \quad (2.137)$$

Because g depends only on T and P , we have

$$dg = \left(\frac{\partial g}{\partial P}\right)_T dP + \left(\frac{\partial g}{\partial T}\right)_P dT \quad (2.138)$$

$$= vdP - sdT, \quad (2.139)$$

where $v = V/N$ and $s = S/N$. The properties of G and the relation (2.139) will be important when we discuss processes involving a change of phase (see Section 7.5).

Another common thermodynamic potential is the *enthalpy* H which we defined in (2.29). This potential is similar to $E(S, V, N)$ except for the requirement of fixed P rather than fixed V .

Problem 2.22. Show that

$$dH = TdS + VdP + \mu dN, \quad (2.140)$$

and

$$T = \left(\frac{\partial H}{\partial S}\right)_{P, N} \quad (2.141)$$

$$V = \left(\frac{\partial H}{\partial P}\right)_{S, N} \quad (2.142)$$

$$\mu = \left(\frac{\partial H}{\partial N}\right)_{S, P}. \quad (2.143)$$

Problem 2.23. Show that H is a minimum for an equilibrium system at fixed entropy.

Landau potential. As we have seen, we can define many thermodynamic potentials depending on which variables we constrain. A very useful thermodynamic potential that has no generally recognized name or symbol is sometimes called the *Landau potential* and is denoted by Ω . Another common name is simply the *grand potential*. The Landau potential is the thermodynamic potential for which the variables T , V , and μ are specified and is given by

$$\Omega(T, V, \mu) = F - \mu N. \quad (2.144)$$

If we take the derivative of Ω and use the fact that $dF = -SdT - PdV + \mu dN$ (see (2.130c)), we obtain

$$d\Omega = dF - \mu dN - Nd\mu \quad (2.145a)$$

$$= -SdT - PdV - Nd\mu. \quad (2.145b)$$

From (2.145a) we have

$$S = -\left(\frac{\partial \Omega}{\partial T}\right)_{V, \mu}. \quad (2.146)$$

$$P = -\left(\frac{\partial \Omega}{\partial V}\right)_{T, \mu}. \quad (2.147)$$

$$N = -\left(\frac{\partial \Omega}{\partial \mu}\right)_{T, V}. \quad (2.148)$$

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

$$\Omega(T, V, \mu) = F - \mu N = F - G = -PV. \quad (2.149)$$

The relation (2.149) will be very useful for obtaining the equation of state of various systems (see Section 6.10).

***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} :

$$W_{\text{by}} = P_{\text{bath}}\Delta V + W_{\text{useful}}. \quad (2.150)$$

Because W_{by} is the work done by the system when its volume changes by ΔV , the first term in (2.150) 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 (2.125) 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

$$\Delta E + P_{\text{bath}}\Delta V + W_{\text{useful}} - T_{\text{bath}}\Delta S \leq 0, \quad (2.151)$$

or the useful work done is

$$W_{\text{useful}} \leq -(\Delta E + P_{\text{bath}}\Delta V - T_{\text{bath}}\Delta S) = -\Delta A, \quad (2.152)$$

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 2.24. (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 $-\Delta G$.

Vocabulary

thermodynamics, system, boundary, surroundings

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 $^{\circ}\text{C}$, Fahrenheit $^{\circ}\text{F}$

heat capacity C , specific heat c

thermal efficiency η

Boltzmann's constant k , gas constant R

Appendix 2A: Equivalence of Different Statements of the Second Law

[xx not done xx]

Appendix 2B: 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 relationships:

$$y = f(x) = x^2, \quad (2.153)$$

and

$$x = g(z) = z^{1/2}. \quad (2.154)$$

If we write x in terms of z , we can write y as

$$y = h(z) = f(g(z)) = z. \quad (2.155)$$

We have given the composite function a different symbol h because it 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 relationship: $S(E(T, V, N), V, N)$. 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](#),¹⁸ have criticized their use. These authors and

¹⁸See Bohren and Albrecht, pp. 93–99.

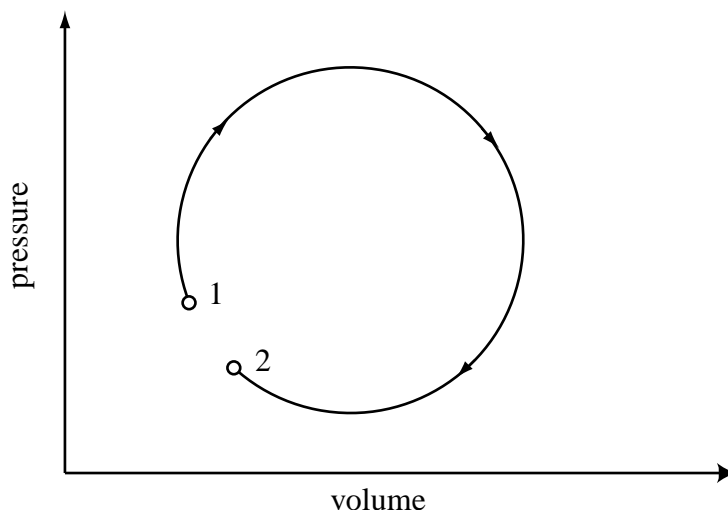


Figure 2.11: The change in internal energy can be made arbitrarily small by making the initial (1) and final (2) states arbitrarily close, but the total work done, which is the area enclosed by the nearly closed curve, is not vanishingly small. Adapted from [Bohren and Albrecht](#).

others argue for example that the first law should be written as

$$\frac{dE}{dt} = \frac{dQ}{dt} + \frac{dW}{dt}, \quad (2.156)$$

rather than

$$dE = \Delta Q + \Delta W, \quad (2.157)$$

An argument for writing the first law in the form (2.156) is that the first law applies to a process, which of course takes place over an interval of time. Here, dE/dt represents the rate of energy change, dW/dt is the rate of doing work or working and dQ/dt is the rate of heating. In contrast, dE in (2.157) 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 2.11, 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, $dy = f(x) dx$. If the use of infinitesimals is confusing to you, we encourage you to replace infinitesimals by rate equations as in (2.156).

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

$$dz = \left(\frac{\partial z}{\partial x} \right)_y dx + \left(\frac{\partial z}{\partial y} \right)_x dy. \quad (2.158)$$

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 7.2.

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

$$\left(\frac{\partial z}{\partial x}\right)_y = \left(\frac{\partial z}{\partial w}\right)_y \left(\frac{\partial w}{\partial x}\right)_y. \quad (2.159)$$

We also can derive a relation whose form is superficially similar to (2.159) when *different* variables are held constant in each term. From (2.158) we set $dz = 0$ and obtain

$$dz = 0 = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy. \quad (2.160)$$

We divide both sides of (2.160) by dx :

$$0 = \left(\frac{\partial z}{\partial x}\right)_y + \left(\frac{\partial z}{\partial y}\right)_x \left(\frac{\partial y}{\partial x}\right)_z, \quad (2.161)$$

and rewrite (2.161) as

$$\left(\frac{\partial z}{\partial x}\right)_y = -\left(\frac{\partial z}{\partial y}\right)_x \left(\frac{\partial y}{\partial x}\right)_z. \quad (2.162)$$

Note that (2.162) involves a relation between the three possible partial derivatives which involve x , y , and z .

Problem 2.25. Consider the function

$$z(x, y) = x^2 y + 2x^4 y^6.$$

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 $\partial^2 z/\partial x \partial y = \partial^2 z/\partial y \partial x$.

Additional Problems

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Listing of inline problems.

Problem 2.26. Compare the notion of mechanical equilibrium and thermodynamic equilibrium.

Problem 2.27. Explain how a barometer works to measure pressure.

Problem 2.28. 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 2.29. Although you were probably taught how to convert between Fahrenheit and Celsius temperatures, you might not remember the details. The fact that 1°C equals $\frac{9}{5}^\circ\text{F}$ 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 $^\circ\text{C}$ or $^\circ\text{F}$ and multiply by $\frac{5}{9}$ if going from $^\circ\text{F}$ to $^\circ\text{C}$ or by $\frac{9}{5}$ if going from $^\circ\text{C}$ to $^\circ\text{F}$. Then subtract 40 from the calculated temperature to obtain the desired conversion. Explain why this procedure works.

Problem 2.30. 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 2.31. Does it make sense to talk about the amount of heat in a room?

Problem 2.32. 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 2.33. Why should we check the pressure in a tire when the tire is cold?

Problem 2.34. 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 2.35. Why do we use the triple point of water to calibrate thermometers? Why not use the melting point or the boiling point?

Problem 2.36. 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.¹⁹ 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 2.37. 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 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 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.

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.

¹⁹See Dugdale, pp. 21–22.

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 2.38. Why are the terms heat capacity and specific heat poor choices of names? Suggest more appropriate names. Criticize the statement: “The heat capacity of a body is a measure of how much heat the body can hold.”

Problem 2.39. The atmosphere of Mars has a pressure that is only 0.007 times that of the Earth and an average temperature of 218 K. What is the volume of 1 mole of the Martian atmosphere?

Problem 2.40. 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 2.41. Gasoline burns in an automobile engine and releases energy at the rate of 160 kW. Energy is exhausted through the car’s radiator at the rate of 51 kW and out the exhaust at 50 kW. An additional 23 kW goes to frictional heating within the machinery of the car. What fraction of the fuel energy is available for moving the car?

Problem 2.42. Two moles of an ideal gas at 300 K occupying a volume of 0.10 m^3 is compressed isothermally by a motor driven piston to a volume of 0.010 m^3 . If this process takes place in 120 s, how powerful a motor is needed?

Problem 2.43. 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 2.44. (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 (2.24))

$$E = \frac{3}{2}NkT - N\frac{N}{V}a, \quad (2.163)$$

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 2.45. 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 2.46. 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 2.12). Assume that the system is an ideal gas. (This problem is adapted from Reif, p. 215.)

(a) The volume is changed quasistatically from $A \rightarrow C$ while the gas is kept thermally isolated.

- (b) The system is compressed from its original volume of $V_A = 8 \text{ m}^3$ to its final volume $V_C = 1 \text{ m}^3$ along the path $A \rightarrow B$ and $B \rightarrow C$. The pressure is kept constant at $P_A = 1 \text{ Pa}$ 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 $P_B = 32 \text{ Pa}$.
- (c) $A \rightarrow D$ and $D \rightarrow C$. The two steps of the preceding process are performed in opposite order.
- (d) $A \rightarrow C$. The volume is decreased and the system is heated so that the pressure is proportional to the volume.

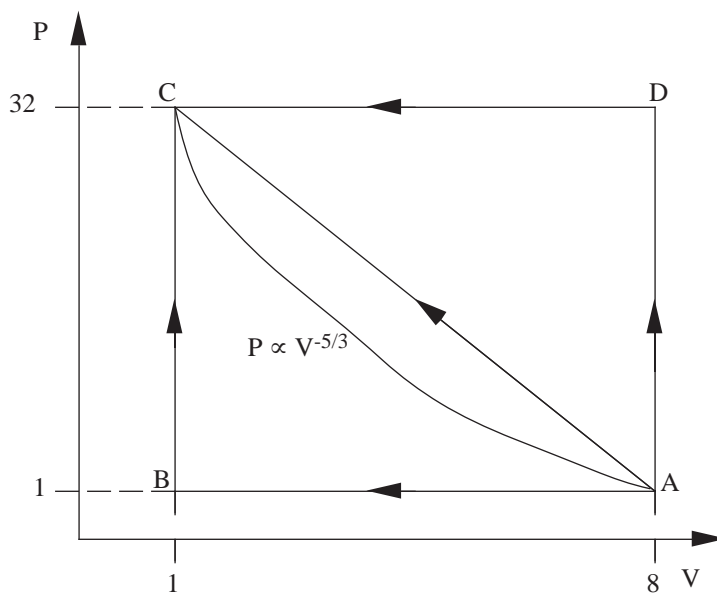


Figure 2.12: Illustration of various thermodynamic processes discussed in Problem 2.46. The units of the pressure P and the volume V are Pa and m^3 , respectively.

Problem 2.47. A 0.5 kg copper block at 80°C is dropped into 1 kg of water at 10°C . What is the final temperature? What is the change in entropy of the system? The specific heat of copper is $386 \text{ J}/(\text{kg K})$.

Problem 2.48. (a) Surface temperatures in the tropical oceans are approximately 25°C , while hundreds of meters below the surface the temperature is approximately 5°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?

Problem 2.49. 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 2.50. Positive change in total entropy

- (a) Show that the total entropy change in Example 2.13 can be written as

$$\Delta S = Cf\left(\frac{T_2}{T_1}\right), \quad (2.164)$$

where

$$f(x) = \ln x + \frac{1}{x} - 1. \quad (2.165)$$

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 2.51. 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 2.52. 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 2.53. 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 2.54. 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 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 2.55. 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 2.56. 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 2.13). 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

$$\text{COP} = \frac{\text{what you get}}{\text{what you pay for}} = \frac{Q_{\text{cold}}}{W}. \quad (2.166)$$

Show that the maximum value of the COP corresponds to a reversible refrigerator and is given by

$$\text{COP} = \frac{T_{\text{cold}}}{T_{\text{hot}} - T_{\text{cold}}}. \quad (2.167)$$

Note that a refrigerator is more efficient for smaller temperature differences.

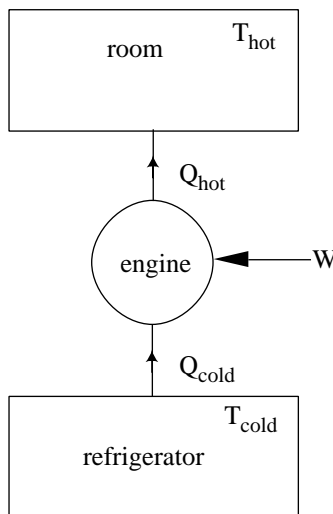


Figure 2.13: The transfer of energy in an idealized refrigerator.

Problem 2.57. 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

$$\text{COP} = \frac{\text{what you get}}{\text{what you pay for}} = \frac{Q_{\text{hot}}}{W}. \quad (2.168)$$

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?

Problem 2.58. Use (2.115) to derive the relation (2.43) between V and T for an ideal gas in a quasistatic adiabatic process.

Problem 2.59. *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 2.14.

$5 \rightarrow 1$. *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

$$\eta = 1 - \left(\frac{V_2}{V_1}\right)^{\gamma-1}. \quad (2.169)$$

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.

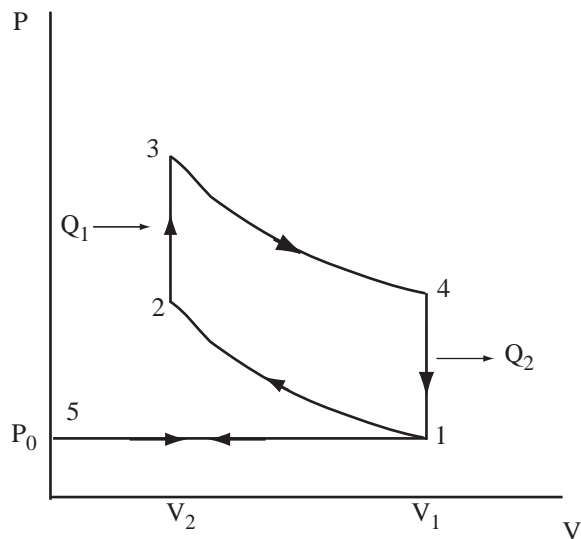


Figure 2.14: The air standard Otto cycle.

Suggestions for Further Reading

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Chapter 3

Concepts of Probability

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We introduce the basic concepts of probability and apply it 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 processes 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 cover more advanced topics, our discussion goes beyond what we will need for most applications of statistical mechanics.

3.1 Probability in everyday life

Chapter 2 provided an introduction to thermodynamics using macroscopic arguments. Our goal, which we will consider again in Chapter 4, 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 than one in a thousand, because you have crossed streets thousands of times and hopefully you have not been hit. Of course 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 ...

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 crashing. 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 80 years, it seems that flying is not too much of a risk. However, suppose that instead of living 80 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 gambling 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 probability 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. 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. 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. 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. 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. 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. What is the predicted average value of A assuming a fair die? What is the average value of A observed in this experiment?

Problem 3.6. 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 .

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 3.7. 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. Suppose that you are offered a choice of the following: a certain \$10 or the chance of rolling a die and receiving \$36 if it comes up 5 or 6, but nothing otherwise. Make arguments in favor of each choice.

Problem 3.9. Suppose that you are offered the following choice: (a) a prize of \$100 if a flip of a coin yields heads or (b) a certain prize of \$40. What choice would you make? Explain your reasoning.

Problem 3.10. Suppose that you are offered the following choice: (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 3.11. Suppose that you were to judge an event to be 99.9999% probable. Would you be willing to bet \$999999 against \$1 that the event would occur? Discuss why probability assessments should be kept separate from decision issues.

Problem 3.12. Suppose that someone gives you a dollar to play the lottery. What sequence of six numbers between 1 and 36 would you choose?

Problem 3.13. Suppose you toss a coin 8 times and obtain heads each time. Estimate the probability that you will obtain heads on your ninth toss.

Problem 3.14. What is the probability that it will rain tomorrow? What is the probability that the Dow Jones industrial average will increase tomorrow?

Problem 3.15. 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

¹In 1933 the Russian mathematician A. N. Kolmogorov formulated a complete set of axioms for the mathematical definition of probability.

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

$$P(i) \geq 0, \quad (3.1)$$

and

$$\sum_i P(i) = 1. \quad (3.2)$$

$P(i) = 0$ 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.

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 (3.4). 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.

Perhaps the interpretation of probability that is the easiest 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. 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.

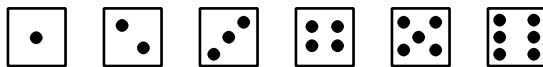


Figure 3.1: The six possible outcomes of the toss of a die.

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

²The 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).

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

$$P(i \text{ or } j) = P(i) + P(j). \quad (\text{addition rule}) \quad (3.3)$$

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

$$\begin{aligned} P(\text{not six}) &= P(1) + P(2) + P(3) + P(4) + P(5) \\ &= 1 - P(6) = \frac{5}{6}, \end{aligned}$$

where the last relation follows from the fact that the sum of the probabilities for all outcomes sums to unity. Although this property of the probability is obvious, 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

$$P(i \text{ and } j) = P(i) P(j). \quad (\text{multiplication rule}) \quad (3.4)$$

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 (3.4) 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 $P(\text{female}) \times P(6^+) = \frac{1}{2} \times \frac{1}{5} = \frac{1}{10}$. 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 3.16. Give an example from your solutions to Problems 3.1–3.6 where you used the addition rule or the multiplication rule.

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

$$P(\text{even}) = P(2) + P(4) + P(6) = \frac{1}{6} + \frac{1}{6} + \frac{1}{6} = \frac{1}{2}.$$

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), \dots (6,6) is $\frac{1}{6} \times \frac{1}{6} = \frac{1}{36}$. Hence, by the addition rule

$$P(\text{same face}) = P(1,1) + P(2,2) + \dots + P(6,6) = 6 \times \frac{1}{36} = \frac{1}{6}.$$

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

$$P(6) = \frac{1}{6} \quad P(\text{not } 6) = \frac{5}{6}.$$

There are four possible outcomes (6,6), (6, not 6), (not 6,6), (not 6, not 6) with the probabilities

$$\begin{aligned} P(6,6) &= \frac{1}{6} \times \frac{1}{6} = \frac{1}{36} \\ P(6, \text{not } 6) &= P(\text{not } 6, 6) = \frac{1}{6} \times \frac{5}{6} = \frac{5}{36} \\ P(\text{not } 6, \text{not } 6) &= \frac{5}{6} \times \frac{5}{6} = \frac{25}{36}. \end{aligned}$$

All outcomes except the last have at least one six. Hence, the probability of obtaining at least one six is

$$\begin{aligned} P(\text{at least one } 6) &= P(6,6) + P(6, \text{not } 6) + P(\text{not } 6, 6) \\ &= \frac{1}{36} + \frac{5}{36} + \frac{5}{36} = \frac{11}{36}. \end{aligned}$$

A more direct way of obtaining this result is to use the normalization condition. That is,

$$P(\text{at least one six}) = 1 - P(\text{not } 6, \text{not } 6) = 1 - \frac{25}{36} = \frac{11}{36}.$$

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

$$P(\text{not } 6, \text{not } 6, \text{not } 6, \text{not } 6) = P(\text{not } 6)^4 = \left(\frac{5}{6}\right)^4,$$

and hence

$$\begin{aligned} P(\text{at least one six}) &= 1 - P(\text{not 6, not 6, not 6, not 6}) \\ &= 1 - \left(\frac{5}{6}\right)^4 = \frac{671}{1296} \approx 0.517. \end{aligned}$$

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 3.17. Find the probability distribution $P(n)$ for throwing a sum n with two dice and plot $P(n)$ as a function of n .

Problem 3.18. What is the probability of obtaining at least one double six in twenty-four throws of a pair of dice?

Problem 3.19. 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 3.20. 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.

Problem 3.21. 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 this reasoning?

3.3 Mean values

The specification of the *probability distribution* $P(1), P(2), \dots, P(n)$ 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 \bar{x} . The definition of the mean value of x is

$$\bar{x} \equiv x_1P(1) + x_2P(2) + \dots + x_nP(n) \quad (3.6a)$$

$$= \sum_{i=1}^n x_iP(i), \quad (3.6b)$$

where $P(i)$ is the probability of x_i , and we have assumed that the probability is normalized. If $f(x)$ is a function of x , then the mean value of $f(x)$ is defined by

$$\overline{f(x)} = \sum_{i=1}^n f(x_i)P(i). \quad (3.7)$$

If $f(x)$ and $g(x)$ are any two functions of x , then

$$\begin{aligned} \overline{f(x) + g(x)} &= \sum_{i=1}^n [f(x_i) + g(x_i)]P(i) \\ &= \sum_{i=1}^n f(x_i)P(i) + \sum_{i=1}^n g(x_i)P(i), \end{aligned}$$

or

$$\overline{f(x) + g(x)} = \overline{f(x)} + \overline{g(x)}. \quad (3.8)$$

Problem 3.22. Show that if c is a constant, then

$$\overline{cf(x)} = c\overline{f(x)}. \quad (3.9)$$

In general, we can define the m th *moment* of the probability distribution P as

$$\overline{x^m} \equiv \sum_{i=1}^n x_i^m P(i), \quad (3.10)$$

where we have let $f(x) = x^m$. The mean of x is the first moment of the probability distribution.

Problem 3.23. Suppose that the variable x takes on the values $-2, -1, 0, 1$, and 2 with probabilities $1/4, 1/8, 1/8, 1/4$, and $1/4$, 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

$$\Delta x \equiv x - \bar{x}, \quad (3.11)$$

and

$$\overline{\Delta x} = \overline{(x - \bar{x})} = \bar{x} - \bar{x} = 0. \quad (3.12)$$

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

$$\overline{\Delta x^2} \equiv \overline{(x - \bar{x})^2}. \quad (3.13)$$

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 \bar{x} , the larger the variance. The use of the square of $x - \bar{x}$ ensures that the contribution of x values that are smaller and larger than \bar{x} enter with the same sign. A useful form for the variance can be found by letting

$$\begin{aligned} \overline{(x - \bar{x})^2} &= \overline{(x^2 - 2x\bar{x} + \bar{x}^2)} \\ &= \overline{x^2} - 2\bar{x}\bar{x} + \bar{x}^2, \end{aligned} \quad (3.14)$$

or

$$\overline{(x - \bar{x})^2} = \overline{x^2} - \bar{x}^2. \quad (3.15)$$

Because $\overline{\Delta x^2}$ is always nonnegative, it follows that $\overline{x^2} \geq \bar{x}^2$.

The variance is the mean value of the square $(x - \bar{x})^2$ 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. The standard deviation of the probability distribution $P(x)$ is given by

$$\sigma_x = \sqrt{\overline{\Delta x^2}} = \sqrt{\overline{x^2} - \bar{x}^2}. \quad (3.16)$$

Example 3.9. Find the mean value \bar{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 $i = 1, \dots, 6$, we have that

$$\begin{aligned} \bar{x} &= \frac{1}{6}(1 + 2 + 3 + 4 + 5 + 6) = \frac{7}{2} = 3.5 \\ \overline{x^2} &= \frac{1}{6}(1 + 4 + 9 + 16 + 25 + 36) = \frac{46}{3} \\ \overline{\Delta x^2} &= \overline{x^2} - \bar{x}^2 = \frac{46}{3} - \frac{49}{4} = \frac{37}{12} \approx 3.08 \\ \sigma_x &\approx \sqrt{3.08} = 1.76 \end{aligned}$$

Example 3.10. 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^2p
4	q^3p

Table 3.2: Probability of a head for the first time on trial i ($q = 1 - p$).

The sum of the probabilities is $p + pq + pq^2 + \cdots = p(1 + q + q^2 + \cdots) = p/(1 - q) = p/p = 1$. The mean number of trials m is

$$\begin{aligned}
 m &= p + 2pq + 3pq^2 + 4pq^3 + \cdots \\
 &= p(1 + 2q + 3q^2 + \cdots) \\
 &= p \frac{d}{dq} (1 + q + q^2 + q^3 + \cdots) \\
 &= p \frac{d}{dq} \frac{1}{1 - q} = \frac{p}{(1 - q)^2} = \frac{1}{p}
 \end{aligned} \tag{3.17}$$

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 the concept 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 already 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 Problems 3.11 and 3.90).

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 3.24. (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 3.25. 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,"

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.

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 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. 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.

Next 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 find a mathematical measure that is consistent with our intuitive sense of uncertainty. Let us define the uncertainty function $S(P_1, P_2, \dots, P_j, \dots)$ where j labels the possible events and P_j is the probability of event j . We first consider the case where all the probabilities P_j are equal. Then $P_1 = P_2 = \dots = P_j = 1/\Omega$, where Ω is the total number of outcomes. In this case we have $S = S(1/\Omega, 1/\Omega, \dots)$ 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

$$S(\Omega = 1) = 0. \quad (3.18)$$

We also have that

$$S(\Omega_1) > S(\Omega_2) \text{ if } \Omega_1 > \Omega_2. \quad (3.19)$$

That is, $S(\Omega)$ is an 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

$$S(\Omega_1 \Omega_2) = S(\Omega_1) + S(\Omega_2). \quad (3.20)$$

It is remarkable that there is an unique functional form that satisfies the three conditions (3.18)–(3.20). We can find this form by writing (3.20) in the form

$$S(xy) = S(x) + S(y), \quad (3.21)$$

and taking the variables x and y to be continuous. (The analysis can be done assuming that x and y are continuous variables, but the analysis is simpler if we assume that x and y are continuous variables. The functional form of S might already be obvious.) This generalization is consistent with $S(\Omega)$ being an increasing function of Ω . First we take the partial derivative of $S(xy)$ with respect to x and then with respect to y . We have

$$\frac{\partial S(z)}{\partial x} = \frac{\partial z}{\partial x} \frac{dS(z)}{dz} = y \frac{dS(z)}{dz} \quad (3.22a)$$

$$\frac{\partial S(z)}{\partial y} = \frac{\partial z}{\partial y} \frac{dS(z)}{dz} = x \frac{dS(z)}{dz}, \quad (3.22b)$$

where $z = xy$. But from (3.21) we have

$$\frac{\partial S(z)}{\partial x} = \frac{dS(x)}{dx} \quad (3.23a)$$

$$\frac{\partial S(z)}{\partial y} = \frac{dS(y)}{dy}. \quad (3.23b)$$

By comparing the right-hand side of (3.22) and (3.23), we have

$$\frac{dS}{dx} = y \frac{dS}{dz} \quad (3.24a)$$

$$\frac{dS}{dy} = x \frac{dS}{dz}. \quad (3.24b)$$

If we multiply (3.24a) by x and (3.24b) by y , we obtain

$$x \frac{dS(z)}{dz} = x \frac{S(x)}{dx} = y \frac{S(y)}{dy}. \quad (3.25)$$

Note that the second part of (3.25) depends only on x and the third part depends only on y . Because x and y are independent variables, the three parts of (3.25) must be equal to a constant. Hence we have the desired condition

$$x \frac{S(x)}{dx} = y \frac{S(y)}{dy} = A, \quad (3.26)$$

where A is a constant. The differential equation in (3.26) can be integrated to give

$$S(x) = A \ln x + B. \quad (3.27)$$

The integration constant B must be equal to zero to satisfy the condition (3.18). The constant A is arbitrary so we choose $A = 1$. Hence for equal probabilities we have that

$$S(\Omega) = \ln \Omega. \quad (3.28)$$

What about the case where the probabilities for the various events are unequal? We will show in Appendix 3A that the general form of the uncertainty S is

$$S = - \sum_j P_j \ln P_j. \quad (3.29)$$

Note that if all the probabilities are equal then

$$P_j = \frac{1}{\Omega} \quad (3.30)$$

for all j . In this case

$$S = - \sum_j \frac{1}{\Omega} \ln \frac{1}{\Omega} = \Omega \frac{1}{\Omega} \ln \Omega = \ln \Omega, \quad (3.31)$$

because there are Ω equal terms in the sum. Hence (3.29) reduces to (3.28) as required. We also see that if outcome i is certain, $P_i = 1$ and $P_j = 0$ 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_j 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

$$S = - \sum_j P_j \ln P_j = -(P_1 \ln P_1 + P_2 \ln P_2) \quad (3.32a)$$

$$= -(P_1 \ln P_1 + (1 - P_1) \ln(1 - P_1)), \quad (3.32b)$$

where we have used the fact that $P_1 + P_2 = 1$. To maximize S we take the derivative with respect to P_1 .³

$$\frac{dS}{dP_1} = -[\ln P_1 + 1 - \ln(1 - P_1) - 1] = -\ln \frac{P_1}{1 - P_1} = 0. \quad (3.33)$$

The solution of (3.33) satisfies

$$\frac{P_1}{1 - P_1} = 1, \quad (3.34)$$

which is satisfied by the choice $P_1 = 1/2$. We can check that this solution is a maximum by calculating the second derivative.

$$\frac{\partial^2 S}{\partial P_1^2} = -\left[\frac{1}{P_1} + \frac{1}{1 - P_1}\right] = -4 < 0, \quad (3.35)$$

which is less than zero as we expected.

Problem 3.26. (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 $P_2 = 1/3$? How does the uncertainty in this case compare to that in part (a)? (c) On page 94 we discussed four experiments with various outcomes. Calculate the uncertainty S of the third and fourth experiments.

Example 3.11. 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

$$S = -[P_1 \ln P_1 + P_2 \ln P_2 + P_3 \ln P_3]. \quad (3.36)$$

We also know that

$$f = (1 \times P_1) + (2 \times P_2) + (3 \times P_3), \quad (3.37)$$

³We have used the fact that $d(\ln x) = 1/x$.

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 (3.37) as

$$f = P_1 + 2P_2 + 3(1 - P_1 - P_2) = 3 - 2P_1 - P_2. \quad (3.38)$$

We then use (3.38) to eliminate P_2 and P_3 from (3.36) using $P_2 = 3 - f - 2P_1$ and $P_3 = f - 2 + P_1$:

$$S = -[P_1 \ln P_1 + (3 - f - 2P_1) \ln(3 - f - 2P_1) + (f - 2 + P_1) \ln(f - 2 + P_1)]. \quad (3.39)$$

Because S in (3.39) depends on only P_1 , we can simply differentiate S with respect P_1 to find its maximum value:

$$\begin{aligned} \frac{dS}{dP_1} &= -\left[\ln P_1 - 1 - 2[\ln(3 - f - 2P_1) - 1] + [\ln(f - 2 + P_1) - 1]\right] \\ &= \ln \frac{P_1(f - 2 + P_1)}{(3 - f - 2P_1)^2} = 0. \end{aligned} \quad (3.40)$$

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 .

Problem 3.27. Fill in the missing steps in Example 3.11 and solve for P_1 , P_2 , and P_3 .

In Appendix 3B we maximize the uncertainty for a case for which there are more than three outcomes.

3.4.2 *Bayesian inference

Let us define $P(A|B)$ as the probability of A occurring given that we know B . We now discuss a few results about conditional probability. Clearly,

$$P(A) = P(A|B) + P(A|\overline{B}), \quad (3.41)$$

where \overline{B} means B does not occur. Also, it is clear that

$$P(A \text{ and } B) = P(A|B)P(B) = P(B|A)P(A), \quad (3.42)$$

Equation (3.42) 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. If we are interested in various possible outcomes A_i for the same B , we can rewrite (3.42) as

$$P(A_i|B) = \frac{P(B|A_i)P(A_i)}{P(B)}. \quad (3.43)$$

If all the A_i are mutually exclusive and if at least one of the A_i must occur, then we can also write

$$P(B) = \sum_i P(B|A_i)P(A_i). \quad (3.44)$$

If we substitute (3.44) for $P(B)$ into (3.43), we obtain the important result:

$$P(A_i|B) = \frac{P(B|A_i)P(A_i)}{\sum_i P(B|A_i)P(A_i)}. \quad (\text{Bayes' theorem}) \quad (3.45)$$

Equation 3.45 is known as Bayes' theorem.

Bayes' theorem is very useful for choosing the most probable explanation of a given data set. In this context A_i represents the possible explanations and B represents the data. As more data becomes available, the probabilities $P(B|A_i)P(A_i)$ change.

As an example, consider the following quandary known as the Monty Hall Problem.⁴ In this show a contestant is shown three doors. Behind one door is an expensive gift 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. The contestant now has a choice – should she stay with her original choice or switch to door 3? What would you do?

Let us use Bayes' theorem to determine her best course of action. We want to calculate

$$P(A_1|B) = P(\text{car behind door 1}|\text{door 2 open after door 1 chosen}),$$

and

$$P(A_3|B) = P(\text{car behind door 3}|\text{door 2 open after door 1 chosen}),$$

where A_i denotes car behind door i . We know that all the $P(A_i)$ equal $1/3$, because with no information we must 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

$$P(\text{door 2 open after door 1 chosen}|\text{car behind 1}) = 1/2 \quad (3.46a)$$

$$P(\text{door 2 open after door 1 chosen}|\text{car behind 2}) = 0 \quad (3.46b)$$

$$P(\text{door 2 open after door 1 chosen}|\text{car behind 3}) = 1. \quad (3.46c)$$

Using Bayes' theorem we have

$$P(\text{car behind 1}|\text{door 2 open after door 1 chosen}) = \frac{(1/2)(1/3)}{\frac{1}{2}\frac{1}{3} + 0\frac{1}{3} + 1\frac{1}{3}} = 1/3 \quad (3.47a)$$

$$P(\text{car behind 3}|\text{door 2 open after door 1 chosen}) = \frac{(1)(1/3)}{\frac{1}{2}\frac{1}{3} + 0\frac{1}{3} + 1\frac{1}{3}} = 2/3. \quad (3.47b)$$

The results in (3.47) 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. A search of the internet for Monty Hall will bring you to many sites that discuss the problem in more detail.

Example 3.12. 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 disease, 98% of the times the test will come out positive, and 2% negative.

⁴This question was posed on the TV game show, "Let's Make A Deal," hosted by Monty Hall.

We will 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? Is this test useful?

Solution. Let $P(+|D) = 0.98$ represent the probability of testing positive and having the disease. If \overline{D} represents not having the disease and $-$ represents testing negative, then we are given: $P(-|D) = 0.02$, $P(-|\overline{D}) = 0.98$, $P(+|\overline{D}) = 0.02$, $P(D) = 0.0001$, and $P(\overline{D}) = 0.9999$. From Bayes' theorem we have

$$\begin{aligned} P(D|+) &= \frac{P(+|D)P(D)}{P(+|D)P(D) + P(+|\overline{D})P(\overline{D})} \\ &= \frac{(0.98)(0.0001)}{(0.98)(0.0001) + (0.02)(0.9999)} \\ &= 0.0047 = 0.47\%. \end{aligned} \tag{3.48}$$

Problem 3.28. 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 3.29. Make a table that determines the necessary accuracy 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, read Problem 3.92 and the reference by D'Agostini.

3.5 Bernoulli processes and the binomial distribution

Because most physicists spend little time gambling,⁵ we will have to develop our intuitive understanding 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.

⁵After a Las Vegas hotel hosted a meeting of the American Physical Society in March, 1986, the physicists were asked never to return.

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

$$M = \mu(s_1 + s_2 + \dots + s_N) = \mu \sum_{i=1}^N s_i. \quad (3.49)$$

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 (3.49). If we use (3.8), we can interchange the sum and the average and write

$$\overline{M} = \overline{\left(\sum_{i=1}^N s_i \right)} = \sum_{i=1}^N \overline{s_i}. \quad (3.50)$$

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, $\overline{s_1} = \overline{s_2} = \dots = \overline{s_N} \equiv \overline{s}$. Therefore the sum in (3.50) consists of N equal terms and can be written as

$$\overline{M} = N\overline{s}. \quad (3.51)$$

The meaning of (3.51) 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

$$\overline{M} = N(p - q). \quad (3.52)$$

Now let us calculate the variance of M , that is, $\overline{(M - \overline{M})^2}$. We write

$$\Delta M = M - \overline{M} = \sum_{i=1}^N \Delta s_i, \quad (3.53)$$

where

$$\Delta s_i \equiv s_i - \overline{s}. \quad (3.54)$$

As an example, let us calculate $\overline{(\Delta M)^2}$ for $N = 3$ spins. In this case $(\Delta M)^2$ is given by

$$\begin{aligned} (\Delta M)^2 &= (\Delta s_1 + \Delta s_2 + \Delta s_3)(\Delta s_1 + \Delta s_2 + \Delta s_3) \\ &= [(\Delta s_1)^2 + (\Delta s_2)^2 + (\Delta s_3)^2] + 2[\Delta s_1 \Delta s_2 + \Delta s_1 \Delta s_3 + \Delta s_2 \Delta s_3]. \end{aligned} \quad (3.55)$$

We take the mean value of (3.55), interchange the order of the sums and averages, and write

$$\overline{(\Delta M)^2} = \overline{[(\Delta s_1)^2 + (\Delta s_2)^2 + (\Delta s_3)^2]} + 2[\overline{\Delta s_1 \Delta s_2} + \overline{\Delta s_1 \Delta s_3} + \overline{\Delta s_2 \Delta s_3}]. \quad (3.56)$$

The first term on the right of (3.56) 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

$$\overline{\Delta s_i \Delta s_j} = \overline{\Delta s_i} \overline{\Delta s_j} = 0, \quad (i \neq j) \quad (3.57)$$

because $\overline{\Delta s_i} = 0$. That is, each cross term vanishes on the average. Hence (3.57) reduces to a sum of squared terms

$$\overline{(\Delta M)^2} = [\overline{(\Delta s_1)^2} + \overline{(\Delta s_2)^2} + \overline{(\Delta s_3)^2}]. \quad (3.58)$$

Because each spin is equivalent on the average, each term in (3.58) is equal. Hence, we obtain the desired result

$$\overline{(\Delta M)^2} = 3\overline{(\Delta s)^2}. \quad (3.59)$$

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

$$\begin{aligned} \overline{(\Delta s)^2} &= \overline{s^2} - \overline{s}^2 = 1 - (p - q)^2 = 1 - (2p - 1)^2 \\ &= 1 - 4p^2 + 4p - 1 = 4p(1 - p) = 4pq, \end{aligned} \quad (3.60)$$

and our desired result for $\overline{(\Delta M)^2}$ is

$$\overline{(\Delta M)^2} = 3(4pq). \quad (3.61)$$

Problem 3.30. Use similar considerations to show that for $N = 3$ that

$$\overline{n} = 3p \quad (3.62)$$

and

$$\overline{(n - \overline{n})^2} = 3pq, \quad (3.63)$$

where n is the number of up spins. Explain the difference between (3.52) and (3.62) for $N = 3$, and the difference between (3.61) and (3.63).

Problem 3.31. In the text we showed that $\overline{(\Delta M)^2} = 3\overline{(\Delta s)^2}$ for $N = 3$ spins (see (3.59) and (3.61)). Use similar considerations for N noninteracting spins to show that

$$\overline{(\Delta M)^2} = N(4pq). \quad (3.64)$$

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 (3.4) to calculate the probabilities of each outcome as shown in Figure 3.2. Although each outcome is distinct, several of the configurations

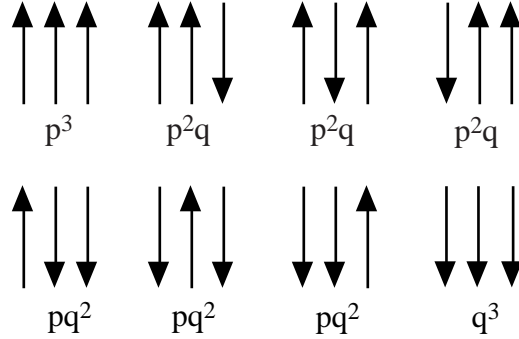


Figure 3.2: An ensemble of $N = 3$ spins. The arrow indicates the direction of the magnetic moment of a spin. The probability of each member of the ensemble is shown.

have the same number of up spins. One quantity of interest is the probability $P_N(n)$ that n spins are up out of a total of N spins. For example, there are three states with $n = 2$, each with probability p^2q so the probability that two spins are up is equal to $3p^2q$. For $N = 3$ we see from Figure 3.2 that

$$P_3(n = 3) = p^3 \quad (3.65a)$$

$$P_3(n = 2) = 3p^2q \quad (3.65b)$$

$$P_3(n = 1) = 3pq^2 \quad (3.65c)$$

$$P_3(n = 0) = q^3. \quad (3.65d)$$

Example 3.13. Find the first two moments of $P_3(n)$.

Solution. The first moment \bar{n} of the distribution is given by

$$\begin{aligned} \bar{n} &= 0 \times q^3 + 1 \times 3pq^2 + 2 \times 3p^2q + 3 \times p^3 \\ &= 3p(q^2 + 2pq + p^2) = 3p(q + p)^2 = 3p. \end{aligned} \quad (3.66)$$

Similarly, the second moment $\overline{n^2}$ of the distribution is given by

$$\begin{aligned} \overline{n^2} &= 0 \times q^3 + 1 \times 3pq^2 + 4 \times 3p^2q + 9 \times p^3 \\ &= 3p(q^2 + 4pq + 3p^2) = 3p(q + 3p)(q + p) \\ &= 3p(q + 3p) = (3p)^2 + 3pq. \end{aligned}$$

Hence

$$\overline{(n - \bar{n})^2} = \overline{n^2} - \bar{n}^2 = 3pq. \quad (3.67)$$

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: $\overline{M} = [\bar{n} - (3 - \bar{n})]$, or $\overline{M} = 3(2p - 1) = 3(p - q)$.

Problem 3.32. 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 $q = 1 - p = 1/2$. What is the probability that in three tosses of a coin, there will be two heads?

Problem 3.33. *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 $N = n + n'$. (a) 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.⁶

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

$$P_N(n) = W_N(n, n') p^n q^{n'}, \quad (3.68)$$

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

- (a) up if there are $(n - 1)$ up spins and n' down spins, or
- (b) down if there are n up spins and $(n' - 1)$ down spins.

Because there are $W_{N-1}(n - 1, n')$ ways of reaching the first case and $W_{N-1}(n, n' - 1)$ ways in the second case, we obtain the recursion relation

$$W_N(n, n') = W_{N-1}(n - 1, n') + W_{N-1}(n, n' - 1). \quad (3.69)$$

⁶These processes are named after the mathematician Jacob Bernoulli, 1654 – 1705.

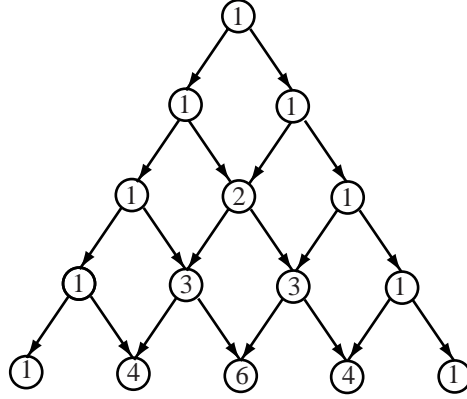


Figure 3.3: The values of the first few coefficients $W_N(n, n')$. Each number is the sum of the two numbers to the left and right above it. This construction is called a Pascal triangle.

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 (3.69) to construct $W_N(n, n')$ for any desired N . For example,

$$W_2(2, 0) = W_1(1, 0) + W_1(2, -1) = 1 + 0 = 1. \quad (3.70a)$$

$$W_2(1, 1) = W_1(0, 1) + W_1(1, 0) = 1 + 1 = 2. \quad (3.70b)$$

$$W_2(0, 2) = W_1(-1, 2) + W_1(0, 1) = 0 + 1. \quad (3.70c)$$

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

$$W_N(n, n') = \frac{N!}{n! n'!} = \frac{N!}{n! (N - n)!} \quad (3.71)$$

satisfies the relation (3.69). Note the convention $0! = 1$. We can combine (3.68) and (3.71) to find the desired result

$$P_N(n) = \frac{N!}{n! (N - n)!} p^n q^{N-n}. \quad (\text{binomial distribution}) \quad (3.72)$$

The form (3.72) is called the *binomial distribution*. Note that for $p = q = 1/2$, $P_N(n)$ reduces to

$$P_N(n) = \frac{N!}{n! (N - n)!} 2^{-N}. \quad (3.73)$$

The probability $P_N(n)$ is shown in Figure 3.4 for $N = 16$.

Problem 3.34. (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 $P_N(n)$. (b) Plot your tabulated results that you calculated in part (a) (see Figure 3.4). Assume $p = q = 1/2$. Visually estimate the width of the distribution

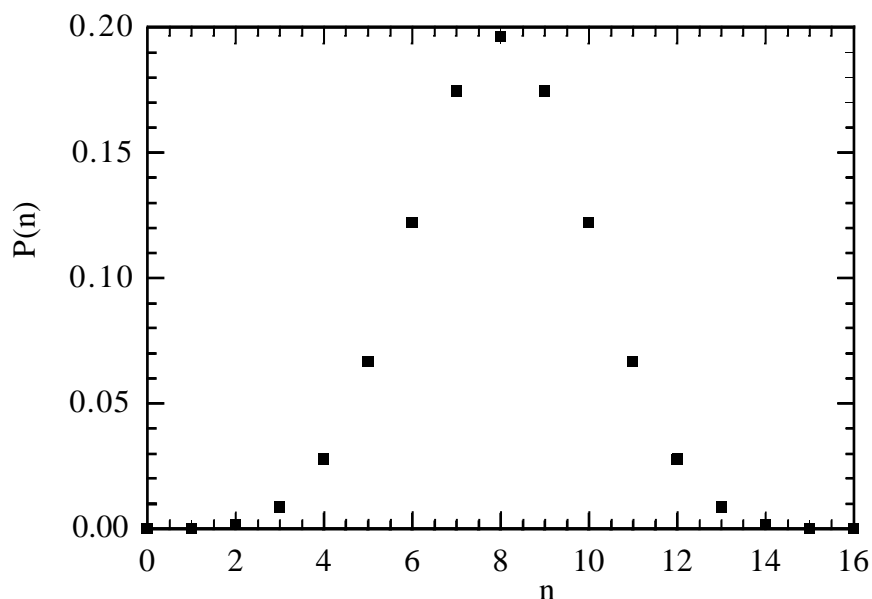


Figure 3.4: The binomial distribution $P_{16}(n)$ for $p = q = 1/2$ and $N = 16$. What is your visual estimate for the width of the distribution?

for each value 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/\bar{n} for $N = 4$ and $N = 16$ on the same graph as in (b). Visually estimate the relative width of the distribution for each value of N . (d) Plot $\ln P_N(n)$ versus n/\bar{n} for $N = 16$. Describe the behavior of $\ln P_N(n)$. Can $\ln P_N(n)$ be fitted to a parabola of the form $A + B(n - \bar{n})^2$, where A and B are fit parameters?

Problem 3.35. (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 3.34? (b) For what value of p and q do you think the width is a maximum for a given N ?

Example 3.14. Show that the expression (3.72) for $P_N(n)$ satisfies the normalization condition (3.2).

Solution. The reason that (3.72) 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

$$(p + q)^N = \sum_{n=0}^N \frac{N!}{n!(N-n)!} p^n q^{N-n}. \quad (3.74)$$

We use (3.72) and write

$$\sum_{n=0}^N P_N(n) = \sum_{n=0}^N \frac{N!}{n!(N-n)!} p^n q^{N-n} = (p + q)^N = 1^N = 1, \quad (3.75)$$

where we have used (3.74) and the fact that $p + q = 1$.

Calculation of the mean value

We now find an analytical expression for the dependence of \bar{n} on N and p . From the definition (3.6) and (3.72) we have

$$\bar{n} = \sum_{n=0}^N n P_N(n) = \sum_{n=0}^N n \frac{N!}{n! (N-n)!} p^n q^{N-n}. \quad (3.76)$$

We evaluate the sum in (3.76) by using a technique that is useful in a variety of contexts.⁷ The technique is based on the fact that

$$p \frac{d}{dp} p^n = n p^n. \quad (3.77)$$

We use (3.77) to rewrite (3.76) as

$$\bar{n} = \sum_{n=0}^N n \frac{N!}{n! (N-n)!} p^n q^{N-n} \quad (3.78)$$

$$= \sum_{n=0}^N \frac{N!}{n! (N-n)!} \left(p \frac{\partial}{\partial p} p^n \right) q^{N-n}. \quad (3.79)$$

We have used a partial derivative in (3.79) to remind us that the derivative operator does not act on q . We interchange the order of summation and differentiation in (3.79) and write

$$\bar{n} = p \frac{\partial}{\partial p} \left[\sum_{n=0}^N \frac{N!}{n! (N-n)!} p^n q^{N-n} \right] \quad (3.80)$$

$$= p \frac{\partial}{\partial p} (p+q)^N, \quad (3.81)$$

where we have temporarily assumed that p and q are independent variables. Because the operator acts only on p , we have

$$\bar{n} = pN(p+q)^{N-1}. \quad (3.82)$$

The result (3.82) is valid for arbitrary p and q , and hence it is applicable for $p+q=1$. Thus our desired result is

$$\bar{n} = pN. \quad (3.83)$$

The dependence of \bar{n} on N and p should be intuitively clear. Compare the general result (3.83) to the result (3.66) for $N=3$. What is the dependence of \bar{n}' on N and p ?

Calculation of the relative fluctuations

⁷The integral $\int_0^\infty x^n e^{-ax^2}$ for $a > 0$ is evaluated in Appendix A using a similar technique.

To determine $\overline{\Delta n^2}$ we need to know $\overline{n^2}$ (see the relation (3.15)). The average value of n^2 can be calculated in a manner similar to that for \overline{n} . We write

$$\overline{n^2} = \sum_{n=0}^N n^2 \frac{N!}{n!(N-n)!} p^n q^{N-n} \quad (3.84)$$

$$\begin{aligned} &= \sum_{n=0}^N \frac{N!}{n!(N-n)!} \left(p \frac{\partial}{\partial p}\right)^2 p^n q^{N-n} \\ &= \left(p \frac{\partial}{\partial p}\right)^2 \sum_{n=0}^N \frac{N!}{n!(N-n)!} p^n q^{N-n} = \left(p \frac{\partial}{\partial p}\right)^2 (p+q)^N \\ &= \left(p \frac{\partial}{\partial p}\right)^2 [pN(p+q)^{N-1}] \\ &= p[N(p+q)^{N-1} + pN(N-1)(p+q)^{N-2}]. \end{aligned} \quad (3.85)$$

Because we are interested in the case $p+q=1$, we have

$$\begin{aligned} \overline{n^2} &= p[N + pN(N-1)] \\ &= p[pN^2 + N(1-p)] = (pN)^2 + p(1-p)N \\ &= \overline{n}^2 + pqN, \end{aligned} \quad (3.86)$$

where we have used (3.83) and let $q=1-p$. Hence, from (3.86) we find that the variance of n is given by

$$\sigma_n^2 = \overline{(\Delta n)^2} = \overline{n^2} - \overline{n}^2 = pqN. \quad (3.87)$$

Compare the calculated values of σ_n from (3.87) with your estimates in Problem 3.34 and to the exact result (3.67) for $N=3$.

The relative width of the probability distribution of n is given by (3.83) and (3.87)

$$\frac{\sigma_n}{\overline{n}} = \frac{\sqrt{pqN}}{pN} = \left(\frac{q}{p}\right)^{\frac{1}{2}} \frac{1}{\sqrt{N}}. \quad (3.88)$$

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

$$\ln N! \approx N \ln N - N. \quad (\text{Stirling's approximation}) \quad (3.89)$$

A more accurate approximation is given by

$$\ln N! \approx N \ln N - N + \frac{1}{2} \ln(2\pi N). \quad (3.90)$$

A simple derivation of Stirling's approximation is given in Appendix A.

Problem 3.36. (a) What is the largest value of $\ln N!$ that you can calculate exactly using a typical hand calculator? (b) Compare the approximations (3.89) and (3.90) 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

$$\ln N! = \sum_{m=1}^N \ln m. \quad (3.91)$$

(c) Use the simple form of Stirling's approximation to show that

$$\frac{d}{dx} \ln x! = \ln x \text{ for } x \gg 1. \quad (3.92)$$

Problem 3.37. 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 $P_N(n = \bar{n})\sigma_n$?

Problem 3.38. 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 3.39. Suppose that a random walker takes n steps to the right and n' steps to the left and each step is of equal length a . Denote x as the net displacement of a walker. What is the mean value \bar{x} for a N -step random walk? What is the analogous expression for the variance $(\Delta x)^2$?

Problem 3.40. *Monte Carlo simulation.* We can gain more insight into the nature of the Bernoulli distribution by doing a Monte Carlo simulation, that is, by using a computer to “flip coins” and average over many measurements.⁸ In the context of random walks, we can implement 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. It is necessary to save the value of x after N steps and average over many walkers. Write a simple program or use the applet at stp.clarku.edu/simulations/OneDimensionalWalk to compute $P_N(x)$. First choose $N = 4$ and $p = 1/2$ and make a sufficient number of measurements so that the various quantities of interest are known to a good approximation. Then take $N = 100$ and describe the qualitative x -dependence of $P_N(x)$.

⁸The name “Monte Carlo” was coined by Nicolas Metropolis in 1949.

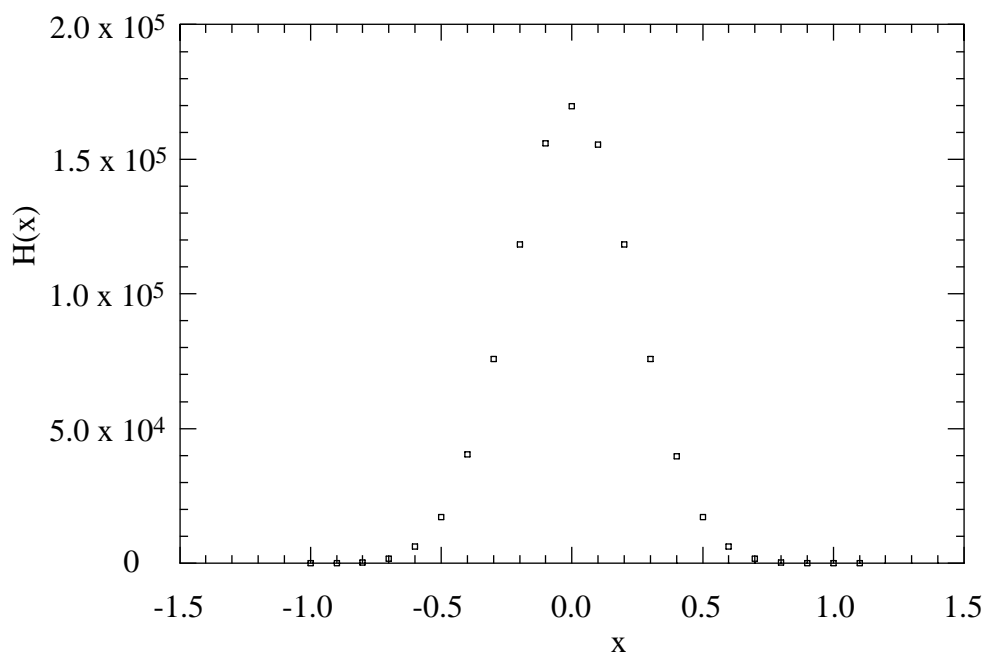


Figure 3.5: Histogram of the number of times that the displacement of a one-dimensional random walker is between x and $x + \Delta x$ after $N = 16$ steps. The data was generated by simulating 10^6 walkers. The length of each step was chosen at random between zero and unity and the bin width is $\Delta x = 0.1$.

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.

For continuous variables, the probability of obtaining a particular value is not meaningful. For example, consider a one-dimensional random walker who steps at random to the right or to the left with equal probability, but with step lengths that are chosen at random between zero and a maximum length a . The continuous nature of the length of each step implies that the position x of the walker is a continuous variable. Because there are an infinite number of possible x values in a finite interval of x , the probability of obtaining any particular value of x is zero. Instead, we have to reformulate the question and ask for the probability that the position of the walker is between x and $x + \Delta x$ after N steps. If we do a simulation of such a walker, we would record the number of times, $H(x, \Delta x)$, that a walker is in a bin of width Δx a distance x from the origin, and plot the histogram $H(x, \Delta x)$ as a function of x (see Figure 3.5). If the number of walkers that is sampled is sufficiently large, we would find that $H(x, \Delta x)$ 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 $H(x, \Delta x)$ 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. Hence, our estimate of the number of walkers in each bin would be less accurate. Because we expect the number to be proportional to the width of the bin, we can write $H(x, \Delta x) = p(x)\Delta x$. The quantity $p(x)$ is the *probability density*. In the limit that $\Delta x \rightarrow 0$, $H(x, \Delta x)$ becomes a continuous function of x , and we can write the probability that a walker is in the range between a and b as

$$P(a \text{ to } b) = \int_a^b p(x) dx. \quad (3.93)$$

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 $p(x)$ are easily generalizable from the discrete case. For example, the normalization condition is given by

$$\int_{-\infty}^{\infty} p(x) dx = 1. \quad (3.94)$$

The mean value of the function $f(x)$ in the interval a to b is given by

$$\bar{f} = \int_a^b f(x) p(x) dx. \quad (3.95)$$

Problem 3.41. The random variable x has the probability density

$$p(x) = \begin{cases} A e^{-\lambda x} & \text{if } 0 \leq x \leq \infty \\ 0 & x < 0. \end{cases} \quad (3.96)$$

(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 less than 0.3.

Problem 3.42. Consider the probability density function $p(\mathbf{v}) = (a/\pi)^{3/2} e^{-av^2}$ for the velocity \mathbf{v} of a particle. 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

$$\int_0^{\infty} e^{-au^2} du = \frac{1}{2} \sqrt{\frac{\pi}{a}}. \quad (3.97)$$

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 3.43. (a) Find the first four moments of the Gaussian probability density

$$p(x) = (2\pi)^{-\frac{1}{2}} e^{-x^2/2}. \quad (-\infty < x < \infty) \quad (3.98)$$

Guess the dependence of the k th 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

$$C_4 = \overline{x^4} - 4\overline{x^3}\overline{x} - 3\overline{x^2}^2 + 12\overline{x^2}\overline{x}^2 - 6\overline{x}^4. \quad (3.99)$$

Problem 3.44. Consider the probability density given by

$$p(x) = \begin{cases} (2a)^{-1} & \text{for } |x| \leq a \\ 0 & \text{for } |x| > a \end{cases} \quad (3.100)$$

(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 (3.99). What is C_4 for the probability density in (3.100)?

Problem 3.45. Not all probability densities have a finite variance. Sketch the *Lorentz* or *Cauchy distribution* given by

$$p(x) = \frac{1}{\pi} \frac{\gamma}{(x-a)^2 + \gamma^2}. \quad (-\infty < x < \infty) \quad (3.101)$$

Choose $a = 0$ and $\gamma = 1$ and compare the form of $p(x)$ in (3.101) to the Gaussian distribution given by (3.98). 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 3.34 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. However, because the logarithm of $P_N(n)$ is a slowly varying function (see Problem 3.34), 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

$$\ln p(n) = \ln p(n = \tilde{n}) + (n - \tilde{n}) \frac{d \ln p(n)}{dn} \Big|_{n=\tilde{n}} + \frac{1}{2} (n - \tilde{n})^2 \frac{d^2 \ln p(n)}{d^2 n} \Big|_{n=\tilde{n}} + \cdots \quad (3.102)$$

Because we have assumed that the expansion (3.102) 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 (3.102) can be neglected and adopt the notation

$$\ln A = \ln p(n = \tilde{n}), \quad (3.103)$$

and

$$B = -\frac{d^2 \ln p(n)}{dn^2} \Big|_{n=\tilde{n}}. \quad (3.104)$$

The approximation (3.102) and the notation in (3.103) and (3.104) allows us to write

$$\ln p(n) \approx \ln A - \frac{1}{2}B(n - \tilde{n})^2, \quad (3.105)$$

or

$$p(n) \approx A e^{-\frac{1}{2}B(n-\tilde{n})^2}. \quad (3.106)$$

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

$$\ln p(n) = \ln N! - \ln n! - \ln(N - n)! + n \ln p + (N - n) \ln q. \quad (3.107)$$

It is straightforward to use the relation (3.92) to obtain

$$\frac{d(\ln p)}{dn} = -\ln n + \ln(N - n) + \ln p - \ln q. \quad (3.108)$$

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

$$\frac{N - \tilde{n}}{\tilde{n}} = \frac{q}{p}, \quad (3.109)$$

or $(N - \tilde{n})p = \tilde{n}q$. If we use the relation $p + q = 1$, we obtain

$$\tilde{n} = pN. \quad (3.110)$$

Note that $\tilde{n} = \bar{n}$, 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 (3.108). We have

$$\frac{d^2(\ln p)}{dn^2} = -\frac{1}{n} - \frac{1}{N - n}. \quad (3.111)$$

Hence, the coefficient B defined in (3.104) is given by

$$B = -\frac{d^2 \ln p}{dn^2} = \frac{1}{\tilde{n}} + \frac{1}{N - \tilde{n}} = \frac{1}{Npq}. \quad (3.112)$$

From the relation (3.87) we see that

$$B = \frac{1}{\sigma^2}, \quad (3.113)$$

where σ^2 is the variance of n .

If we use the simple form of Stirling's approximation (3.89) 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 (3.90). The result is

$$A = \frac{1}{(2\pi Npq)^{1/2}} = \frac{1}{(2\pi\sigma^2)^{1/2}}. \quad (3.114)$$

Problem 3.46. Derive (3.114) using the more accurate form of Stirling's approximation (3.90) with $n = pN$ and $N - n = qN$.

If we substitute our results for \tilde{n} , B , and A into (3.106), we find the standard form for the Gaussian distribution

$$p(n) = \frac{1}{\sqrt{2\pi\sigma^2}} e^{-(n-\bar{n})^2/2\sigma^2}. \quad (\text{Gaussian probability density}) \quad (3.115)$$

An alternative derivation of the parameters A , B , and \tilde{n} is given in Problem 3.74.

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 distribution (3.115) for $p = q = 1/2$.

From our derivation we see that (3.115) is valid for large values of N and for values of n near \bar{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 distribution is that its relative width, σ_n/\bar{n} , decreases as $N^{-1/2}$. Of course, the binomial distribution shares this feature.

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

$$S = \sum_{i=1}^N s_i, \quad (3.116)$$

where

$$s_i = \begin{cases} 1, & \text{if the } i\text{th throw gives 1} \\ 0 & \text{otherwise.} \end{cases} \quad (3.117)$$

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 3.6 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 3.47 we calculate the absolute and relative width of the distributions.

Problem 3.47. Estimate the absolute width and the relative width of the distributions shown in Figure 3.6 for $N = 100$ and $N = 800$. Does the error of any one measurement of S decrease with increasing N as expected? How would the plot change if M were increased to $M = 10,000$?

In Appendix 3A we show that in the limit of large N , the probability density $p(S)$ is given by

$$p(S) = \frac{1}{\sqrt{2\pi\sigma_S^2}} e^{-(S-\bar{S})^2/2\sigma_S^2}, \quad (3.118)$$

where

$$\bar{S} = N\bar{s} \quad (3.119)$$

$$\sigma_S^2 = N\sigma^2, \quad (3.120)$$

with $\sigma^2 = \overline{s^2} - \bar{s}^2$. 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 (3.118) is equivalent to the central limit theorem. Note that the Gaussian form in (3.118) 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 sum of a large number of random variables will approximate a Gaussian distribution. Moreover, the approximation steadily improves as the number of variables in the sum increases.

For the throw of a die, $\bar{s} = \frac{1}{6}$, $\overline{s^2} = \frac{1}{6}$, and $\sigma^2 = \overline{s^2} - \bar{s}^2 = \frac{1}{6} - \frac{1}{36} = \frac{5}{36}$. For N throws of a die, we have $\bar{S} = N/6$ 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 $\sigma_S/\bar{S} = \sqrt{5/N}$.

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 (3.118)–(3.120) 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 distribution 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.

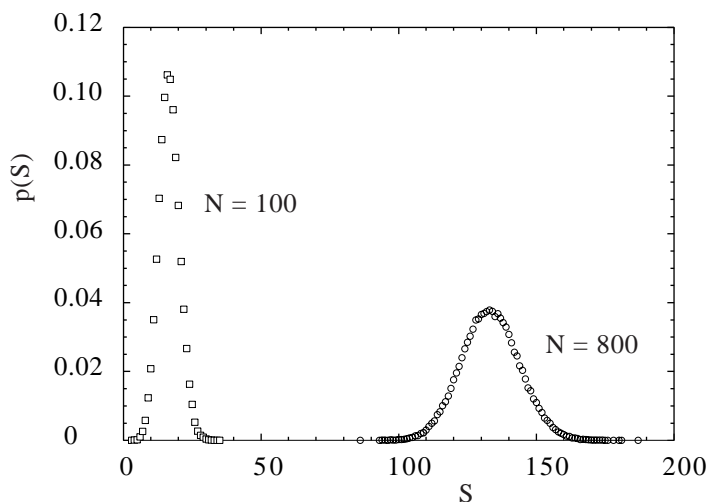


Figure 3.6: The distribution of the measured values of $M = 10,000$ different measurements of the sum S for $N = 100$ and $N = 800$ terms in the sum. The quantity S is the number of times that face 1 appears in N throws of a die. For $N = 100$, the measured values are $\bar{S} = 16.67$, $\overline{S^2} = 291.96$, and $\sigma_S = 3.74$. For $N = 800$, the measured values are $\bar{S} = 133.31$, $\overline{S^2} = 17881.2$, and $\sigma_S = 10.52$. What are the estimated values of the relative width for each case?

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 3.48. 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 3.49. Write a program to test the applicability of the central limit theorem. For simplicity, assume that the variable s_i is uniformly distributed between 0 and 1. First compute the mean and standard deviation of s and compare your numerical results with your analytical calculation. Then sum $N = 10\,000$ values of s_i to obtain one measurement of S . Compute the sum for many measurements, say $M = 1000$. Store in an array $H(S)$ the number of times S is between S and $S + \Delta S$. Plot your results for $H(S)$ and determine how $H(S)$ depends on N . How do your results change if $M = 10000$? Do your results for the form of $H(S)$ depend strongly on the number of measurements M ?

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 lived eighty years and 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 such 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:

$$P(n) = \frac{N!}{n!(N-n)!} p^n (1-p)^{N-n}. \quad (3.121)$$

(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

$$\begin{aligned} \ln \frac{N!}{(N-n)!} &= \ln N! - \ln(N-n)! \\ &\approx N \ln N - (N-n) \ln(N-n) \\ &\approx N \ln N - (N-n) \ln N \\ &= N \ln N - N \ln N + n \ln N \\ &= n \ln N. \end{aligned} \quad (3.122)$$

From (3.123) we obtain

$$\frac{N!}{(N-n)!} \approx e^{n \ln N} = N^n. \quad (3.124)$$

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

$$P(n) \approx \frac{N^n}{n!} p^n e^{-pN} = \frac{(Np)^n}{n!} e^{-pN}, \quad (3.125)$$

or

$$P(n) = \frac{\bar{n}^n}{n!} e^{-\bar{n}}, \quad (\text{Poisson distribution}) \quad (3.126)$$

where

$$\bar{n} = pN. \quad (3.127)$$

The form (3.126) 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 $\bar{N} = pN$ 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 3.50. 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 . 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, \dots 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

$$\int_0^t w(t) \Delta t, \quad (3.128)$$

and the probability that no event occurs in the interval t is

$$1 - \int_0^t w(t) \Delta t. \quad (3.129)$$

Thus the probability that the duration of the interval between the two events is between t and $t + \Delta t$ is given by

$$\begin{aligned} w(t) \Delta t &= \text{probability that no event occurs in the interval } [0, t] \\ &\quad \times \text{probability that an event occurs in interval } [t, t + \Delta t] \\ &= \left[1 - \int_0^t w(t) dt\right] \lambda \Delta t. \end{aligned} \quad (3.130)$$

If we cancel Δt from each side of (3.130) and differentiate both sides with respect to t , we find

$$\frac{dw}{dt} = -\lambda w,$$

so that

$$w(t) = Ae^{-\lambda t}. \quad (3.131)$$

The constant of integration A is determined from the normalization condition:

$$\int_0^\infty w(t)dt = 1 = A \int_0^\infty e^{-\lambda t} dt = A/\lambda. \quad (3.132)$$

Hence, $w(t)$ is the exponential function

$$w(t) = \lambda e^{-\lambda t}. \quad (3.133)$$

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.

The above 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:

$$P_n(t) = \frac{(\lambda t)^n}{n!} e^{-\lambda t}. \quad (3.134)$$

We first consider the case $n = 0$. If $n = 0$, the probability that no event occurs in the interval t is (see (3.130))

$$P_{n=0}(t) = 1 - \lambda \int_0^t e^{-\lambda t'} dt' = e^{-\lambda t}. \quad (3.135)$$

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

$$P_{n=1}(t) = \int_0^t \lambda e^{-\lambda t'} e^{-\lambda(t-t')} dt', \quad (3.136)$$

where we have used (3.135) with $t \rightarrow (t' - t)$. Hence,

$$P_{n=1}(t) = \int_0^t \lambda e^{-\lambda t} dt = (\lambda t) e^{-\lambda t}. \quad (3.137)$$

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,

$$P_n(t) = \int_0^t \lambda e^{-\lambda t'} P_{n-1}(t - t') dt'. \quad (3.138)$$

Equation (3.138) is a recurrence formula that can be used to derive (3.134) by induction. It is easy to see that (3.134) satisfies (3.138) for $n = 0$ and 1. As is usual when solving recursion formula by induction, we assume that (3.134) is correct for $(n - 1)$. We substitute this result into (3.138) and find

$$P_n(t) = \lambda^n e^{-\lambda t} \int_0^t (t - t')^{n-1} dt' / (n - 1)! = \frac{(\lambda t)^n}{n!} e^{-\lambda t}. \quad (3.139)$$

An application of the Poisson distribution is given in Problem 3.51.

Problem 3.51. 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. Is the distribution of the number of vehicles consistent with the Poisson distribution? If so, what is the value of the parameter λ ?

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 the sum is a Gaussian. 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. 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^2w , pqw , qpw , and q^2w . What is the distribution of the fragments after N blows of the hammer?

To answer this question, 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 $\bar{\Pi}$, the mean value of Π . To compute $\bar{\Pi}$, we define $P(n)$ as 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:

$$P(n) = \frac{N!}{n!(N-n)!} p^n q^{N-n}. \quad (3.140)$$

The mean value of the product is given by

$$\bar{\Pi} = \sum_{n=0}^N P(n) x_1^n x_2^{N-n} \quad (3.141)$$

$$= (px_1 + qx_2)^N. \quad (3.142)$$

The most probable event is one in which the product contains Np factors of x_1 and Nq factors of x_2 . Hence, the most probable value of the product is

$$\tilde{\Pi} = (x_1^p x_2^q)^N. \quad (3.143)$$

We have found that the average value of the sum of random variables is a good approximation to the most probable value of the sum. Let us see if there is a similar relation for a random multiplicative process. We first consider $x_1 = 2$, $x_2 = 1/2$, and $p = q = 1/2$. Then $\bar{\Pi} = [(1/2) \times 2 + (1/2) \times (1/2)]^N = (5/4)^N = e^{N \ln 5/4}$. In contrast $\tilde{\Pi} = 2^{1/2} \times (1/2)^{1/2} = 1$.

The reason for the large discrepancy between $\bar{\Pi}$ and $\tilde{\Pi}$ is the relatively 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 $\bar{\Pi}$ and a dominant contribution to the higher moments $\bar{\Pi}^m$.

***Problem 3.52.** (a) Confirm the above general results for $N = 4$ by showing explicitly all the possible values of the product. (b) Consider the case $x_1 = 2$, $x_2 = 1/2$, $p = 1/3$, and $q = 2/3$, and calculate $\bar{\Pi}$ and $\tilde{\Pi}$.

***Problem 3.53.** (a) Show that $\bar{\Pi}^m$ reduces to $(px_1^m)^N$ as $m \rightarrow \infty$. This result implies that for $m \gg 1$, the m th moment is determined solely by the most extreme event. (b) 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 $N \gg 1$. (c) More insight can be gained by running the applet at stp.clarku.edu/simulations/product 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 $p = q = 1/2$ for which we have already calculated the analytical results for $\bar{\Pi}$ and $\tilde{\Pi}$. First choose $N = 4$ and estimate $\bar{\Pi}$ and $\tilde{\Pi}$. Do your estimated values converge more or less uniformly to the exact 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. An excellent discussion is given by Redner (see references).

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

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 $p(x)$

Appendix 3A: The uncertainty for unequal probabilities

Consider a loaded die for which the probabilities P_j are not equal. We wish to motivate the form (3.29) 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, \dots . 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 (3.28) for the associated uncertainty S_N :

$$S_N = \ln \Omega = \ln \left[\frac{N!}{\prod_j N_j!} \right], \quad (3.144)$$

The right-hand side of (3.144) equals the total number of possible sequences.

To understand the form (3.144) 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

$$M = \frac{N!}{\prod_j N_j} = \frac{4!}{2!2!} = 6. \quad (3.145)$$

Now that we understand the form of S_N in (3.144), we can find the desired form of S . The uncertainty S_N in (3.144) is the uncertainty associated with all N rolls. The uncertainty associated with one roll is

$$S = \lim_{N \rightarrow \infty} \frac{1}{N} S_N = \lim_{N \rightarrow \infty} \frac{1}{N} \ln \left[\frac{N!}{\prod_j N_j!} \right] = \lim_{N \rightarrow \infty} \frac{1}{N} [\ln N! - \sum_j \ln N_j!]. \quad (3.146)$$

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.

We can reduce (3.146) to a simpler form by using Stirling's approximation, $\ln N! \approx N \ln N - N$ for large N and substituting $N_j = NP_j$:

$$S = \lim_{N \rightarrow \infty} \frac{1}{N} [N \ln N - N - \sum_j (NP_j) \ln(NP_j) - \sum_j (NP_j)] \quad (3.147)$$

$$= \lim_{N \rightarrow \infty} \frac{1}{N} [N \ln N - N - \ln N \sum_j (NP_j) + N \sum_j P_j \ln P_j - N \sum_j P_j] \quad (3.148)$$

$$= \lim_{N \rightarrow \infty} \frac{1}{N} [N \ln N - N - N \ln N - N \sum_j P_j \ln P_j] \quad (3.149)$$

$$= - \sum_j P_j \ln P_j. \quad (3.150)$$

Appendix 3B: 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

$$df - \lambda dg = 0, \quad (3.151)$$

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 (3.151), we have

$$(y^2 - 2\lambda x)dx + 2(xy - \lambda y)dy = 0. \quad (3.152)$$

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 $f(x_1, x_2, \dots, x_N)$ subject to the constraints $g_j(x_1, x_2, \dots, x_N) = 0$ where $j = 1, 2, \dots, M$ with $M < N$. The maximum of f is given by

$$df = \sum_{i=1}^N \left(\frac{\partial f}{\partial x_i} \right) dx_i = 0, \quad (3.153)$$

and the constraint can be expressed as

$$dg = \sum_{i=1}^N \left(\frac{\partial g_j}{\partial x_i} \right) dx_i = 0. \quad (3.154)$$

As in our example, we can combine (3.153) and (3.154) and write $df - \sum_{j=1}^M \lambda_j dg_j = 0$ or

$$\sum_{i=1}^N \left[\left(\frac{\partial f}{\partial x_i} \right) - \sum_{j=1}^M \lambda_j \left(\frac{\partial g_j}{\partial x_i} \right) \right] dx_i = 0. \quad (3.155)$$

We are free to choose all M values of λ_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

$$\left(\frac{\partial f}{\partial x_i} \right) - \sum_{j=1}^M \lambda_j \left(\frac{\partial g_j}{\partial x_i} \right) = 0. \quad (3.156)$$

In Example 3.11 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 is f . Then we wish to determine P_1, P_2, \dots, P_6 subject to the constraints

$$\sum_{j=1}^6 P_j = 1, \quad (3.157)$$

$$\sum_{j=1}^6 jP_j = f. \quad (3.158)$$

For a perfect die $f = 3.5$. Equation (3.156) becomes

$$\sum_{j=1}^6 \left[(1 + \ln P_j) + \alpha + \beta j \right] dP_j = 0, \quad (3.159)$$

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

$$\alpha = \ln P_2 - 2 \ln P_1 - 1 \quad (3.160a)$$

$$\beta = \ln P_1 - \ln P_2. \quad (3.160b)$$

We can solve (3.160b) for $\ln P_2 = \ln P_1 - \beta$ and use (3.160a) to find $\ln P_1 = -1 - \alpha - \beta$ and use this result to write $P_2 = -1 - \alpha - \beta$. We can independently vary dP_3, \dots, dP_6 because the two constraints are satisfied by the values of P_1 and P_2 . We let

$$\ln P_j = -1 - \alpha - j\beta, \quad (3.161)$$

or

$$P_j = e^{-1-\alpha} e^{-\beta j}. \quad (3.162)$$

We can eliminate the constant α by the normalization condition (3.157):

$$P_j = \frac{e^{-\beta j}}{\sum_j e^{-\beta j}}. \quad (3.163)$$

The constant β is determined by the constraint (3.38):

$$f = \frac{e^{-\beta} + 2e^{-\beta 2} + 3e^{-\beta 3} + 4e^{-\beta 4} + 5e^{-\beta 5} + 6e^{-\beta 6}}{e^{-\beta} + e^{-\beta 2} + e^{-\beta 3} + e^{-\beta 4} + e^{-\beta 5} + e^{-\beta 6}}. \quad (3.164)$$

In general, (3.164) must be solved numerically.

Problem 3.54. Show that the solution to (3.164) is $\beta = 0$ for $f = 7/2$, $\beta = +\infty$ for $f = 2$, $\beta = -\infty$ for $f = 6$, and $\beta = -0.1746$ for $f = 4$.

Appendix 3C: 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 $p(x)$:

$$\phi(k) = \overline{e^{ikx}} = \int_{-\infty}^{\infty} dx e^{ikx} p(x). \quad (3.165)$$

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:

$$p(x) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dk e^{-ikx} \phi(k). \quad (3.166)$$

Problem 3.55. 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 $p(x)$:

$$\phi(k) = \sum_{n=0}^{\infty} \frac{k^n}{n!} \frac{d^n \phi(k)}{dk^n} \Big|_{k=0}, \quad (3.167)$$

$$= \overline{e^{ikx}} = \sum_{n=0}^{\infty} \frac{(ik)^n \overline{x^n}}{n!}. \quad (3.168)$$

By comparing coefficients of k^n in (3.167) and (3.168), we see that

$$\bar{x} = -i \frac{d\phi}{dk} \Big|_{k=0}. \quad (3.169)$$

In Problem 3.56 we show that

$$\overline{x^2} - \bar{x}^2 = -\frac{d^2}{dk^2} \ln \phi(k) \Big|_{k=0} \quad (3.170)$$

and that certain convenient combinations of the moments are related to the power series expansion of the logarithm of the characteristic function.

Problem 3.56. The characteristic function generates the *cumulants* C_m defined by

$$\ln \phi(k) = \sum_{m=1}^{\infty} \frac{(ik)^m}{m!} C_m. \quad (3.171)$$

Show that the cumulants are combinations of the moments of x and are given by

$$C_1 = \bar{x} \quad (3.172a)$$

$$C_2 = \sigma^2 = \overline{x^2} - \bar{x}^2 \quad (3.172b)$$

$$C_3 = \overline{x^3} - 3\overline{x^2}\bar{x} + 2\bar{x}^3 \quad (3.172c)$$

$$C_4 = \overline{x^4} - 4\overline{x^3}\bar{x} - 3\overline{x^2}^2 + 12\overline{x^2}\bar{x}^2 - 6\bar{x}^4. \quad (3.172d)$$

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

$$z = x + y. \quad (3.173)$$

How do the probability densities combine? The answer is

$$p(z) = \int dx dy p_1(x) p_2(y) \delta(z - x - y). \quad (3.174)$$

The integral in (3.174) 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 (3.174) 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

$$\phi_z(k) = \int dz e^{ikz} p(z) \quad (3.175)$$

$$\begin{aligned} &= \int dz \int dx \int dy e^{ikz} p_1(x) p_2(y) \delta(z - x - y) \\ &= \int dx e^{ikx} p_1(x) \int dy e^{iky} p_2(y) \\ &= \phi_1(k) \phi_2(k). \end{aligned} \quad (3.176)$$

It is straightforward to generalize this result to a sum of N random variables. We write

$$z = x_1 + x_2 + \dots + x_N. \quad (3.177)$$

Then

$$\phi_z(k) = \prod_{i=1}^N \phi_i(k). \quad (3.178)$$

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 (3.178), we obtain

$$\ln \phi_z(k) = \sum_{i=1}^N \ln \phi_i(k). \quad (3.179)$$

Each side of (3.179) 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 n th order cumulants satisfy the relation:

$$C_n^z = C_n^1 + C_n^2 + \dots + C_n^N. \quad (3.180)$$

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 \bar{x} and σ respectively, then from (3.172a) and (3.180) we find that the mean weight of N adult males is given by $N\bar{x}$. Similarly from (3.172b) 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, \dots, 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 $\bar{x} = 0$, 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

$$p(S) = \frac{1}{\sqrt{2\pi N\sigma_x^2}} e^{-S^2/2N\sigma_x^2} \quad (3.181)$$

From (3.172b) 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 :

$$\overline{\left(\frac{x_1 + x_2 + \dots + x_N}{N}\right)^2} = \frac{N\sigma_x^2}{N^2} = \frac{\sigma_x^2}{N}. \quad (3.182)$$

From (3.182) we see that it is useful to define a scaled sum:

$$z = \frac{1}{\sqrt{N}}(x_1 + x_2 + \dots + x_N), \quad (3.183)$$

and to write the central limit theorem in the form

$$p(z) = \frac{1}{\sqrt{2\pi\sigma^2}} e^{-z^2/2\sigma^2}. \quad (3.184)$$

To obtain the result (3.184), we write the characteristic function of z as

$$\begin{aligned} \phi_z(k) &= \int dx e^{ikz} \int dx_1 \int dx_2 \cdots \int dx_N \delta\left(z - \left[\frac{x_1 + x_2 + \cdots + x_N}{N^{1/2}}\right]\right) \\ &\quad \times p(x_1) p(x_2) \cdots p(x_N) \\ &= \int dx_1 \int dx_2 \cdots \int dx_N e^{ik(x_1 + x_2 + \cdots + x_N)/N^{1/2}} p(x_1) p(x_2) \cdots p(x_N) \\ &= \phi\left(\frac{k}{N^{1/2}}\right)^N. \end{aligned} \quad (3.185)$$

We next take the logarithm of both sides of (3.185) and expand the right-hand side in powers of k to find

$$\ln \phi_z(k) = \sum_{m=2}^{\infty} \frac{(ik)^m}{m!} N^{1-m/2} C_m. \quad (3.186)$$

The $m = 1$ term does not contribute in (3.186) because we have assumed that $\bar{x} = 0$. More importantly, note that as $N \rightarrow \infty$, the higher-order terms are suppressed so that

$$\ln \phi_z(k) \rightarrow -\frac{k^2}{2} C_2, \quad (3.187)$$

or

$$\phi_z(k) \rightarrow e^{-k^2\sigma^2/2} + \cdots \quad (3.188)$$

Because the inverse Fourier transform of a Gaussian is also a Gaussian, we find that

$$p(z) = \frac{1}{\sqrt{2\pi\sigma^2}} e^{-z^2/2\sigma^2}. \quad (3.189)$$

The leading correction to $\phi(k)$ in (3.189) gives rise to a term of order $N^{-1/2}$, and therefore does not contribute in the limit $N \rightarrow \infty$.

The conditions for the rigorous applicability of the central limit theorem can be found in textbooks on probability. The only requirements 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 3.45). It is not necessary that all the x_i have the same distribution.

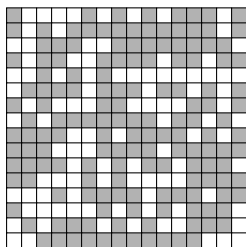


Figure 3.7: Representation of a square lattice of 16×16 sites. The sites are represented by squares and are either occupied (shaded) or empty (white).

Additional Problems

Problems	page
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3.42, 3.43, 3.44, 3.45	111
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3.55, 3.56	125

Listing of inline problems.

Problem 3.57. In Figure 3.7 we show a square lattice of 16^2 sites each of which is either occupied or empty. Estimate the probability that a site in the lattice is occupied.

Problem 3.58. Three coins are tossed in succession. Assume that the simple events are equiprobable. Find the probabilities of the following: (a) the first coin is a heads, (b) exactly two heads have occurred, (c) not more than two heads have occurred.

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 3.59. A student tries to solve Problem 3.18 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 3.60. 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.

Problem 3.61. 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. Consider the ten pairs of numbers, (x_i, y_i) , given in Table 3.7. The numbers are all 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

$$F = \int_0^1 dx \sqrt{(1-x^2)}. \quad (3.190)$$

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*.⁹ An applet for estimating integrals by Monte Carlo integration can be found at stp.clarku.edu/simulations/estimation.

Problem 3.63. 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.

⁹Monte Carlo methods were first developed to estimate integrals that could not be performed by other ways.

Problem 3.65. What is the probability that five children produced by the same couple will consist of (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. 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. 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.insidescience.org/reports/2003/080.html.

Problem 3.68. The Galton board (named after Francis Galton (1822–1911)), is a triangular array of pegs. The rows are numbered $0, 1, \dots$ 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. (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. 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 (3.61) for $\overline{(\Delta M)^2}$ differs by a factor of four from the result for σ_n^2 in (3.87). Why? Compare (3.61) to the result of Problem 3.39.

Problem 3.73. 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 \bar{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 \bar{n} compare for the two values of N ? Explain your results. (c) Compute \bar{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 3.74. In Section 3.7 we evaluated the derivatives of $P(n)$ to determine the parameters A , B , and \tilde{n} in (3.106). 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

$$P(n) = Ae^{-\frac{1}{2}B(n-\tilde{n})^2}, \quad (3.191)$$

and require that

$$\int_0^N P(n) dn = 1. \quad (3.192)$$

Because $P(n)$ depends on the difference $n - \tilde{n}$, it is convenient to change the variable of integration in (3.192) to $x = n - \tilde{n}$. We have

$$\int_{-\tilde{n}}^{N-\tilde{n}} P(x) dx = 1, \quad (3.193)$$

where

$$P(x) = Ae^{-\frac{1}{2}Bx^2}. \quad (3.194)$$

In the limit of large N , we can extend the upper and lower limits of integration in (3.193) and write

$$\int_{-\infty}^{\infty} P(x) dx = 1, \quad (3.195)$$

The first moment of $P(n)$ is given by

$$\bar{n} = \int_0^N nP(n) dn = pN. \quad (3.196)$$

Make a change of variables and show that

$$\int_{-\infty}^{\infty} xP(x) dx = \bar{n} - \tilde{n}. \quad (3.197)$$

Because the integral in (3.197) is zero, we can conclude that $\tilde{n} = \bar{n}$. We also have that

$$\overline{(n - \bar{n})^2} = \int_0^N (n - \bar{n})^2 P(n) dn = pqN. \quad (3.198)$$

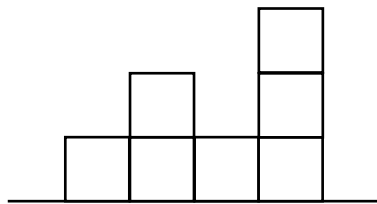


Figure 3.8: Example of a castle wall as explained in Problem 3.75.

Do the integrals in (3.198) and (3.195) (see (A.17) and (A.21)) and confirm that the values of B and A are given by (3.112) and (3.114), 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.

Problem 3.75. Consider a two-dimensional “castle wall” constructed from N squares as shown in Figure 3.8. 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 3.76. 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 3.77. 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 3.78.** 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 $\ln P(n)$:

$$\frac{1}{3!}(n - \tilde{n})^3 C + \frac{1}{4!}(n - \tilde{n})^4 D, \quad (3.199)$$

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 (3.102)) and determine the conditions for which the terms beyond $(n - \tilde{n})^2$ can be neglected. (b) Define the error as

$$E(n) = 1 - \frac{\text{Binomial}(n)}{\text{Gaussian}(n)} \quad (3.200)$$

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 3.79. 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 3.80. 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 3.81. 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 3.82. 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 3.83.** 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 3.84.** 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 $n = 1, \dots, 9$? 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

$$P(n) = \log_{10} \left(1 + \frac{1}{n} \right). \quad (3.201)$$

The distribution (3.201) 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," *Amer. Sci.* **86**, 358–363 (1998).

***Problem 3.85.** 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 3.86.** Analyze a text and do a ranking of the word frequencies. The word with rank r is the r th 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

$$f \sim \frac{1}{r \ln(1.78R)}, \quad (3.202)$$

where R is the number of different words. Note the inverse power law behavior. The relation (3.202) 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 3.87.** 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.

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 3.88. 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

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.

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 3.89. 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 3.90.** 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 3.91.** 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? Visit chance.dartmouth.edu/chancewiki/ and www.dartmouth.edu/~chance/ and read about other interesting issues involving probability and statistics.

***Problem 3.92.** D’Agostini has given a simple example where it is clear that determining the probability of various events using all the available information is more appropriate than estimating the probability from a relative frequency. [xx not finished xx]

***Problem 3.93.** 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.

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.

The www.dartmouth.edu/~chance/ Chance database 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 an excellent 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, eds., 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 some 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).

Charles A. Whitney, *Random Processes in Physical Systems: An Introduction to Probability-Based Computer Simulations*, John Wiley & Sons (1990).

R. K. P. Zia and B. Schmittmann, “Watching a drunkard for 10 nights: A study of distributions of variances,” *Am. J. Phys.* **71**, 859 (2003). See Problem 3.73.

Chapter 4

The Methodology of Statistical Mechanics

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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 types of calculations that we do in statistical mechanics.

Consider an isolated system of $N = 5$ noninteracting 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 an enumeration of the *microstates* or *configurations* of the system. For $N = 5$, there are $2^5 = 32$ microstates, each specified by the orientation of each spin. 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 4.1a 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 4.1b).

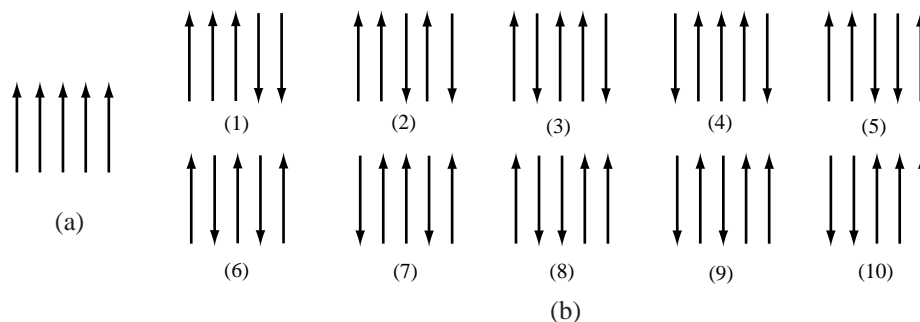


Figure 4.1: (a) Example of an inaccessible macrostate for the ensemble specified by $E = -\mu B$, $N = 5$. (b) The ten accessible members of the ensemble with $E = -\mu B$ and $N = 5$. Spin 1 is the left most spin.

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

$$p_n = \frac{1}{\Omega}, \quad (4.1)$$

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 4.1b). Because s_1 assumes the value ± 1 , we have

$$\begin{aligned} \langle s_1 \rangle &= \sum_{n=1}^{10} p_n s_n \\ &= \frac{1}{10} [(+1) + (+1) + (+1) + (-1) + (+1) + (+1) + (-1) + (+1) + (-1) + (-1)] \\ &= \frac{2}{10} = \frac{1}{5}. \end{aligned} \quad (4.2)$$

The sum is over all the accessible microstates and s_n is the value of spin 1 in the n th member of the ensemble. We see from (4.2) that the mean value of s_1 is $\langle s_1 \rangle = 1/5$.

Problem 4.1. (a) What is the mean value of spin 2 in the above example? (b) What is the mean magnetic moment per spin? (c) What is the probability p that a given spin points up? (d) What is the probability that if spin 1 is up, spin 2 also is up?

Of course 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. (a) Consider $N = 4$ noninteracting spins with magnetic moment μ and spin $1/2$ in a magnetic field B . 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 $\pm\mu$? Compare these probabilities to the analogous ones calculated in part (a).

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*, that is, a system with fixed 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 is 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

We will now 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 will not be 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 given by integer values, $\epsilon_n = 0, 1, 2, 3, \dots$. We can distinguish the particles by their colors. (Or we can assume that the particles have the same color, but are fixed on lattice sites.) For reasons that we will discuss in Section 6.12, we will refer to this model system as an Einstein solid.¹

Suppose that we have an Einstein solid with $N = 3$ particles (with color red, white, and blue) in an isolated box and that their total energy is $E = 3$. For these small values of N and E , we can enumerate the accessible microstates by hand. The ten accessible microstates of this system are

¹These 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 $\epsilon_n = n$.

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, ...

shown in Table 4.1. If 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

$$\Omega = \frac{(E + N - 1)!}{E!(N - 1)!}. \quad (4.3)$$

(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

$$E = E_A + E_B = 5 + 1 = 6. \quad (4.4)$$

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

$$\Omega = \Omega_A \times \Omega_B = 6 \times 2 = 12. \quad (4.5)$$

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.)

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

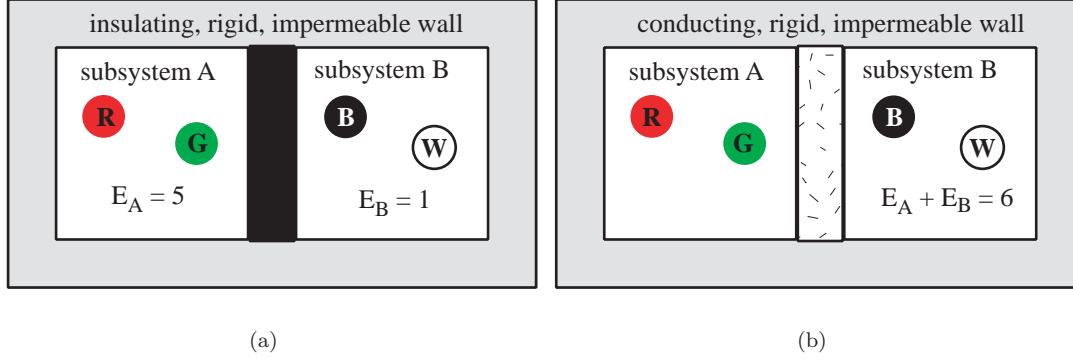


Figure 4.2: Two subsystems, each with two distinguishable particles, surrounded by (a) insulating, rigid, and impermeable outer walls and (b) separated by a conducting, rigid, and impermeable wall. The other walls remain the same.

E_A	accessible microstates		E_B	accessible microstates	
5	5,0	0,5	1	1,0	0, 1
	4,1	1,4			
	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 $E_B = 1$.

hence the single particle energy eigenvalues 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

$$\Omega(E_A, E_B) = \Omega_A(E_A) \times \Omega_B(E_B). \quad (4.6)$$

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 $E_A + E_B = 6$. Hence, Ω can be expressed as

$$\Omega = \sum_{E_A} \Omega_A(E_A)\Omega_B(E - E_A). \quad (4.7)$$

From Table 4.3 we see that

$$\Omega = (7 \times 1) + (6 \times 2) + (5 \times 3) + (4 \times 4) + (3 \times 5) + (2 \times 6) + (1 \times 7) = 84. \quad (4.8)$$

E_A	microstates	$\Omega_A(E_A)$	E_B	microstates	$\Omega_B(E_B)$	$\Omega_A \Omega_B$
6	6,0 0,6 5,1 1,5 4,2 2,4 3,3	7	0	0,0	1	7
5	5,0 0,5 4,1 1,4 3,2 2,3	6	1	1,0 0,1	2	12
4	4,0 0,4 3,1 1,3 2,2	5	2	2,0 0,2 1,1	3	15
3	3,0 0,3 2,1 1,2	4	3	3,0 0,3 2,1 1,2	4	16
2	2,0 0,2 1,1	3	4	4,0 0,4 3,1 1,3 2,2	5	15
1	1,0 0,1	2	5	5,0 0,5 4,1 1,4 3,2 2,3	6	12
0	0,0	1	6	6,0 0,6 5,1 1,5 4,2 2,4 3,3	7	7

Table 4.3: The 84 equally probable microstates accessible to 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 $N_B = 2$.

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 composite system is in any one of the microstates in which $E_A = 2$ 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

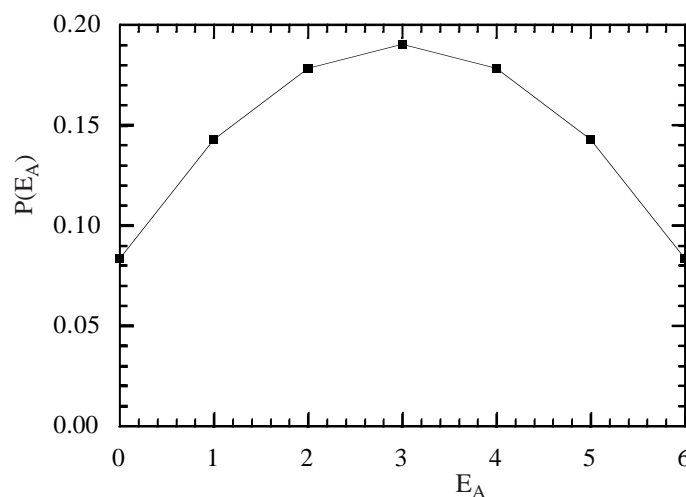
$$P_A(E_A) = \frac{\Omega_A(E_A)\Omega_B(E - E_A)}{\Omega}. \quad (4.9)$$

We show in Table 4.4 and Figure 4.3 the various values of $P_A(E_A)$.

The mean energy of subsystem A is found by doing an ensemble average over the 84 microstates accessible to the composite system. We have that

$$\overline{E}_A = (0 \times \frac{7}{84}) + (1 \times \frac{12}{84}) + (2 \times \frac{15}{84}) + (3 \times \frac{16}{84}) + (4 \times \frac{15}{84}) + (5 \times \frac{12}{84}) + (6 \times \frac{7}{84}) = 3. \quad (4.10)$$

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.

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 $P_A(E_A)$.

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

$$S = k \ln \Omega, \quad (4.11)$$

where k is an arbitrary constant. Note the similarity to the expression for the missing information on page 95. 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 4.5. 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. Use the relation (4.3) to determine the initial number of accessible microstates for the composite system. 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. 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 4.6. The applet/application at stp.clarku.edu/simulations/einsteinsolid 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) Plot P_A versus E_A and discuss its qualitative energy dependence. (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 given by $k \ln \Omega_A(\tilde{E}_A) \Omega_B(E - \tilde{E}_A)$. Compare this contribution to 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. Use Stirling’s approximation (3.89) to calculate the entropies in part (e).

Problem 4.7. 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 4.7 and the example in (4.12) should convince you, 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 the most probable energies and hence thermal equilibrium corresponds to $\tilde{E}_A = 4$ and $\tilde{E}_B = 6$. Note that $\tilde{E}_A \neq \tilde{E}_B$. The mean energy of system A is given by

$$\begin{aligned}\bar{E}_A &= \frac{1}{8008}[(10 \times 66) + (9 \times 220) + (8 \times 450) + (7 \times 720) + (6 \times 980) + (5 \times 1176) \\ &\quad + (4 \times 1260) + (3 \times 1200) + (2 \times 990) + (1 \times 660) + (0 \times 286)] \\ &= 34320/8008 = 4.286.\end{aligned}\tag{4.12}$$

In this case we see that $\bar{E}_A \neq \tilde{E}_A$.

In this example, the quantity that is the same for both systems in thermal equilibrium is not the most probable energy nor the mean energy. (In this case, the energy per particle of the two systems is the same, but this equality does not hold in general.) 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 of systems A and B calculated from the central difference approximation for the slope at E :

$$\frac{1}{T(E)} \approx \frac{[S(E + \Delta E) - S(E - \Delta E)]}{2\Delta E}.\tag{4.13}$$

(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 $S_A(E_A = 2)$, 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. As we discussed in Chapter 2 the association of the inverse temperature with the energy derivative of the entropy is more fundamental than the association of the temperature with the mean kinetic energy per particle.

Problem 4.8. The applet/application at stp.clarku.edu/simulations/entropy/ computes the entropies of two Einstein solids in thermal contact. Explore the effect of increasing the values

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. Note that most probable energy of subsystem A is $\bar{E}_S = 4$ and the fraction of microstates associated with the most probable macrostate is $1260/8008 \approx 0.157$. This relative fraction will approach unity as the number of particles in the systems become larger.

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 ?

The interested reader may 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 same model system 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 $\epsilon_n = n$. 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, there is a one-to-one correspondence between the quantum state and the energy of a microstate.

The number of accessible microstates of the composite system is shown in Table 4.6 using the

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.

relation (4.3). From Table 4.6 we can determine the mean energy of the subsystem of one particle:

$$\begin{aligned}
\bar{\epsilon} &= \sum_{n=0}^{12} \epsilon_n p_n \\
&= \frac{1}{6188} [(0 \times 1820) + (1 \times 1365) + (2 \times 1001) + (3 \times 715) + (4 \times 495) \\
&\quad + (5 \times 330) + (6 \times 210) + (7 \times 126) + (8 \times 70) \\
&\quad + (9 \times 35) + (10 \times 15) + (11 \times 5) + (12 \times 1)] = 2.
\end{aligned} \tag{4.14}$$

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

$$p_n = \frac{1}{Z} e^{-\beta \epsilon_n}, \tag{4.15}$$

where $\epsilon_n = n$ in this example and Z is a normalization constant. Given the form (4.15), we can estimate the parameter β from the slope of $\ln p_n$ versus ϵ_n . The result is that $\beta \approx 0.57$. The interested reader might wish to skip to Section 4.6 to read about the generalization of these results.

Problem 4.9. Consider an Einstein solid with $N_A = 1$ and $N_B = 3$ with a total energy $E = 6$. (A similar system of four particles was considered on page 142.) Calculate the probability p_n that system A is in microstate n . Why is this probability the same as the probability that the system has energy ϵ_n ? Is p_n a decreasing or increasing function of ϵ_n ?

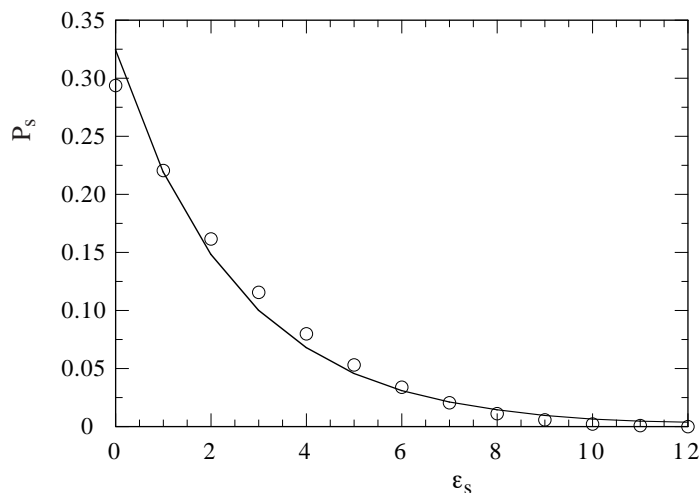


Figure 4.4: The probability p_n for the subsystem to be in state n with energy $\epsilon_n = n$. The subsystem can exchange energy with a system of $N = 5$ particles. The total energy of the composite system of six particles is $E = 12$. The circles are the values of p_n given in Table 4.6. The continuous line corresponds to p_n calculated from (4.15) with $\beta = 0.57$.

Problem 4.10. 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 4.11. Use the applet/application at stp.clarku.edu/simulations/einsteinsolid 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 $E = 36$. (The total number of particles in the composite system is 12.) Compare your result for p_n to the form (4.15) 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 $\epsilon \approx 1/\beta$. 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 4.12. (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. (b) Explain why the probability $P_A(E_A)$ that system A has energy E_A has a Gaussian-like form. (c) What is the difference between $P(E_A)$ and $p_n(E_n)$? Why do these two probabilities have qualitatively different dependencies on the energy?

Problem 4.13. (a) Consider an Einstein solid of $N = 10$ distinguishable oscillators. How does the total number of accessible microstates $\Omega(E)$ change for $E = 10, 10^2, 10^3, \dots$? Is $\Omega(E)$ a rapidly increasing function of E for fixed N ? (b) Is Ω a rapidly increasing function of N for fixed E ?

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

$$E = n(-\mu B) + (N - n)(\mu B) = -(2n - N)\mu B. \quad (4.16)$$

For a given N and B , n specifies the energy and vice versa. If we solve (4.16) for n , we find

$$n = \frac{N}{2} - \frac{E}{2\mu B}. \quad (4.17)$$

As we found in (3.71), 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

$$\Omega(n, N) = \frac{N!}{n!(N - n)!}, \quad (4.18)$$

where n is related to E by (4.17). We will apply this result in Example 4.2 on page 163.

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. It turns out that the general expression for $\Omega(E, N)$ for the one-dimensional Ising model for even N is

$$\Omega(E, N) = 2 \binom{N}{i} = 2 \frac{N!}{i!(N - i)!}, \quad (i = 0, 2, 4, \dots, N) \quad (4.19)$$

where $E = 2i - N$. We will discuss the Ising model in more detail in Chapter 5.

Problem 4.14. Verify that (4.19) gives the correct answers for $N = 2$ and 4.

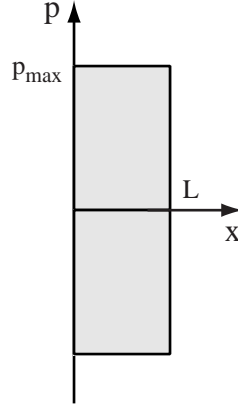


Figure 4.5: The phase space for a single particle of mass m and energy E in a one-dimensional box of length L . The maximum value of the momentum is $p_{\max} = \sqrt{2mE}$. Any point within the shaded rectangle corresponds to a microstate with energy less than or equal to E .

4.3.3 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 want 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 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

$$g(E)\Delta E = \Gamma(E + \Delta E) - \Gamma(E) \approx \frac{d\Gamma(E)}{dE} \Delta E. \quad (4.20)$$

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 $p_{\max} = \sqrt{2mE}$. However, 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

²We 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.

of cells or microstates equals

$$\Gamma_{\text{cl}}(E) = \frac{2p_{\text{max}}L}{\Delta x \Delta p} = 2 \frac{L}{\Delta x \Delta p} (2mE)^{1/2}, \quad (4.21)$$

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

$$\lambda = 2L. \quad (4.22)$$

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 $x = L$ are given by

$$\lambda_n = \frac{2L}{n}, \quad (n = 1, 2, 3, \dots) \quad (4.23)$$

where the index n labels the quantum state of the particle and can be any nonzero, positive integer. From the de Broglie relation,

$$p = \frac{h}{\lambda}, \quad (4.24)$$

and the nonrelativistic relation between the energy E and the momentum p , we find that the eigenvalues of the particle are given by

$$E_n = \frac{p_n^2}{2m} = \frac{h^2}{2m \lambda_n^2} = \frac{n^2 h^2}{8mL^2}. \quad (4.25)$$

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 (4.25))

$$n = \frac{2L}{h} (2mE)^{1/2}. \quad (4.26)$$

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

$$\Gamma_{\text{qm}}(E) = n = \frac{2L}{h} (2mE)^{1/2}. \quad (4.27)$$

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

³Note that the semiclassical limit is not equivalent to simply letting $\hbar \rightarrow 0$.

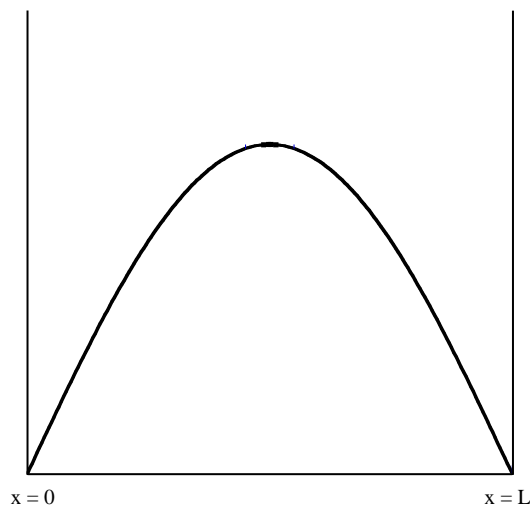


Figure 4.6: Representation of the ground state wave function of a particle in a one-dimensional box. Note that the wave function equals zero at $x = 0$ and $x = L$.

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

$$\Delta x \Delta p = h. \quad (4.28)$$

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.

Problem 4.15. 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 count the number of microstates in both the classical and quantum cases. The total energy of the harmonic oscillator is given by

$$E = \frac{p^2}{2m} + \frac{1}{2}kx^2, \quad (4.29)$$

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 (4.29) by dividing both sides by E and substituting $\omega^2 = k/m$:

$$\frac{x(t)^2}{2E/m\omega^2} + \frac{p(t)^2}{2mE} = 1. \quad (4.30)$$

where the total energy E is a constant of the motion.

From the form of (4.30) we see that the shape of phase space of a one-dimensional harmonic oscillator is an ellipse,

$$\frac{x^2}{a^2} + \frac{p^2}{b^2} = 1, \quad (4.31)$$

with $a^2 = 2E/(m\omega^2)$ and $b^2 = 2mE$. Because the area $\pi ab = 2\pi E/\omega$, the number of states with energy less than or equal to E is given by

$$\Gamma_{\text{cl}}(E) = \frac{\pi ab}{\Delta x \Delta p} = \frac{2\pi E}{\omega \Delta x \Delta p}. \quad (4.32)$$

Quantum mechanical calculation. The energy eigenvalues of the harmonic oscillator are given by

$$E_n = \left(n + \frac{1}{2}\right) \hbar\omega. \quad (n = 0, 1, 2, \dots) \quad (4.33)$$

Hence the number of microstates is given by

$$\Gamma_{\text{qm}}(E) = n = \frac{E}{\hbar\omega} - \frac{1}{2} \rightarrow \frac{E}{\hbar\omega}. \quad (4.34)$$

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.

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 wave function takes the form of a standing wave in two dimensions. The energy of the particle is given by

$$E = \frac{\mathbf{p}^2}{2m} = \frac{1}{2m}(p_x^2 + p_y^2), \quad (4.35)$$

where $\mathbf{p} = \hbar\mathbf{k}$. The wave vector \mathbf{k} satisfies the conditions for a standing wave:

$$k_x = \frac{\pi}{L_x}n_x, \quad k_y = \frac{\pi}{L_y}n_y. \quad (n_x, n_y = 1, 2, 3, \dots) \quad (4.36)$$

The corresponding eigenvalues are given by

$$E_{n_x, n_y} = \frac{\hbar^2}{8m} \left[\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} \right]. \quad (4.37)$$

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

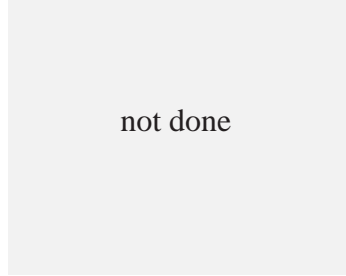


Figure 4.7: The points represent possible values of n_x and n_y such that $R^2 = n_x^2 + n_y^2 = 10^2$ and $n_x > 0$ and $n_y > 0$. The number of states for $R = 10$ is 69. The corresponding number from the asymptotic relation is $\Gamma(E) = \pi 10^2/4 \approx 78.5$.

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

$$R^2 = n_x^2 + n_y^2 = \left(\frac{2L}{h}\right)^2 (2mE). \quad (4.38)$$

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

$$R = \frac{2L}{h}(2mE)^{1/2}. \quad (4.39)$$

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

$$\Gamma(E) = \frac{1}{4}\pi R^2 = \pi \frac{L^2}{h^2}(2mE). \quad (4.40)$$

Note that $V = L^2$ in this case.

Problem 4.16. The expression (4.40) 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 . Explore how the relation $\Gamma = \pi R^2/4$ approximates the actual number of microstates by writing a program that computes the number of nonzero, positive integers that satisfy the condition $n_x^2 + n_y^2 \leq R^2$. Pseudocode for such a program is listed in the following:

```

R = 10
R2 = R*R
states = 0
do nx = 1,R
  do ny = 1,R
    if ((nx*nx + ny*ny) <= R2) then
      states = states + 1
    end if
  end do
end do

```

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

$$E = \frac{h^2}{8mL^2}[n_x^2 + n_y^2 + n_z^2]. \quad (4.41)$$

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

$$R^2 = n_x^2 + n_y^2 + n_z^2 = \left(\frac{2L}{h}\right)^2 (2mE). \quad (4.42)$$

Hence

$$\Gamma(E) = \frac{1}{8} \left(\frac{4}{3}\pi R^3\right) = \frac{\pi}{6} \left(\frac{2L}{h}\right)^3 (2mE)^{3/2} = \frac{4\pi}{3} \frac{V}{h^3} (2mE)^{3/2}, \quad (4.43)$$

where we have let $V = L^3$.

Problem 4.17. The expression (4.43) 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 . Explore how the relation $\Gamma = \pi R^3/6$ approximates the total number of microstates by writing a program that computes the number of nonzero, positive integers that satisfy the condition $n_x^2 + n_y^2 + n_z^2 \leq R^2$.

Problem 4.18. Estimate the number of microstates accessible to a gas molecule at typical room temperatures and pressures. We can proceed by estimating 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 cm^3). Consider a small energy interval $\Delta E = 10^{-27} \text{ J}$ that is much smaller than E itself, 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

$$E_{n_1, n_2} = \frac{h^2}{8mL^2}[n_1^2 + n_2^2], \quad (4.44)$$

where the quantum numbers n_1 and n_2 are positive nonzero integers. However, 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 $n_1^2 + n_2^2 \leq 25$. The values of n_1 and n_2 that satisfy this constraint are

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 $n_1^2 + n_2^2 \leq 25$.

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 $n_1^2 + n_2^2 \leq 25$. 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 $\hbar \rightarrow 0$. Because the classical limit corresponds to very large quantum numbers (see Problem 6.27) 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 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 4.19, 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 (4.39)). 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 the $3N$ -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

$$V_n(R) = \int_{r_1^2 + r_2^2 + \dots + r_n^2 < R^2} d\mathbf{r}_1 d\mathbf{r}_2 \dots d\mathbf{r}_n. \quad (4.45)$$

It is shown in Appendix 4A that $V_n(R)$ is given by (for integer n)

$$V_n(R) = \frac{2\pi^{n/2}}{n\Gamma(n/2)} R^n, \quad (4.46)$$

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

$$\Gamma(R) = \left(\frac{1}{2}\right)^n V_n(R). \quad (4.47)$$

(The volume $\Gamma(R)$ 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

$$\Gamma(E, V, N) = \left(\frac{1}{2}\right)^{3N} \frac{2\pi^{3N/2}}{3N(3N/2 - 1)!} R^{3N/2} \quad (4.48a)$$

$$= \left(\frac{1}{2}\right)^{3N} \frac{\pi^{3N/2}}{(3N/2)!} R^{3N/2} \quad (4.48b)$$

$$= \left(\frac{1}{2}\right)^{3N} \left(\frac{2L}{h}\right)^{3N/2} \frac{\pi^{3N/2}}{(3N/2)!} (2mE)^{3N/2} \quad (4.48c)$$

$$= \left(\frac{V}{h^3}\right)^N \frac{(2\pi mE)^{3N/2}}{(3N/2)!}. \quad (4.48d)$$

If we include the factor of $1/N!$ to correct for the overcounting of microstates in the semiclassical limit, we obtain the desired result:

$$\Gamma(E, V, N) = \frac{1}{N!} \left(\frac{V}{h^3}\right)^N \frac{(2\pi mE)^{3N/2}}{(3N/2)!}. \quad (\text{semiclassical limit}) \quad (4.49)$$

A more convenient expression for Γ can be found by using Stirling's approximation for $N \gg 1$. We have

$$\ln \Gamma = -\ln N! + N \ln \frac{V}{h^3} + \frac{3}{2} N \ln(2\pi mE) - \ln \left(\frac{3N}{2}\right)! \quad (4.50a)$$

$$= -N \ln N + N + N \ln V - \frac{3N}{2} \ln h^2 + \frac{3}{2} N \ln(2\pi mE) - \frac{3}{2} N \ln \frac{3N}{2} + \frac{3N}{2} \quad (4.50b)$$

$$= N \ln \frac{V}{N} + \frac{3}{2} N \ln \frac{4\pi mE}{3N h^2} + \frac{5}{2} N \quad (4.50c)$$

$$= N \ln \frac{V}{N} + \frac{3}{2} N \ln \frac{mE}{3N \pi \hbar^2} + \frac{5}{2} N, \quad (4.50d)$$

where we have let $h = 2\pi\hbar$ to obtain (4.50d) from (4.50c).

Problem 4.19. We can obtain an equivalent expression for $\Gamma(E, V, N)$ using simpler physical considerations. We write

$$\Gamma(E, V, N) \approx \frac{1}{N!} \Gamma_1\left(\frac{E}{N}, V\right) \Gamma_1\left(\frac{E}{N}, V\right) \dots \Gamma_1\left(\frac{E}{N}, V\right), \quad (4.51)$$

where $\Gamma_1(E, V)$ is the number of states for a 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 (4.43) for Γ_1 . Compare the V and E -dependencies of $\Gamma(E, V, N)$ obtained from this simple argument to (4.49). What about the N -dependence?

Problem 4.20. 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

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 (4.50d) 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

$$\Omega = \Omega_A(E_A, V_A, N_A) \Omega_B(E_B, V_B, N_B). \quad (4.52)$$

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 famous formula, first proposed by Planck:

$$\boxed{S = k \ln \Omega.} \quad (4.53)$$

Note that if we substitute (4.52) in (4.53), 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? In general, we expect that there are many more microstates available after the constraint is removed. 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 distinct microstates accessible to the

⁴For 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.

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

$$\Omega(E) = \sum_{E_A} \Omega_A(E_A)\Omega_B(E - E_A). \quad (4.54)$$

The probability that system A has energy E_A is given by

$$P(E_A) = \frac{\Omega_A(E_A)\Omega_B(E - E_A)}{\Omega(E)}. \quad (4.55)$$

Note that the logarithm of (4.54) does not yield a sum of two functions. However, the dominant contribution to the right-hand side of (4.54) 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

$$\Omega \approx \Omega_A(\tilde{E}_A)\Omega_B(E - \tilde{E}_A). \quad (4.56)$$

The approximation (4.56) becomes more and more accurate as the thermodynamic limit ($N, V \rightarrow \infty, \rho = N/V = \text{constant}$) is approached and allows us to write

$$S = k \ln \Omega = S_A + S_B \quad (4.57)$$

before and after the constraint is removed.

The relation $S = k \ln \Omega$ is not very mysterious. It is simply a matter of counting the number of accessible microstates and assuming that they are all equally probable. We see immediately that one consequence of this definition is that the entropy increases or remains unchanged after an internal constraint is relaxed. Given the definition (4.53) of S as a function of E , V , and N , it is natural to adopt the thermodynamic definitions of temperature, pressure, and chemical potential:

$$\frac{1}{T} = \frac{\partial S}{\partial E}. \quad (4.58)$$

$$\frac{P}{T} = \frac{\partial S}{\partial V}. \quad (4.59)$$

$$\frac{\mu}{T} = -\frac{\partial S}{\partial N}. \quad (4.60)$$

We have made the connection between statistical mechanics and thermodynamics.

How should we define the entropy for a system in which the energy is a continuous variable? Three possibilities are

$$S = k \ln \Gamma \quad (4.61a)$$

$$S = k \ln g(E)\Delta E \quad (4.61b)$$

$$S = k \ln g(E). \quad (4.61c)$$

It is easy to show that in the limit $N \rightarrow \infty$, the three definitions yield the same result (see Problem 4.21). 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 (4.61), we find that the entropy of an ideal gas in the semiclassical limit for $N \rightarrow \infty$ is given by

$$S(E, V, N) = Nk \left[\ln \frac{V}{N} + \frac{3}{2} \ln \frac{mE}{3N\pi\hbar^2} + \frac{5}{2} \right]. \quad (4.62)$$

Problem 4.21. (a) Justify the statement made in the text that any of the definitions of S given in (4.61) yield the result (4.62). (b) Verify the result (4.62) for the entropy S of an ideal gas.

Problem 4.22. Compare the form of S given in (4.62) with the form of S determined from thermodynamic considerations in Section 2.19.

We now use the result (4.62) for S to obtain the thermal equation of state of an ideal classical gas. From (4.62) we see that

$$\frac{1}{T} = \left(\frac{\partial S}{\partial E} \right)_{V,N} = \frac{3}{2} \frac{Nk}{E}, \quad (4.63)$$

and hence we obtain the familiar result

$$E = \frac{3}{2} NkT. \quad (4.64)$$

The pressure equation of state follows from (4.59) and (4.62) and is given by

$$\frac{P}{T} = \left(\frac{\partial S}{\partial V} \right)_{E,N} = \frac{Nk}{V},$$

and hence

$$PV = NkT. \quad (4.65)$$

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 (4.49)?

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 4.23. Use the relations (4.62) and (4.64) 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 4.24. Use (4.60) and (4.62) to derive the dependence of the chemical potential μ on E , V , and N for a ideal classical gas. Then use (4.64) 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

$$E = -(n - n')\mu B = -[n - (N - n)]\mu B = -(2n - N)\mu B, \quad (4.16)$$

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 (4.18):

$$\Omega(n) = \frac{N!}{n!(N - n)!}. \quad (4.18)$$

From (4.16), we find that the value of n corresponding to a given E is given by

$$n = \frac{1}{2} \left(N - \frac{E}{\mu B} \right). \quad (4.66)$$

The thermodynamic temperature T is given by

$$\frac{1}{T} = \frac{\partial S}{\partial E} = \frac{dS(n)}{dn} \frac{dn}{dE} = -\frac{1}{2\mu B} \frac{dS}{dn}. \quad (4.67)$$

It is understood that the magnetic field B is held fixed.

To calculate dS/dn , we use the approximation (3.92) for large n :

$$\frac{d}{dn} \ln n! = \ln n, \quad (4.68)$$

and find

$$\frac{dS(n)}{dn} = k[-\ln n + \ln(N - n)], \quad (4.69)$$

where $S(n) = k \ln \Omega(n)$ from (4.18). Hence

$$\frac{1}{T} = -k \frac{1}{2\mu B} \ln \frac{N - n}{n}. \quad (4.70)$$

Equation (4.70) yields T as a function of E by eliminating n using (4.66).

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 4.25, we can rewrite this relation to express E as a function T . The result is

$$E = -N\mu B \tanh \frac{\mu B}{kT} = -N\mu B \tanh \beta \mu B, \quad (4.71)$$

where $\beta = 1/kT$.

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 common ensembles. Note that Ω is the number of accessible microstates in the microcanonical ensemble and the thermodynamic potential in the grand canonical ensemble.

The probability p that a given spin is up is equal to the ratio n/N . We can solve (4.70) for n/N and obtain (see Problem 4.25)

$$p = \frac{n}{N} = \frac{1}{1 + e^{-2\mu B/kT}}, \quad (4.72a)$$

$$= \frac{e^{\mu B/kT}}{e^{\mu B/kT} + e^{-\mu B/kT}} = \frac{e^{\beta\mu B}}{e^{\beta\mu B} + e^{-\beta\mu B}}, \quad (4.72b)$$

We have obtained the result for p that we promised in Section 3.5.

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 (4.72) by a more straightforward method in Section 4.6.

Problem 4.25. Solve (4.70) for n/N and verify (4.72). Then use (4.16) 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 4.26. 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 4.52.

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 the *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 $E_{\text{bath}} = E - E_n$. Because the system of interest is much smaller than the heat bath, we know that $E_n \ll E$. For small systems 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. However, if the number of particles is large, the number of particles near the interface 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.

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 (4.52))

$$p_n = \frac{1 \times \Omega(E - E_n)}{\sum_n \Omega(E - E_n)}, \quad (4.73)$$

where $\Omega(E - E_n)$ is the number of microstates of the heat bath for a given microstate n of the system of interest. As E_n increases, $\Omega(E - E_n)$, 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 $E_n \ll E$. However, we cannot approximate $\Omega(E - E_n)$ directly because Ω is a rapidly varying function of the energy. For this reason we

take the logarithm of (4.73) and write

$$\ln p_n = C + \ln \Omega(E_{\text{bath}} = E - E_n) \quad (4.74a)$$

$$\approx C + \ln \Omega(E) - E_n \left(\frac{\partial \ln \Omega(E_{\text{bath}})}{\partial E_{\text{bath}}} \right)_{E_{\text{bath}}=E} \quad (4.74b)$$

$$= C + \ln \Omega(E) - \frac{E_n}{kT}, \quad (4.74c)$$

where C is related to the denominator of (4.73) and does not depend on E_n . We have used the relation

$$\beta \equiv \frac{1}{kT} = \left(\frac{\partial \ln \Omega(E_{\text{bath}})}{\partial E_{\text{bath}}} \right)_{N,V}. \quad (4.75)$$

As can be seen from (4.75), β is proportional to the inverse temperature of the heat bath. From (4.74c) we obtain

$$\boxed{p_n = \frac{1}{Z} e^{-\beta E_n}}. \quad (\text{Boltzmann distribution}) \quad (4.76)$$

The function Z is found from the normalization condition $\sum_n p_n = 1$ and is given by

$$\boxed{Z = \sum_n e^{-\beta E_n}}. \quad (\text{partition function}) \quad (4.77)$$

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 4.27. Discuss the relation between the qualitative results that we obtained in Table 4.6 and the Boltzmann distribution in (4.76).

Problem 4.28. The hydrocarbon 2-butene, $\text{CH}_3\text{-CH}=\text{CH-CH}_3$ occurs in two conformations (geometrical structures) called the *cis*- and *trans*-conformations. 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 \bar{E} is given by

$$\bar{E} = \sum_n p_n E_n = \frac{1}{Z} \sum_n E_n e^{-\beta E_n}, \quad (4.78)$$

where we have substituted the Boltzmann form (4.76) for the probability distribution. We use a trick similar to that used in Section 3.5 to obtain a simpler form for \bar{E} . First we write

$$\bar{E} = -\frac{1}{Z} \frac{\partial}{\partial \beta} \sum_n e^{-\beta E_n}, \quad (4.79)$$

where we have used the fact that derivative $\frac{\partial}{\partial\beta}(e^{-\beta E_n}) = -E_n e^{-\beta E_n}$. Because

$$\frac{\partial Z}{\partial\beta} = -\sum_n E_n e^{-\beta E_n}, \quad (4.80)$$

we can write

$$\overline{E} = -\frac{1}{Z} \frac{\partial Z}{\partial\beta} = -\frac{\partial}{\partial\beta} \ln Z. \quad (4.81)$$

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

$$C_V = \frac{\partial \overline{E}}{\partial T} = \frac{d\beta}{dT} \frac{\partial \overline{E}}{\partial\beta}, \quad (4.82)$$

$$= \frac{1}{kT^2} \left[\frac{1}{Z} \frac{\partial^2 Z}{\partial\beta^2} - \frac{1}{Z^2} \left(\frac{\partial Z}{\partial\beta} \right)^2 \right], \quad (4.83)$$

where $\partial \overline{E} / \partial\beta$ has been calculated from (4.81). Because

$$\overline{E^2} = \frac{1}{Z} \sum_n E_n^2 e^{-\beta E_n} = \frac{1}{Z} \frac{\partial^2 Z}{\partial\beta^2}, \quad (4.84)$$

we obtain the relation

$$C_V = \frac{1}{kT^2} [\overline{E^2} - \overline{E}^2]. \quad (4.85)$$

Equation (4.85) 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.⁵

***Problem 4.29.** The isothermal compressibility of a system is defined as $\kappa = -(1/V)(\partial V / \partial P)_T$. In what way is κ a linear response? In analogy to the relation of C_V to the fluctuations in the energy, how do you think κ is related to the fluctuations in the volume of the system 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 (4.85) 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

$$\frac{\sqrt{\overline{E^2} - \overline{E}^2}}{\overline{E}} = \frac{\sqrt{kT^2 C_V}}{\overline{E}} \sim \frac{N^{1/2}}{N} \sim N^{-1/2}. \quad (4.86)$$

⁵The relation (4.85) 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 (4.82).

From (4.86) 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 (see Appendix 4B).

Problem 4.30. The Boltzmann probability given by (4.76) 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 E 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 \bar{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

$$dE_n = \frac{dE_n}{dV} dV = -P_n dV. \quad (4.87)$$

The quantity dE_n in (4.87) is the work done on the system in state n to produce the volume change dV . The relation (4.87) defines the pressure P_n of the system in state n . Hence, the mean pressure of the system is given by

$$\bar{P} = - \sum_n p_n \frac{dE_n}{dV}. \quad (4.88)$$

From (4.77) and (4.88) we can express the mean pressure as

$$\bar{P} = kT \left(\frac{\partial \ln Z}{\partial V} \right)_{T,N}. \quad (4.89)$$

Note that in defining the pressure, we assumed that a small change in the volume does not change the probability distribution of the microstates. In general, a perturbation of the system will induce transitions between the different microstates of the system so that if initially the system is in a microstate n , it will not stay in that 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 its same state. As discussed in Chapter 2, such a change is called quasistatic.

We can use the relation $\bar{E} = \sum_n p_n E_n$ to write the total change in the energy as

$$d\bar{E} = \sum_n dp_n E_n + \sum_n p_n dE_n. \quad (4.90)$$

The second term in (4.90) can be written as

$$\sum_n p_n dE_n = \sum_n p_n \frac{dE_n}{dV} dV. \quad (4.91)$$

The identification of the second term in (4.90) with the work done on the system allows us to write

$$d\bar{E} = \sum_n E_n dp_n - P dV. \quad (4.92)$$

If we use the fundamental thermodynamic relation (2.110), $dE = TdS - PdV$ (for fixed N), we can identify the first term in (4.92) with the change in entropy of the system. Hence, we have

$$TdS = \sum_n E_n dp_n. \quad (4.93)$$

From (4.93) we see that a change in entropy of the system is related to a change in the probability distribution.

We can use (4.93) 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 (4.93):

$$TdS = \sum_n E_n dp_n = -kT \sum_n \ln Z dp_n - kT \sum_n \ln p_n dp_n. \quad (4.94)$$

The first term in (4.94) is zero because the total change in the probability must sum to zero. From (4.94) we write

$$dS = -k \sum_n \ln p_n dp_n, \quad (4.95)$$

or

$$= -k \sum_n d(p_n \ln p_n). \quad (4.96)$$

We can integrate both sides of (4.96) to obtain the desired result:

$$\boxed{S = -k \sum_n p_n \ln p_n}. \quad (4.97)$$

We have assumed that the constant of integration is zero. The quantity defined by (4.11) and (4.97) is known as the *statistical entropy* in contrast to the thermodynamic entropy introduced in Chapter 2. Note the similarity of (4.97) to (3.29).

The relation (4.97) 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,

$$S = -k \sum_{n=1}^{\Omega} \frac{1}{\Omega} \ln \frac{1}{\Omega} = -k\Omega \frac{1}{\Omega} \ln \frac{1}{\Omega} = k \ln \Omega. \quad (4.98)$$

Note that the constant of integration in going from (4.96) to (4.97) must be set to zero so that S reduces to its form in the microcanonical ensemble. We see that we can interpret (4.97) 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 (4.97) is equivalent to its thermodynamic definition which can be expressed as

$$dS = \int \frac{dQ}{T}. \quad (4.99)$$

The relation (4.97) is of fundamental importance and shows that the entropy is uniquely determined by the probability distribution p_n of the different possible states. 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, and the equation $S = k \ln \Gamma$ (his notation) appears on his tombstone.⁶ 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 be able to 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. One statement of the third law of thermodynamics is

The entropy approaches a constant value as the temperature approaches zero.

The third law was first formulated by Nernst in 1906 based on experimental observations. We can easily see that the law follows simply from the statistical definition of the entropy. At $T = 0$, the system is in the ground state which we will label by 0. From (4.97) we see that if $p_n = 1$ for state 0 and is zero for all other microstates, then $S = 0$. We conclude that $S \rightarrow 0$ as $T \rightarrow 0$ if the system has a unique ground state. This behavior is the type that we would expect for simple systems.

If there are $g(0)$ microstates with the same ground state energy, then the corresponding entropy is $S(T = 0) = k \ln g(0)$. As an example, because an electron has spin $\frac{1}{2}$, it has two quantum states for each value of its momentum. Hence, an electron in zero magnetic field has degeneracy⁷ $g_n = 2$, because its energy is independent of its spin orientation, and the ground state entropy of a system of electrons would be $kN \ln 2$. However, there are some complex systems for which $g(0) \sim N$. In any case, we can conclude that the heat capacities must go to zero as $T \rightarrow 0$ (see Problem 4.45).

4.7 Connection between statistical mechanics and thermodynamics

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 (4.81) and (4.89)). 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

$$\boxed{F = -kT \ln Z}. \quad (\text{statistical mechanics definition of the free energy}) \quad (4.100)$$

⁶See www.lecb.ncifcrf.gov/~toms/icons/aust2002/photos-by-tds/all/index.105.html.

⁷An energy level is said to be degenerate if there are two or more microstates with the same energy.

At this stage the quantity defined in (4.100) has no obvious relation to the thermodynamic potential $F = E - TS$ that we defined earlier.

We now show that F as defined by (4.100) is equivalent to the thermodynamic definition $F = E - TS$. The relation (4.100) 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

$$\begin{aligned} d(\beta F) &= -\frac{1}{Z} \frac{\partial Z}{\partial \beta} d\beta - \frac{1}{Z} \frac{\partial Z}{\partial V} dV \\ &= \bar{E} d\beta - \beta \bar{P} dV, \end{aligned} \quad (4.101)$$

where we have used (4.81) and (4.88). We add and subtract $\beta d\bar{E}$ to the right-hand side of (4.101) to find

$$\begin{aligned} d(\beta F) &= \bar{E} d\beta + \beta d\bar{E} - \beta d\bar{E} - \beta \bar{P} dV \\ &= d(\beta \bar{E}) - \beta(d\bar{E} + \bar{P} dV). \end{aligned} \quad (4.102)$$

Hence, we can write

$$d(\beta F - \beta \bar{E}) = -\beta(d\bar{E} + \bar{P} dV). \quad (4.103)$$

From the thermodynamic relation $dE = TdS - PdV$ (for fixed N), we can rewrite (4.103) as

$$d(\beta F - \beta \bar{E}) = -\beta(d\bar{E} + \bar{P} dV) = -\beta T dS = -dS/k. \quad (4.104)$$

If we integrate (4.104), we find

$$S/k = \beta(\bar{E} - F) + \text{constant}, \quad (4.105)$$

or

$$F = \bar{E} - TS + \text{constant}. \quad (4.106)$$

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 (4.106) equal to zero, and we obtain

$$F = \bar{E} - TS. \quad (4.107)$$

Equation (4.107) is equivalent to the thermodynamic definition of the Helmholtz free energy with E replaced by \bar{E} . In the following, we will write E instead of \bar{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

$$S = -\left(\frac{\partial F}{\partial T}\right)_{V,N}. \quad (4.108)$$

$$P = -\left(\frac{\partial F}{\partial V}\right)_{T,N} \quad (4.109)$$

$$\mu = \left(\frac{\partial F}{\partial N}\right)_{T,V}. \quad (4.110)$$

These relations still hold with $F = -kT \ln Z$.

In the above we started with the statistical mechanical relation $F = -kT \ln Z$ (see (4.100)) and found that it was consistent with the thermodynamic relation $F = E - TS$ (see (4.107)). 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 (4.108)) and find

$$F = E - TS = -\frac{\partial \ln Z}{\partial \beta} - \beta \left(\frac{\partial F}{\partial \beta} \right)_{V,N}. \quad (4.111)$$

We rewrite (4.111) as

$$F + \beta \left(\frac{\partial F}{\partial \beta} \right)_{V,N} = -\frac{\partial \ln Z}{\partial \beta} = \left(\frac{\partial \beta F}{\partial \beta} \right)_{V,N}. \quad (4.112)$$

If we integrate both sides of (4.112), we find (up to a constant) that

$$F = -kT \ln Z. \quad (4.113)$$

4.8 Simple applications of the canonical ensemble

To gain experience with the canonical ensemble, we consider some relatively simple examples. In all these examples, the goal is to calculate the sum over microstates in the partition function. Then we can calculate the free energy using (4.100), the entropy from (4.108), and the mean energy from (4.81). (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 systems. However, we will find that summing over microstates to evaluate the partition function is usually a formidable task.

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

$$\begin{aligned} Z_2 &= \sum_{n=1}^4 e^{-\beta E_n} \\ &= 1 + 2e^{-\beta \Delta} + e^{-2\beta \Delta} \end{aligned} \quad (4.114)$$

$$= (1 + e^{-\beta \Delta})^2. \quad (4.115)$$

As might be expected, we can express Z_2 in terms of Z_1 , the partition function for one particle:

$$Z_1 = \sum_{n=1}^2 e^{-\beta \epsilon_n} = 1 + e^{-\beta \Delta}. \quad (4.116)$$

By comparing the forms of (4.115) and (4.116), we find that

$$Z_2 = Z_1^2. \quad (4.117)$$

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 (4.76) we find the probability that the system is in each of its two possible states is given by:

$$p_1 = \frac{1}{Z_1} = \frac{1}{1 + e^{-\beta\Delta}} \quad (4.118a)$$

$$p_2 = \frac{e^{-\beta\Delta}}{Z_1} = \frac{e^{-\beta\Delta}}{1 + e^{-\beta\Delta}}. \quad (4.118b)$$

The average energy is given by

$$\begin{aligned} \bar{\epsilon} &= \sum_{n=1}^2 p_n \epsilon_n \\ &= \frac{\Delta e^{-\beta\Delta}}{1 + e^{-\beta\Delta}}. \end{aligned} \quad (4.119)$$

Of course, $\bar{\epsilon}$ could also be found from the relation $\bar{\epsilon} = -\partial \ln Z / \partial \beta$. (We have used the symbol ϵ to denote the energy of a single particle.) The energy of N noninteracting, distinguishable particles of the same type is given by $\bar{E} = N\bar{\epsilon}$.

It is easy to calculate the various thermodynamic quantities directly from the partition function in (4.115). The free energy per particle, f , is given by

$$f = -kT \ln Z_1 = -kT \ln[1 + e^{-\beta\Delta}], \quad (4.120)$$

and s , the entropy per particle, is given by

$$s = -\left(\frac{\partial f}{\partial T}\right)_V = k \ln[1 + e^{-\beta\Delta}] + k \frac{\beta\Delta}{1 + e^{\beta\Delta}}. \quad (4.121)$$

If we had not already calculated the average energy $\bar{\epsilon}$, we could also obtain it from the relation $\bar{\epsilon} = f - Ts$. (As before, we have used lower case symbols to denote that the results are for one particle.) Confirm that the various ways of determining $\bar{\epsilon}$ yield the same results as found in (4.119). The behavior of the various thermodynamic properties of this system are explored in Problem 4.49.

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

$$\epsilon_n = \left(n + \frac{1}{2}\right)\hbar\omega. \quad (n = 0, 1, 2, \dots) \quad (4.122)$$

The partition function is given by

$$Z = \sum_{n=0}^{\infty} e^{-\beta\hbar\omega(n+1/2)} = e^{-\beta\hbar\omega/2} \sum_{n=0}^{\infty} e^{-n\beta\hbar\omega} \quad (4.123)$$

$$= e^{-\beta\hbar\omega/2} (1 + e^{-\beta\hbar\omega} + e^{-2\beta\hbar\omega} + \dots) = e^{-\beta\hbar\omega/2} (1 + x + x^2 + \dots), \quad (4.124)$$

where $x = e^{-\beta\hbar\omega}$. The infinite sum in (4.124) is a geometrical series in x and can be summed using the result that $1 + x + x^2 + \dots = 1/(1 - x)$ (see Appendix A). The result is

$$Z = \frac{e^{-\beta\hbar\omega/2}}{1 - e^{-\beta\hbar\omega}}, \quad (4.125)$$

and

$$\ln Z = -\frac{1}{2}\beta\hbar\omega - \ln(1 - e^{-\beta\hbar\omega}). \quad (4.126)$$

We leave it as an exercise for the reader to show that

$$f = \frac{1}{2}\hbar\omega + kT \ln(1 - e^{-\beta\hbar\omega}) \quad (4.127)$$

$$s = k \left[\frac{\beta\hbar\omega}{e^{\beta\hbar\omega} - 1} - \ln(1 - e^{-\beta\hbar\omega}) \right] \quad (4.128)$$

$$e = \hbar\omega \left[\frac{1}{2} + \frac{1}{e^{\beta\hbar\omega} - 1} \right]. \quad (4.129)$$

Equation (4.129) is Planck's formula for the mean energy of an oscillator at temperature T . The heat capacity is discussed in Problem 4.52.

Problem 4.31. What is the mean energy of a system of N harmonic oscillators in equilibrium with a heat bath at temperature T ? Compare your result with the result for the energy of N harmonic oscillators calculated in the microcanonical ensemble in Problem 4.26. Do the two ensembles give identical answers?

Equation (4.77) 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 (4.77) as

$$Z = \sum_{\text{levels}} g(E_n) e^{-\beta E_n}, \quad (4.130)$$

where $g(E_n)$ is the number of microstates of the system with energy E_n . The sum in (4.130) is over all the energy levels 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 $g(\epsilon_n)$ 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 (4.130))

$$Z_1 = 1 + 3e^{-\beta\epsilon} + e^{-2\beta\epsilon}.$$

Hence, the mean energy of a single particle is given by

$$\bar{e} = \epsilon \frac{3e^{-\beta\epsilon} + 2e^{-2\beta\epsilon}}{1 + 3e^{-\beta\epsilon} + e^{-2\beta\epsilon}}.$$

What is the energy of N such particles?

Problem 4.32. In Section 4.3.2 we were given the number of states with energy E for the one-dimensional Ising model. Use the result (4.19) to calculate the free energy of the one-dimensional Ising model for $N = 2$ and 4.

4.9 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.

Problem 4.33. The demon can be considered to be a small system in equilibrium with a much larger system. Because the demon is only one particle, its microstate is specified by its energy. Given these considerations, what is the form of the probability that the demon is in a particular microstate?

In Problems 4.34 and 4.35 we use the demon algorithm to determine the probability that the demon is in a particular microstate.

Problem 4.34. 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. Choose 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 usually chosen so that the percentage of accepted changes is between 30% to 50%. The applet/application at stp.clarku.edu/simulations/demon implements this algorithm.

(a) First consider a small number of particles, say $N = 10$. The applet chooses the special microstate for which all the velocities of the particles in the system are identical such that the system has the desired initial energy. After the demon and the system have reached equilibrium, what is the mean kinetic energy per particle, the mean velocity per particle, and the mean energy of the demon? (b) Compare the initial mean velocity of the particles in the system to the mean value after equilibrium has been established and explain the result. (c) Compute the probability, $p(E_d)dE_d$, that the demon has an energy between E_d and $E_d + dE_d$. 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 and compare your prediction with your numerical results. (d) What is form of the distribution of the velocities and the kinetic energies of the system after it has reached equilibrium? (e) How would your results change for an ideal gas in two and three dimensions? (f) For simplicity, the initial demon energy was set to zero. Would your results be different if the demon had a non-zero initial energy if the total energy of the demon plus the system was the same as before?

Problem 4.35. Consider a demon that exchanges energy with an Einstein solid of N particles. First do the simulation by hand choosing $N = 4$ and $E = 8$. For simplicity, choose the initial demon energy to be zero. Choose a particle at random and randomly raise or lower its energy by one unit consistent with the constraint that the energy of the demon $E_d \geq 0$. In this case the energy of the particle chosen also must remain nonnegative. Note that if a trial change is not accepted, the existing microstate is counted in all averages.

After you are satisfied that you understand how the algorithm works, use the applet at stp.clarku.edu/simulations/demon/einsteinsolid and 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? What is the probability that the demon has energy E_d ? What is the mean and standard deviation of the energy of the system? What are the relative fluctuations of the energy in the system? Compute the probability, $P(E_d)$, that the demon has an energy E_d . Fit your results to the form $P(E_d) \propto \exp(-\beta E_d)$, 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_d .

Example 4.6. A demon exchanges energy with a system of N quantized harmonic oscillators (see Problem 4.35). What is the mean energy of the demon?

Solution. The demon can be thought of as a system in equilibrium with a heat bath at temperature T . For simplicity, we will choose units such that the harmonic oscillators have energy $0, 1, 2, \dots$, and hence, the energy of the demon is also restricted to integer values. Because the probability of a demon microstate is given by the Boltzmann distribution, the demon's mean energy is given by

$$\overline{E}_d = \frac{\sum_{n=0}^{\infty} n e^{-\beta n}}{\sum_{n=0}^{\infty} e^{-\beta n}}. \quad (4.131)$$

Explain why the relation (4.131) for the demon energy is reasonable, and do the sums in (4.131)

to determine the temperature dependence of \overline{E}_d . (It is necessary to only do the sum in the denominator of (4.131).)

Example 4.7. A demon exchanges energy with an ideal classical gas of N particles in one dimension (see Problem 4.34). What is the mean energy of the demon?

Solution. In this case the demon energy is a continuous variable. Hence,

$$\overline{E}_d = \frac{\int_0^\infty E_d e^{-\beta E_d}}{\int_0^\infty e^{-\beta E_d}}. \quad (4.132)$$

Explain why the relation (4.132) for the demon energy is reasonable and determine the temperature dependence of \overline{E}_d . Would this temperature dependence be different if the gas were three-dimensional? Compare the temperature dependence of \overline{E}_d for a demon in equilibrium with an ideal classical gas to a demon in equilibrium with a system of harmonic oscillators. Why is the temperature dependence different?

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 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 (4.64). (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 the model introduced in Section 4.2 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 $0, 1, 2, \dots$. 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 (distinguishable) 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 that would leave the total energy unchanged.)

A more interesting example is a system of particles interacting via the Lennard-Jones potential which has the form

$$u(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right], \quad (4.133)$$

where r is the separation between two particles, σ is a measure of the diameter of a particle, and ϵ is a measure of the depth of the attractive part of the force. Note that $u(r)$ is repulsive at short distances and attractive at large distances. The 12-6 potential describes the interaction of the monatomic atoms of the noble gases and some diatomic molecules such as nitrogen and oxygen reasonably well. The parameters ϵ and σ can be determined from experiments or approximate calculations. The values $\epsilon = 1.65 \times 10^{-21}$ J and $\sigma = 3.4$ Å yield good agreement with the experimental properties of liquid Argon.

As we will see in Chapter 6, we can ignore the velocity coordinates and consider only the positions of the particles and their potential energy. If we were to choose one particle at random, and make a random displacement, the potential energy of the system would almost certainly change. The only way we could keep the energy constant (or within a fixed interval ΔE) as required by the microcanonical ensemble is to displace two particles chosen at random and hope that their random displacements would somehow keep the potential energy constant. Very unlikely!

The condition that the total energy is fixed makes sampling the accessible microstates difficult. This difficulty is analogous to the difficulty that we have already found doing calculations in the microcanonical ensemble. We can get around this difficulty by relaxing the condition that the total energy be fixed. One way is to add to the system of N particles an extra degree of freedom called the demon, as we discussed in Sec. 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 $N \rightarrow \infty$. Another way of relaxing the condition that the total energy is fixed is to use the canonical ensemble.

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

$$\overline{E}(T) = \frac{\sum_{n=1}^M E_n e^{-\beta E_n}}{\sum_{n=1}^M e^{-\beta E_n}}, \quad (4.134)$$

where E_n is the energy of microstate n and the sum is over the M states that have been sampled. However, this procedure would be very inefficient because the M states would include many states whose weight in averages such as (4.134) 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 then 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 4.36. Use the Metropolis probability to simulate an Einstein solid of N particles. Choose $N = 20$ and $\beta = 1$. Choose a particle at random and randomly lower or raise its energy by one unit. If the latter choice is made, generate a number at random in the unit interval and accept the change if $r \leq e^{-\beta}$. If a trial change is not accepted, the existing microstate is counted in all averages. Does the energy of the system eventually reach a well defined average? If so, vary β and determine $\overline{E}(T)$. 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 mean energy of the system. We now generalize this derivation and find the probability distribution for a system in equilibrium

with a heat bath at temperature $T = 1/k\beta$ and a particle reservoir with chemical potential μ . In this case the role of the particle reservoir is to fix 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 N_n particles is given by (see (4.73))

$$p_n = \frac{1 \times \Omega(E - E_n, N - N_n)}{\sum_n \Omega(E - E_n, N - N_n)}. \quad (4.135)$$

The difference between (4.73) and (4.135) 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 (4.135) and exploit the fact that $E_n \ll E$ and $N_n \ll N$. We have

$$\ln p_n \approx \text{constant} - E_n \frac{\partial \ln \Omega(E)}{\partial E} - N_n \frac{\partial \ln \Omega(N)}{\partial N}. \quad (4.136)$$

The derivatives in (4.136) are evaluated at $E_{\text{bath}} = E$ and $N_{\text{reservoir}} = N$, respectively. If we substitute $\beta = \partial \ln \Omega / \partial E$ and $\beta\mu = -\partial \ln \Omega / \partial N$, we obtain

$$\ln p_n = \text{constant} - \frac{E_n}{kT} + \frac{\mu N_n}{kT}, \quad (4.137)$$

or

$$\boxed{p_n = \frac{1}{\mathcal{Z}} e^{-\beta(E_n - \mu N_n)}}. \quad (\text{Gibbs distribution}) \quad (4.138)$$

Equation (4.138) is the Gibbs distribution for a variable number of particles. That is, p_n is the probability that the system is in state n with energy E_n and N_n particles. The *grand partition function* \mathcal{Z} in (4.138) is found from the normalization condition

$$\sum_n p_n = 1. \quad (4.139)$$

Hence, we obtain

$$\mathcal{Z} = \sum_n e^{-\beta(E_n - \mu N_n)}. \quad (4.140)$$

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 (2.144) and the grand partition function. Because the derivation of this relation proceeds as in Sec. 4.6, we simply give the relation:

$$\Omega = -kT \ln \mathcal{Z}. \quad (4.141)$$

Example 4.8. 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 \uparrow and \downarrow are possible. An impurity atom has three

allowed states: state 1 without an electron (atom ionized), state 2 with an electron attached with spin \uparrow , and state 3 with an electron attached with spin \downarrow . 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 \uparrow	1	0
3	electron attached, spin \downarrow	1	0

The grand partition function of the impurity atom is given by

$$\mathcal{Z} = e^{\beta\Delta} + 2e^{\beta\mu}. \quad (4.142)$$

Hence, the probability that an atom is ionized (state 1) is given by

$$P(\text{ionized}) = \frac{e^{\beta\Delta}}{e^{\beta\Delta} + 2e^{\beta\mu}} = \frac{1}{1 + e^{-\beta(\Delta-\mu)}}. \quad (4.143)$$

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 entropy in the context of information theory 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 us 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 we are going on a short trip and need to pack our suitcase with only a few articles.⁸ In this case the volume of the suitcase is much greater than the total volume of the articles we wish to pack, and we 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 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.

⁸This example is due to Laird.

Now suppose that we 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 we know from experience that randomly throwing the articles into the suitcase won't allow us to shut the suitcase. Such a configuration is incompatible with the volume constraints of the suitcase. If we randomly throw the articles in the suitcase many times, we might find a few configurations that would allow us to close the suitcase. In contrast, if we 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 suitcase articles) 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

$$u(r) = \begin{cases} \infty & r < \sigma \\ 0 & r \geq \sigma. \end{cases} \quad (4.144)$$

In Chapter 8 we will learn that the properties of a liquid at high density are determined mainly by the repulsive part of the interparticle potential. 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 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 Chapter 8 we will do simulations that indicate that a transition from a fluid at low density to a crystal at high density exists (at fixed temperature). (More extensive simulations and theory show the the crystal has fcc symmetry and that the co-existence densities of the crystal and fluid are between $\rho\sigma^3 = 0.945$ and 1.043 .) 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.

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

Appendix 4A: The volume of a hypersphere

We derive the volume of a hypersphere of n dimensions given in (4.46). As in (4.45), the volume is given by

$$V_n(R) = \int_{x_1^2 + x_2^2 + \dots + x_n^2 < R^2} dx_1 dx_2 \dots dx_n. \quad (4.145)$$

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

$$V_n = C_n R^n, \quad (4.146)$$

where C_n is the (unknown) constant of proportionality that depends only on n . We rewrite the volume element $dV_n = dx_1 dx_2 \dots dx_n$ as

$$dV_n = dx_1 dx_2 \dots dx_n = S_n(R) dR = n C_n R^{n-1} dR, \quad (4.147)$$

where $S_n = n C_n R^{n-1}$ 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)

$$I_n = \int_{-\infty}^{\infty} dx_1 \dots \int_{-\infty}^{\infty} dx_n e^{-(x_1^2 + \dots + x_n^2)} = \left[\int_{-\infty}^{\infty} dx e^{-x^2} \right]^n = \pi^{n/2}. \quad (4.148)$$

The left-hand side of (4.148) can be written as

$$\begin{aligned} I_n &= \int_{-\infty}^{\infty} dx_1 \dots \int_{-\infty}^{\infty} dx_n e^{-(x_1^2 + \dots + x_n^2)} = \int_0^{\infty} dR S_n(R) e^{-R^2} \\ &= n C_n \int_0^{\infty} dR R^{n-1} e^{-R^2}. \end{aligned} \quad (4.149)$$

We can relate the integral in (4.149) to the Gamma function $\Gamma(n)$ defined by the relation

$$\Gamma(n) = \int_0^{\infty} dx x^{n-1} e^{-x}. \quad (4.150)$$

The relation (4.150) holds for $n > -1$ and whether or not n is an integer. We make the change of variables $x = R^2$ so that

$$I_n = \frac{1}{2} n C_n \int_0^{\infty} dx x^{n/2-1} e^{-x} = \frac{1}{2} n C_n \Gamma(n/2). \quad (4.151)$$

A comparison of (4.151) with (4.148) yields the relation

$$C_n = \frac{2\pi^{n/2}}{n\Gamma(n/2)} = \frac{\pi^{n/2}}{(n/2)\Gamma(n/2)}. \quad (4.152)$$

It follows that

$$V_n(R) = \frac{2\pi^{n/2}}{n\Gamma(n/2)} R^n. \quad (4.153)$$

Appendix 4B: Fluctuations in the canonical ensemble

To gain more insight into the spread of energies that are actually observed in the canonical ensemble, we calculate the probability $P(E)\Delta E$ that a system in equilibrium with a heat bath at temperature T has a 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_n can be written as

$$p_n = \frac{g(E_n)e^{-\beta E_n}}{\sum_n g(E_n)e^{-\beta E_n}}, \quad (4.154)$$

where $g(E_n)$ is the number of microstates with energy E_n . In the thermodynamic limit $N, V \rightarrow \infty$, 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 is 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 (4.154) as

$$P(E)dE = \frac{g(E)e^{-\beta E}dE}{\int_0^\infty g(E)e^{-\beta E}dE}. \quad (4.155)$$

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 (4.155):

$$\left(\frac{\partial \ln P}{\partial E} \right)_{E=\tilde{E}} = \left(\frac{\partial \ln g}{\partial E} \right)_{E=\tilde{E}} - \beta = 0. \quad (4.156)$$

and

$$\left(\frac{\partial^2 \ln P}{\partial E^2} \right)_{E=\tilde{E}} = \left(\frac{\partial^2 \ln g}{\partial E^2} \right)_{E=\tilde{E}}. \quad (4.157)$$

We have

$$\left(\frac{\partial^2 \ln g}{\partial E^2} \right)_{E=\tilde{E}} = \frac{\partial}{\partial E} \left(\frac{\partial \ln g}{\partial E} \right)_{E=\tilde{E}} = \frac{\partial \beta}{\partial E}. \quad (4.158)$$

Finally, we obtain

$$\frac{\partial \beta}{\partial E} = -\frac{1}{kT^2} \frac{\partial T}{\partial E} = -\frac{1}{kT^2 C_V}. \quad (4.159)$$

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

$$\ln P(E) = \ln P(\tilde{E}) - \frac{(E - \tilde{E})^2}{2kT^2 C_V} + \dots \quad (4.160)$$

or

$$P(E) = P(\tilde{E}) e^{-(E - \tilde{E})^2 / 2kT^2 C_V}. \quad (4.161)$$

If we compare (4.161) to the standard form of a Gaussian distribution (3.115), we see that $\bar{E} = \tilde{E}$ and $\sigma_E^2 = kT^2 C_V$ as expected.

Additional Problems

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Table 4.9: Listing of inline problems.

Problem 4.37. 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 4.38. 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 4.39. 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 ? (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 4.40. 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 4.41. Show that the relations (4.58)–(4.60) follow from the thermodynamic relation $dE = TdS - PdV + \mu dN$ (see (2.110)).

Problem 4.42. 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

$$g(E)\Delta E = c(V - bN)^N \left(E + \frac{N^2 a}{V}\right)^{3N/2} \Delta E, \quad (4.162)$$

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 4.43. Discuss the assumptions that are needed to derive the classical ideal gas equations of state, (4.64) and (4.65).

Problem 4.44. 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

$$\overline{E} = \frac{\int_0^\infty E g(E) e^{-\beta E} dE}{\int_0^\infty g(E) e^{-\beta E} dE}. \quad (4.163)$$

Problem 4.45. Explain why the various heat capacities must go to zero as $T \rightarrow 0$.

Problem 4.46. The partition function of a hypothetical system is given by

$$\ln Z = aT^4 V, \quad (4.164)$$

where a is a constant. Evaluate the mean energy E , the pressure P , and the entropy S .

Problem 4.47. (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 4.48. 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:

$$Z_{12} = Z_1 Z_2. \quad (4.165)$$

Problem 4.49. (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 heat 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 4.50. 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 4.51. 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 4.52. (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 $C = dE/dT$. (c) Show that $E \rightarrow kT$ 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 (4.129). (d) 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? (e) Verify that $S \rightarrow 0$ as $T \rightarrow 0$ in agreement with the third law of thermodynamics, and that at high T , $S \rightarrow kN \ln(kT/\hbar\omega)$. 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 4.53. In the canonical ensemble the temperature is fixed and the constant volume heat capacity is related to the variance of the energy fluctuations (see (4.85)). As discussed on page 177, the temperature fluctuates in the microcanonical ensemble. Guess how the constant volume heat capacity might be expressed in the microcanonical ensemble.

Problem 4.54. Consider the system illustrated in Figure 4.8. The system consists of two distinguishable particles, each of which can be in either of two boxes. Assume that the energy of a

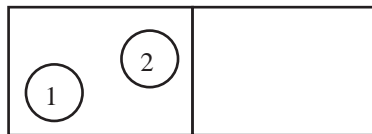


Figure 4.8: The two particles considered in Problem 4.54. The two distinguishable particles can each be in one of the two boxes. The energy of the system depends on which box the particles occupy.

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 . (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 4.55. 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 4.56. 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

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Chapter 5

Magnetic Systems

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In Chapter 4 we developed the general formalism of statistical mechanics. We now apply this formalism to several magnetic systems 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. We also introduce several other quantities of physical interest.

5.1 Paramagnetism

We first review the behavior of a system of noninteracting magnetic moments with spin 1/2 in equilibrium with a thermal 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 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

$$E = -\boldsymbol{\mu} \cdot \mathbf{B} = -\mu_z B = -\mu B s, \quad (5.1)$$

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 $s = \pm 1$.

We assume that the spins are fixed on a lattice so that they are *distinguishable* even though the spins are intrinsically quantum mechanical (because of the association of a magnetic moment with a spin angular momentum). 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. However, in the presence of an external magnetic field, the net magnetic moment and the energy of the system are nonzero.

Because each spin is independent of the others, 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 can derive this relation 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

$$Z_N = \sum_{s_1=\pm 1} \sum_{s_2=\pm 1} \dots \sum_{s_N=\pm 1} e^{\beta \mu B \sum_{i=1}^N s_i} \quad (5.2)$$

$$\begin{aligned} &= \sum_{s_1=\pm 1} \sum_{s_2=\pm 1} \dots \sum_{s_N=\pm 1} e^{\beta \mu B s_1} e^{\beta \mu B s_2} \dots e^{\beta \mu B s_N} \\ &= \sum_{s_1=\pm 1} e^{\beta \mu B s_1} \sum_{s_2=\pm 1} e^{\beta \mu B s_2} \dots \sum_{s_N=\pm 1} e^{\beta \mu B s_N} \\ &= \left[\sum_{s_1=\pm 1} e^{\beta \mu B s_1} \right]^N = Z_1^N. \end{aligned} \quad (5.3)$$

To find Z_1 we write

$$Z_1 = \sum_{s=\pm 1} e^{-\beta \mu B s} = e^{\beta \mu B (-1)} + e^{\beta \mu B (+1)} = 2 \cosh \beta \mu B, \quad (5.4)$$

where we have performed the sum over $s = \pm 1$. The partition function for N spins is simply

$$Z_N = (2 \cosh \beta \mu B)^N. \quad (5.5)$$

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 . In the following, we will use the notation $\langle A \rangle$ instead of \bar{A} to designate an ensemble average. We will also frequently omit the brackets $\langle \dots \rangle$, because it will be clear from the context when an average is implied.

The free energy is given by

$$F = -kT \ln Z_N = -NkT \ln Z_1 = -NkT \ln(2 \cosh \beta \mu B). \quad (5.6)$$

The mean energy E is

$$E = -\frac{\partial \ln Z_N}{\partial \beta} = \frac{\partial(\beta F)}{\partial \beta} = -N\mu B \tanh \beta \mu B. \quad (5.7)$$

Note that we have omitted the brackets because it is clear that E is the mean energy in the present context. From (5.7) we see that $E \rightarrow 0$ as $T \rightarrow \infty$ ($\beta \rightarrow 0$).

Problem 5.1. Compare the result (5.7) for the mean energy in the canonical ensemble to the corresponding result that you found in Problem 4.25 in the microcanonical ensemble.

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

$$C = \frac{\partial E}{\partial T} = -k\beta^2 \frac{\partial E}{\partial \beta}. \quad (5.8)$$

(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

$$C = N(\beta\mu B)^2 \operatorname{sech}^2 \beta\mu B. \quad (5.9)$$

Note that the heat capacity is always positive, goes to zero as $T \rightarrow 0$ 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)

$$\langle M \rangle = \mu \sum_{i=1}^N \langle s_i \rangle, \quad (5.10)$$

and the isothermal susceptibility χ :

$$\chi = \left(\frac{\partial M}{\partial B} \right)_T. \quad (5.11)$$

The susceptibility χ 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 in terms of derivatives of $\ln Z$ by noting that the total energy can be written in the general form as

$$E = E_0 - MB, \quad (5.12)$$

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 $E_0 = 0$.) This form of E implies that we can write Z in the form

$$Z = \sum_s e^{-\beta(E_{0,s} - M_s B)}, \quad (5.13)$$

where M_s and $E_{0,s}$ are the values of M and E_0 in microstate s . From (5.13) we have

$$\frac{\partial Z}{\partial B} = \sum_s \beta M_s e^{-\beta(E_{0,s} - M_s B)}, \quad (5.14)$$

and hence the mean magnetization is given by

$$\langle M \rangle = \frac{1}{Z} \sum_s M_s e^{-\beta(E_{0,s} - M_s B)} \quad (5.15a)$$

$$= \frac{1}{\beta Z} \frac{\partial Z}{\partial B} \quad (5.15b)$$

$$= kT \frac{\partial \ln Z}{\partial B}. \quad (5.15c)$$

If we substitute the relation $F = -kT \ln Z$, we obtain

$$\langle M \rangle = - \frac{\partial F}{\partial B}. \quad (5.16)$$

Often we are more interested in the mean magnetization per spin $\langle m \rangle$, which is simply

$$\langle m \rangle = \frac{1}{N} \langle M \rangle. \quad (5.17)$$

We leave it as an exercise for the reader to show that in the limit $B \rightarrow 0$ (see Problem 5.31)

$$\chi = \frac{1}{kT} [\langle M^2 \rangle - \langle M \rangle^2]. \quad (5.18)$$

The quantity χ in (5.18) is the *zero-field susceptibility*.¹ Note the similarity of the form (5.18) with the form (4.85) for the heat capacity C_V . That is, the response functions C_V and χ are related to the corresponding equilibrium fluctuations in the system.

From (5.6) and (5.16) we find that the magnetization of a system of noninteracting spins is

$$M = N\mu \tanh \beta\mu B. \quad (5.19)$$

The susceptibility can be calculated using (5.11) and (5.19) and is given by

$$\chi = N\mu^2 \beta \operatorname{sech}^2 \beta\mu B. \quad (5.20)$$

For high temperatures (small β), $\operatorname{sech} \beta\mu B \rightarrow 1$, and the leading behavior of χ is given by

$$\chi \rightarrow N\mu^2 \beta = \frac{N\mu^2}{kT}. \quad (\text{high temperature}) \quad (5.21)$$

The result (5.21) is known as the Curie form for the isothermal susceptibility and is commonly observed for magnetic materials at high temperatures ($kT \gg \mu B$).

We see that M is zero at $B = 0$ for all T implying that the system is paramagnetic. For $B \neq 0$, we note that $M \rightarrow 0$ as $\beta \rightarrow 0$ (high T), which implies that $\chi \rightarrow 0$ as $T \rightarrow \infty$. 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 5.2. (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 $T = \infty$. (b) Plot the isothermal susceptibility χ versus T for fixed B and describe its limiting behavior for low and high T .

Problem 5.3. Calculate the entropy of a system of N noninteracting spins and discuss its limiting behavior at low and high temperatures.

Problem 5.4. (a) 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 thermal bath at temperature T . The magnetic moment is $\mu = 9.274 \times 10^{-24}$ J/tesla. 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 thermal 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*.

¹We 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.

5.2 Thermodynamics of magnetism

Note that the free energy F defined by the relation $F = -kT \ln Z$ implies that F is a function of T , B , and N . The magnetization M fluctuates. It can be shown (see Appendix 5B) that the magnetic work done on a magnetic system with magnetization M in an external magnetic field B is given by $dW = -MdB$. For fixed N , we have the thermodynamic relation

$$dF(T, B) = -SdT - MdB. \quad (5.22)$$

From (5.22) we obtain (5.16) for the magnetization in terms of the free energy. As an aside, we note that if M is a constant and B is allowed to vary, we can define $G = F + MB$ so that

$$dG(T, M) = -SdT + BdM. \quad (5.23)$$

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 (or fruit fly) 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 Ernest Ising in 1925.³ Ising was very disappointed because the one-dimensional case does not have a phase transition. Lars Onsager 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.⁴ 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 spins are parallel and $+J$ if the spins are antiparallel. The total energy can be expressed in the form⁵

$$E = -J \sum_{i,j=\text{nn}(i)}^N s_i s_j - B \sum_{i=1}^N s_i, \quad (\text{Ising model}) \quad (5.24)$$

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.⁶ 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

²Each 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.

³A biographical note about Ising's life is at www.bradley.edu/las/phy/personnel/isingobit.html.

⁴The model is sometimes known as the Lenz-Ising model. The history of the Ising model is discussed by Stephen Brush.

⁵If we interpret the spin as an operator, then the energy is really a Hamiltonian. The distinction is unimportant in the present context.

⁶Because the spin \mathbf{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 \mathbf{S} with the Hamiltonian is zero, and we can treat the spins in the Ising model as if they were classical.

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 B 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 is given in Appendix 5A.

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. In other cases we need to use approximation methods and computer simulations.⁷ In the following section 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 some straightforward simulations of the Ising model to gain more insight into the behavior of the Ising model. In Section 5.6 we will discuss a simple approximation known as mean-field theory that is applicable to a wide variety of systems. A more advanced treatment of the Ising model is given in Chapter 9.

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 $N \rightarrow \infty$. The difficulty is that the total number of states, 2^N , is too many for N large. However, for the one-dimensional Ising model or *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 5.1a). Another choice is toroidal boundary conditions as shown in Figure 5.1b. This choice implies that the N th 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, $N \rightarrow \infty$.

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

⁷In three dimensions it has been shown that the Ising model is *NP-complete*, that it is computationally intractable. That is, the three-dimensional Ising model (and the two-dimensional Ising model with next nearest-neighbor interactions in addition to the nearest-neighbor kind) falls into the same class as other hard problems such as the traveling salesman problem.

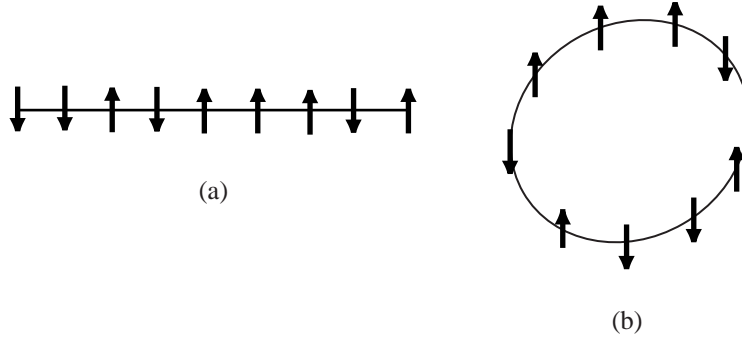


Figure 5.1: (a) Example of free boundary conditions for $N = 9$ spins. The spins at each end interact with only one spin. In contrast, all the other spins interact with two spins. (b) Example of toroidal boundary conditions. The N th spin interacts with the first spin so that the chain forms a ring. As a result, all the spins have the same number of neighbors and the chain does not have a surface.

of an external magnetic field is given explicitly by

$$E = -J \sum_{i=1}^{N-1} s_i s_{i+1}. \quad (\text{free boundary conditions}) \quad (5.25)$$

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

$$Z_2 = 2e^{\beta J} + 2e^{-\beta J} = 4 \cosh \beta J. \quad (5.26)$$

$$\begin{array}{cccc} \uparrow\uparrow & \downarrow\downarrow & \uparrow\downarrow & \downarrow\uparrow \\ -J & -J & +J & +J \end{array}$$

Figure 5.2: The four possible configurations of the $N = 2$ Ising chain.

In the same way we can enumerate the eight microstates for $N = 3$ (see Problem 5.6). We find that

$$Z_3 = 2e^{2\beta J} + 4 + 2e^{-2\beta J} \quad (5.27a)$$

$$= 2(e^{\beta J} + e^{-\beta J})^2 = 8(\cosh \beta J)^2 \quad (5.27b)$$

$$= (e^{\beta J} + e^{-\beta J})Z_2 = (2 \cosh \beta J)Z_2. \quad (5.27c)$$

The relation (5.27c) between Z_3 and Z_2 suggests a general relation between Z_N and Z_{N-1} :

$$Z_N = (2 \cosh \beta J)Z_{N-1} = 2(2 \cosh \beta J)^{N-1}. \quad (5.28)$$

We can derive the recursion relation (5.28) directly by writing Z_N for the Ising chain in the form

$$Z_N = \sum_{s_1=\pm 1} \cdots \sum_{s_N=\pm 1} e^{\beta J \sum_{i=1}^{N-1} s_i s_{i+1}}. \quad (5.29)$$

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 $N = 3$:

$$Z_3 = \sum_{s_1=\pm 1} \sum_{s_2=\pm 1} \sum_{s_3=\pm 1} e^{\beta J s_1 s_2 + \beta J s_2 s_3}. \quad (5.30)$$

The sum over s_3 can be done independently of s_1 and s_2 , and we have

$$Z_3 = \sum_{s_1=\pm 1} \sum_{s_2=\pm 1} e^{\beta J s_1 s_2} [e^{\beta J s_2} + e^{-\beta J s_2}] \quad (5.31a)$$

$$= \sum_{s_1=\pm 1} \sum_{s_2=\pm 1} e^{\beta J s_1 s_2} 2 \cosh \beta J s_2 = 2 \sum_{s_1=\pm 1} \sum_{s_2=\pm 1} e^{\beta J s_1 s_2} \cosh \beta J. \quad (5.31b)$$

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,

$$Z_3 = (2 \cosh \beta J) Z_2, \quad (5.32)$$

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} ,

$$\sum_{s_N=\pm 1} e^{\beta J s_{N-1} s_N} = 2 \cosh \beta J. \quad (5.33)$$

Hence we can write Z_N as

$$Z_N = (2 \cosh \beta J) Z_{N-1}. \quad (5.34)$$

Problem 5.5. Use the recursion relation (5.34) and the result (5.32) for Z_2 to confirm the result (5.28) for Z_N .

We can use the general result (5.28) for Z_N to find the Helmholtz free energy:

$$F = -kT \ln Z_N = -kT [\ln 2 + (N-1) \ln(2 \cosh \beta J)]. \quad (5.35)$$

In the thermodynamic limit $N \rightarrow \infty$, the term proportional to N in (5.35) dominates, and we have the desired result:

$$F = -NkT \ln(2 \cosh \beta J). \quad (5.36)$$

Problem 5.6. Enumerate the 2^N microstates for the $N = 4$ Ising chain and find the corresponding contributions to Z_4 for free boundary conditions. Then show that Z_4 satisfies the recursion relation (5.34) for free boundary conditions.

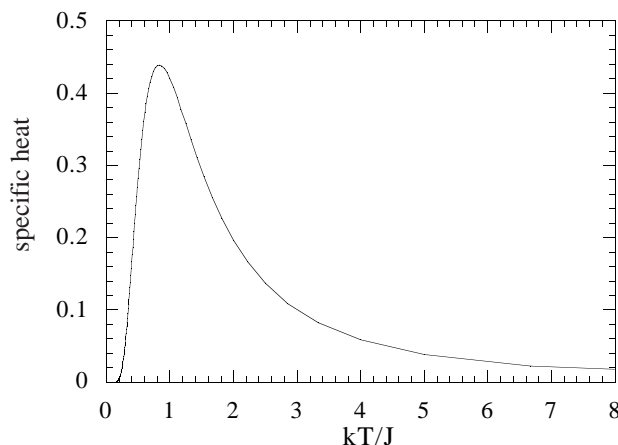


Figure 5.3: The temperature dependence of the heat capacity C of an Ising chain in the absence of an external magnetic field. At what value of kT/J does C exhibit a maximum? Explain.

Problem 5.7. (a) What is the ground state of the Ising chain? (b) What is the behavior of S in the limits $T \rightarrow 0$ and $T \rightarrow \infty$? 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:

$$S = Nk \left[\ln(e^{2\beta J} + 1) - \frac{2\beta J}{1 + e^{-2\beta J}} \right]. \quad (5.37)$$

$$E = -NJ \tanh \beta J. \quad (5.38)$$

$$C = Nk(\beta J)^2 (\operatorname{sech} \beta J)^2. \quad (5.39)$$

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.

***Problem 5.8.** In Problem 4.19 the density of states was given (without proof) for the one-dimensional Ising model for even N and toroidal boundary conditions:

$$\Omega(E, N) = 2 \binom{N}{i} = 2 \frac{N!}{i!(N-i)!}, \quad (i = 0, 2, 4, \dots, N) \quad (4.19)$$

with $E = 2i - N$. Use this form of Ω and the relation

$$Z_N = \sum_E \Omega(E, N) e^{-\beta E} \quad (5.40)$$

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

$$G(r) = \langle s_k s_{k+r} \rangle - \langle s_k \rangle \langle s_{k+r} \rangle. \quad (5.41)$$

Because the average of s_k is independent of the choice of the site k and equals m , the magnetization per spin $m = M/N$ and $G(r)$ can be written as

$$G(r) = \langle s_k s_{k+r} \rangle - m^2. \quad (5.42)$$

The average denoted by the brackets $\langle \dots \rangle$ 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 B), where r is the separation between spins in units of the lattice constant. Note that for $r = 0$, $G(r) = \langle m^2 \rangle - \langle m \rangle^2 \propto \chi$ (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 $G(r) \rightarrow 0$ for fixed r . For fixed T and B , 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 $G(r) \rightarrow 0$ as $r \rightarrow \infty$.

We will show in the following that $G(r)$ can be calculated exactly for the Ising chain. The result is

$$G(r) = (\tanh \beta J)^r. \quad (5.43)$$

A plot of $G(r)$ for $\beta J = 2$ is shown in Figure 5.4. Note that $G(r) \rightarrow 0$ for increasing r as expected.

We will find it useful to define the *correlation length* ξ by writing $G(r)$ in the form

$$G(r) = e^{-r/\xi}. \quad (5.44)$$

For the one-dimensional Ising model

$$\xi = -\frac{1}{\ln(\tanh \beta J)}. \quad (5.45)$$

At low temperatures, $\tanh \beta J \approx 1 - 2e^{-2\beta J}$, and

$$\ln(\tanh \beta J) \approx -2e^{-2\beta J}. \quad (5.46)$$

Hence

$$\xi = \frac{1}{2}e^{2\beta J}. \quad (\beta J \gg 1) \quad (5.47)$$

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 5.9. 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 .

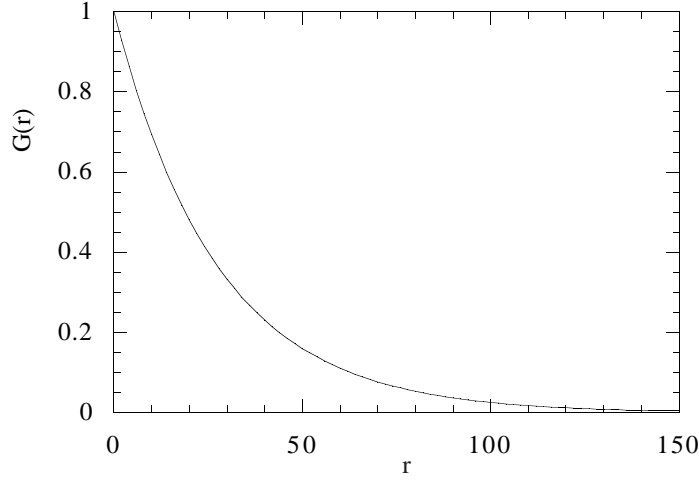


Figure 5.4: Plot of the spin-spin correlation function $G(r)$ as given by (5.43) for the Ising chain for $\beta J = 2$.

To calculate $G(r)$, we assume free boundary conditions as before 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

$$E = - \sum_{i=1}^{N-1} J_i s_i s_{i+1}, \quad (5.48)$$

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 $G(r) = \langle s_k s_{k+r} \rangle$. For the form (5.48) of the energy, $\langle s_k s_{k+r} \rangle$ is given by

$$\langle s_k s_{k+r} \rangle = \frac{1}{Z_N} \sum_{s_1=\pm 1} \cdots \sum_{s_N=\pm 1} s_k s_{k+r} \exp \left[\sum_{i=1}^{N-1} \beta J_i s_i s_{i+1} \right], \quad (5.49)$$

where

$$Z_N = 2 \prod_{i=1}^{N-1} 2 \cosh \beta J_i. \quad (5.50)$$

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 $G(r = 1) = \langle s_k s_{k+1} \rangle$ for the Ising model with

$J_i = J$ can be expressed as

$$\langle s_k s_{k+1} \rangle = \frac{1}{Z_N} \sum_{s_1=\pm 1} \cdots \sum_{s_N=\pm 1} s_k s_{k+1} \exp \left[\sum_{i=1}^{N-1} \beta J_i s_i s_{i+1} \right], \quad (5.51)$$

$$\begin{aligned} &= \frac{1}{Z_N} \frac{1}{\beta} \frac{\partial}{\partial J_k} \sum_{s_1=\pm 1} \cdots \sum_{s_N=\pm 1} \exp \left[\sum_{i=1}^{N-1} \beta J_i s_i s_{i+1} \right], \\ &= \frac{1}{Z_N} \frac{1}{\beta} \frac{\partial Z_N(J_1, \dots, J_{N-1})}{\partial J_k} \bigg|_{J_i=J} \\ &= \frac{\sinh \beta J}{\cosh \beta J} = \tanh \beta J, \end{aligned} \quad (5.52)$$

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 $s_k s_{k+2} = s_k s_{k+1} s_{k+1} s_{k+2}$ and

$$G(r=2) = \frac{1}{Z_N} \sum_{\{s_j\}} s_k s_{k+1} s_{k+1} s_{k+2} \exp \left[\sum_{i=1}^{N-1} \beta J_i s_i s_{i+1} \right], \quad (5.53)$$

$$= \frac{1}{Z_N} \frac{1}{\beta^2} \frac{\partial^2 Z_N(J_1, \dots, J_{N-1})}{\partial J_k \partial J_{k+1}} = [\tanh \beta J]^2. \quad (5.54)$$

It is clear that the method used to obtain $G(r=1)$ and $G(r=2)$ can be generalized to arbitrary r . We write

$$G(r) = \frac{1}{Z_N} \frac{1}{\beta^r} \frac{\partial}{\partial J_k} \frac{\partial}{\partial J_{k+1}} \cdots \frac{\partial}{\partial J_{k+r-1}} Z_N, \quad (5.55)$$

and use (5.50) for Z_N to find that

$$\begin{aligned} G(r) &= \tanh \beta J_k \tanh \beta J_{k+1} \cdots \tanh \beta J_{k+r-1}, \\ &= \prod_{k=1}^r \tanh \beta J_{k+r-1}. \end{aligned} \quad (5.56)$$

For a uniform interaction, $J_i = J$, and (5.56) reduces to the result for $G(r)$ in (5.43).

Problem 5.10. Consider an Ising chain of $N = 4$ spins and calculate $G(r)$ by exact enumeration of the 2^4 microstates. What are the possible values of r for free and toroidal boundary conditions? Choose one of these boundary conditions and calculate $G(r=1)$ and $G(r=2)$ using the microstates that were enumerated in Problem 5.6. Assume that the system is in equilibrium with a thermal bath at temperature T and in zero magnetic field. (For convenience choose $k=1$.)

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 thermal 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 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 $\langle E \rangle$, $\langle M \rangle$, 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 5.11. Use the applet/application at stp.clarku.edu/simulations/ising1d 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 $B = 0$.

- (a) Choose $N = 500$ 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 your criterion for equilibrium? What is the approximate relaxation time for the system to reach 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.
- (c) Approximately how many spins should you choose to avoid finite size effects at $T = 0.5$?

Problem 5.12. The thermodynamic quantities of interest for the Ising model include the mean energy E , the specific heat C , and the isothermal susceptibility χ . 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 specific heat and susceptibility be computed during the simulation at a given temperature?

- (c) Use the applet at stp.clarku.edu/simulations/ising1d 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 $B \neq 0$ is more difficult. We now 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.

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:

$$E = -J \sum_{i=1}^N s_i s_{i+1} - \frac{1}{2} B \sum_{i=1}^N (s_i + s_{i+1}). \quad (\text{toroidal boundary conditions}) \quad (5.57)$$

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

$$T_{s,s'} = e^{\beta[Jss' + \frac{1}{2}B(s+s')]} \quad (5.58)$$

The explicit form of the matrix elements is

$$T_{++} = e^{\beta(J+B)} \quad (5.59a)$$

$$T_{--} = e^{\beta(J-B)} \quad (5.59b)$$

$$T_{-+} = T_{+-} = e^{-\beta J}, \quad (5.59c)$$

or

$$\begin{aligned} \mathbf{T} &= \begin{pmatrix} T_{++} & T_{+-} \\ T_{-+} & T_{--} \end{pmatrix} \\ &= \begin{pmatrix} e^{\beta(J+B)} & e^{-\beta J} \\ e^{-\beta J} & e^{\beta(J-B)} \end{pmatrix}. \end{aligned} \quad (5.60)$$

The definition (5.58) of \mathbf{T} allows us to write Z_N in the form

$$Z_N(T, B) = \sum_{s_1} \sum_{s_2} \cdots \sum_{s_N} T_{s_1, s_2} T_{s_2, s_3} \cdots T_{s_N, s_1}. \quad (5.61)$$

The form of (5.61) 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

$$(\mathbf{T}^2)_{s_1, s_3} = \sum_{s_2} T_{s_1, s_2} T_{s_2, s_3}. \quad (5.62)$$

If we multiply N matrices together, we obtain:

$$(\mathbf{T}^N)_{s_1, s_{N+1}} = \sum_{s_2} \sum_{s_3} \cdots \sum_{s_N} T_{s_1, s_2} T_{s_2, s_3} \cdots T_{s_N, s_{N+1}}. \quad (5.63)$$

This result is very close to what we have in (5.61). To make it identical, we use periodic boundary conditions and set $s_{N+1} = s_1$, and sum over s_1 :

$$\sum_{s_1} (\mathbf{T}^N)_{s_1, s_1} = \sum_{s_1} \sum_{s_2} \sum_{s_3} \cdots \sum_{s_N} T_{s_1, s_2} T_{s_2, s_3} \cdots T_{s_N, s_1} = Z_N. \quad (5.64)$$

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

$$Z_N = \text{trace}(\mathbf{T}^N). \quad (5.65)$$

Because the trace of a matrix is independent of the representation of the matrix, the trace in (5.65) may be evaluated by bringing \mathbf{T} into diagonal form:

$$\mathbf{T} = \begin{pmatrix} \lambda_+ & 0 \\ 0 & \lambda_- \end{pmatrix}. \quad (5.66)$$

The matrix \mathbf{T}^N is diagonal with the diagonal matrix elements λ_+^N, λ_-^N . If we choose the diagonal representation for \mathbf{T} in (5.66), we have

$$\text{trace}(\mathbf{T}^N) = \lambda_+^N + \lambda_-^N, \quad (5.67)$$

where λ_+ and λ_- are the eigenvalues of \mathbf{T} . Hence, we can express Z_N as

$$Z_N = \lambda_+^N + \lambda_-^N. \quad (5.68)$$

The fact that Z_N is the trace of the N th power of a matrix is a consequence of our assumption of toroidal boundary conditions.

The eigenvalues λ_{\pm} are given by the solution of the determinant equation

$$\begin{vmatrix} e^{\beta(J+B)} - \lambda & e^{-\beta J} \\ e^{-\beta J} & e^{\beta(J-B)} - \lambda \end{vmatrix} = 0. \quad (5.69)$$

The roots of (5.69) are

$$\lambda_{\pm} = e^{\beta J} \cosh \beta B \pm [e^{-2\beta J} + e^{2\beta J} \sinh^2 \beta B]^{1/2}. \quad (5.70)$$

It is easy to show that $\lambda_+ > \lambda_-$ for all B and β , and consequently $(\lambda_-/\lambda_+)^N \rightarrow 0$ as $N \rightarrow \infty$. In the thermodynamic limit ($N \rightarrow \infty$), we obtain from (5.68) and (5.70)

$$\frac{1}{N} \ln Z_N(T, B) = \ln \lambda_+ + \ln \left[1 + \left(\frac{\lambda_-}{\lambda_+} \right)^N \right] \xrightarrow{N \rightarrow \infty} \ln \lambda_+, \quad (5.71)$$

and the free energy per spin is given by

$$\frac{1}{N}F(T, B) = -kT \ln [e^{\beta J} \cosh \beta J + (e^{2\beta J} \sinh^2 \beta B + e^{-2\beta J})^{1/2}]. \quad (5.72)$$

We can use (5.72) to find the magnetization M at nonzero T and B :

$$M = \frac{\partial F}{\partial B} = N \frac{\sinh \beta B}{(\sinh^2 \beta B + e^{-4\beta J})^{1/2}}. \quad (5.73)$$

We know that a system is paramagnetic if $M \neq 0$ only for $B \neq 0$, and is ferromagnetic if $M \neq 0$ for $B = 0$. For the one-dimensional Ising model, we see from (5.73) that $M = 0$ for $B = 0$, 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 $\beta B \gg 1$), $\sinh \beta B \approx \frac{1}{2}e^{\beta B} \gg e^{-2\beta J}$ and $m = M/N \approx 1$ for $B \neq 0$. Hence, at low temperatures only a small field is needed to produce saturation, corresponding to $m = 1$.

Problem 5.13. More insight into the properties of the Ising chain in nonzero magnetic field can be found by calculating the isothermal susceptibility χ . Calculate χ using (5.73). What is the limiting behavior of χ in the limit $T \rightarrow 0$? Express this limiting behavior in terms of the correlation length ξ .

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 except at $T = 0$. 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 $S = 0$.⁸ 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

$$\Delta F = 2J - kT \ln(N - 1). \quad (5.74)$$

We see from (5.74) that for $T > 0$ and $N \rightarrow \infty$, 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 $N \rightarrow \infty$.

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.

⁸The ground state for $B = 0$ corresponds to all spins up or all spins down. It is convenient to break this symmetry by assuming that $B = 0^+$ and letting $T \rightarrow 0$ before setting $B = 0$.

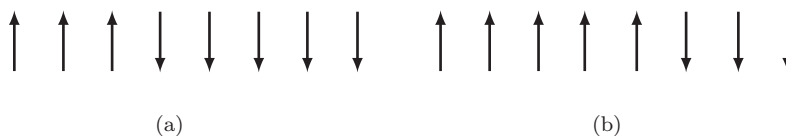


Figure 5.5: A domain wall in one dimension for a system of $N = 8$ spins. In (a) the energy of the system is $E = -5J$ with free boundary conditions. Because the energy of the ground state equals $7J$, the energy cost for forming a domain wall is $2J$. In (b) the domain wall has moved with no cost in energy.

5.5 The Two-Dimensional Ising Model

We first give an argument similar to the one that given in Appendix 5C to suggest the existence of a phase transition (to ferromagnetism) in two dimensions. We need to 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 expansion requires longer boundaries and hence more energy.

In two dimensions the points between pairs of spins of opposite signs can be joined to form boundary lines dividing the lattice into domains (see Figure 5.6). The net magnetization is proportional to the area of the positive domains minus the area of the negative domains. At $T = 0$ all the spins are in the same (positive) direction and there are no boundary lines. At $T > 0$, there is sufficient energy to create boundary lines and negative domains will appear. If the perimeter of a negative domain is b , then the energy needed to create it is $2Jb$. Hence, the probability of having a negative domain is $e^{-2\beta bJ}$. Because b must be at least 4, negative regions of large area are unlikely at low T . 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 1944.⁹ 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

⁹A short biography of Onsager can be found at www.nobel.se/chemistry/laureates/1968/onsager-bio.html.

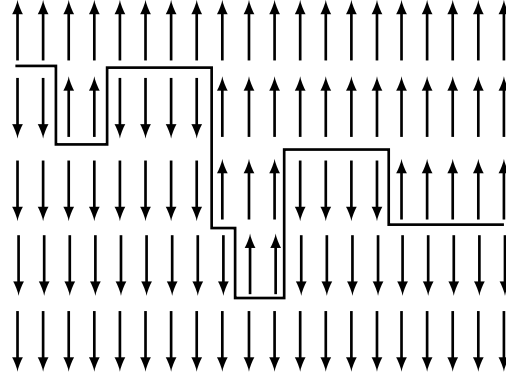


Figure 5.6: Example of a domain wall in the two-dimensional Ising model.

generalized to other systems. For these reasons few workers in statistical mechanics have gone through the Onsager solution in great detail. (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.) In the following, we give only the results of the two-dimensional solution for a square lattice and concentrate on approximation methods of more general applicability.

The critical temperature T_c is given by

$$\sinh \frac{2J}{kT_c} = 1, \quad (5.75)$$

or

$$kT_c/J = \frac{2}{\ln(1 + \sqrt{2})} \approx 2.269. \quad (5.76)$$

It is convenient to express the mean energy in terms of the dimensionless parameter κ defined as

$$\kappa = 2 \frac{\sinh 2\beta J}{(\cosh 2\beta J)^2}. \quad (5.77)$$

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

$$E = -2NJ \tanh 2\beta J - NJ \frac{\sinh^2 2\beta J - 1}{\sinh 2\beta J \cosh 2\beta J} \left[\frac{2}{\pi} K_1(\kappa) - 1 \right], \quad (5.78)$$

where

$$K_1(\kappa) = \int_0^{\pi/2} \frac{d\phi}{\sqrt{1 - \kappa^2 \sin^2 \phi}}. \quad (5.79)$$

K_1 is known as the complete elliptic integral of the first kind. The first term in (5.78) is similar to the result (5.38) for the energy of the one-dimensional Ising model with a doubling of the exchange

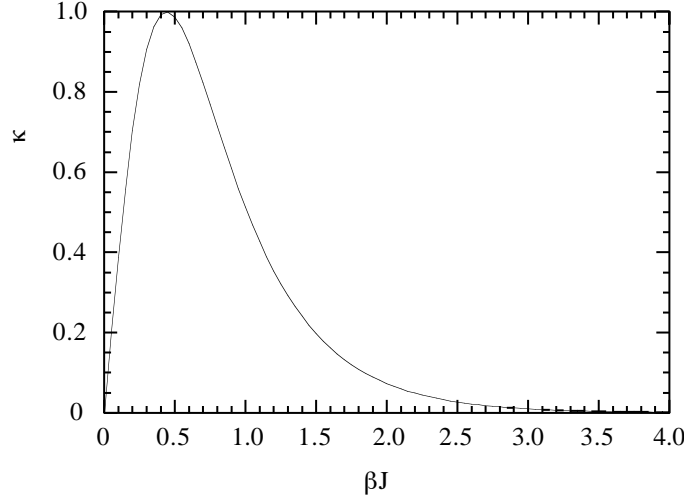


Figure 5.7: Plot of the function κ defined in (5.77) as a function of J/kT .

interaction J for two dimensions. The second term in (5.78) vanishes at low and high temperatures (because of the term in brackets) and at $T = T_c$ because of the vanishing of the term $\sinh^2 2\beta J - 1$. However, $K_1(\kappa)$ has a logarithmic singularity at $T = T_c$ at which $\kappa = 1$. Hence, the entire 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.

The heat capacity can be obtained by differentiating $E(T)$ with respect to temperature. It can be shown after some tedious algebra that

$$C(T) = Nk \frac{4}{\pi} (\beta J \coth 2\beta J)^2 [K_1(\kappa) - E_1(\kappa) - (1 - \tanh^2 2\beta J) \left(\frac{\pi}{2} + (2 \tanh^2 2\beta J - 1) K_1(\kappa) \right)], \quad (5.80)$$

where

$$E_1(\kappa) = \int_0^{\pi/2} d\phi \sqrt{1 - \kappa^2 \sin^2 \phi}. \quad (5.81)$$

E_1 is the complete elliptic integral of the second kind. Near T_c , C is given by

$$C \approx -Nk \frac{2}{\pi} \left(\frac{2J}{kT_c} \right)^2 \ln \left| 1 - \frac{T}{T_c} \right| + \text{constant}. \quad (T \approx T_c) \quad (5.82)$$

The most important property of the Onsager solution is that the heat capacity diverges logarithmically at $T = T_c$:

$$C(T) \sim \ln |\epsilon|, \quad (5.83)$$

where the reduced temperature difference is given by

$$\epsilon = (T_c - T)/T_c. \quad (5.84)$$

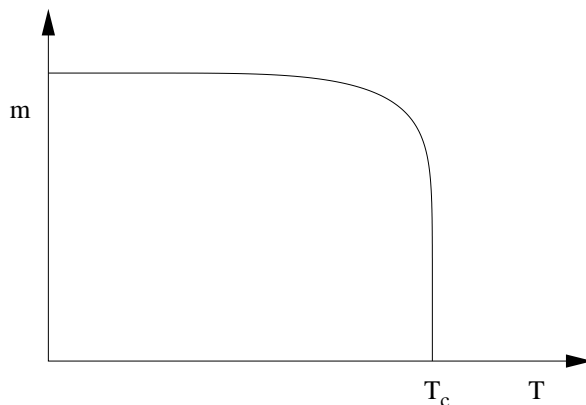


Figure 5.8: The temperature-dependence of the spontaneous magnetization of the two-dimensional Ising model.

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 (5.83).

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 range of $T > 0$ such that $M \neq 0$ for $B = 0$? However, 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 B for finite B and then let $B = 0$. The exact behavior of the two-dimensional Ising model as a function of the magnetic field B is not known. In 1952, Yang was able to calculate the magnetization for $T < T_c$ and the zero-field susceptibility.¹⁰ Yang's exact result for the magnetization per spin can be expressed as

$$m(T) = \begin{cases} 0 & T > T_c \\ (1 - [\sinh 2\beta J]^{-4})^{1/8} & T < T_c \end{cases} \quad (5.85)$$

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 $T \rightarrow T_c$ is given by

$$\chi \sim |\epsilon|^{-7/4}. \quad (5.86)$$

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

¹⁰The result (5.85) 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/.

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 $B = 0$, the transition occurs at a *critical point*.

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 known to be

$$G(r) \sim \frac{1}{r^{d-2+\eta}} e^{-r/\xi}. \quad (\text{large } r \text{ and } |\epsilon| \ll 1), \quad (5.87)$$

where d is the spatial dimension and η is another critical exponent. The *correlation length* ξ diverges as

$$\xi \sim |\epsilon|^{-\nu}. \quad (5.88)$$

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:

$$G(r) = \frac{1}{r^\eta}. \quad (r \gg 1 \text{ and } T = T_c) \quad (5.89)$$

The power-law behavior in (5.89). 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
	η	1/4	0.031(5)	0
correlation length	ν	1	0.629(4)	1/2
power law decay at $T = T_c$	η	1/4	0.04	0

Table 5.1: Values of the static critical exponents for the Ising model.

There is a fundamental difference between the exponential behavior of $G(r)$ for $T \neq T_c$ in (5.87) and the power law behavior of $G(r)$ for $T = T_c$ in (5.89). 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 $x \rightarrow ax$ 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 $x \rightarrow ax$ 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 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. Use the applet at [<stp.clarku.edu/simulations/ising2d/>](http://stp.clarku.edu/simulations/ising2d/) to simulate the two-dimensional Ising model at a given temperature. First choose $N = L^2 = 32^2$. Set the external magnetic field $B = 0$ 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.

- Is the orientation of the spins random, that is, is the mean magnetization equal to zero? Is there a slight tendency for a spin to align with its neighbors?
- Next choose a low temperature such as $T = 0.5$. Are the spins still random or do a majority choose a preferred direction?
- Choose $L = 4$ and $T = 2.0$. Does the sign of the magnetization change during the simulation? Choose a larger value of N and observe if the sign of the magnetization changes.
- 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.

Problem 5.16. We can use the applet at [<stp.clarku.edu/simulations/ising2d/>](http://stp.clarku.edu/simulations/ising2d/) to obtain more quantitative information. Choose $N = 32^2$ and set $B = 0$. 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 $\Delta T = 0.2$ until about $T = 1.6$. Describe the qualitative behavior of these quantities.

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 easy to treat, usually yield qualitatively correct results, and provide insight into the nature of phase transitions. We will see that their main disadvantage is that they ignore long-range correlations and are insensitive to the dimension of space. In Section 8.9 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 other spins. That is, spin i “feels” an effective field B_{eff} given by

$$B_{\text{eff}} = J \sum_{j=1}^q s_j + B, \quad (5.90)$$

where the sum over j in (5.90) is over the q neighbors of i . Because the orientation of the neighboring spins depends on the orientation of spin i , B_{eff} fluctuates from its mean

$$\langle B_{\text{eff}} \rangle = J \sum_{j=1}^q \langle s_j \rangle + B, \quad (5.91a)$$

$$= Jqm + B, \quad (5.91b)$$

where $\langle s_j \rangle = m$ for all j . In the mean-field approximation, we ignore the deviations of B_{eff} from $\langle B_{\text{eff}} \rangle$ and assume that the field at i is $\langle B_{\text{eff}} \rangle$, independent of the orientation of s_i . This assumption is clearly an approximation because if s_i is up, then its neighbors are more likely to be up. This correlation is ignored in the mean-field approximation.

It is straightforward to write the partition function for one spin in an effective field:

$$Z_1 = \sum_{s_1=\pm 1} e^{\beta s_1 B_{\text{eff}}} = 2 \cosh \beta(Jqm + B). \quad (5.92)$$

The free energy per spin is

$$f = -\frac{1}{\beta} \ln Z_1 = -kT \ln [2 \cosh \beta(Jqm + B)], \quad (5.93)$$

and the magnetization is

$$m = -\frac{\partial f}{\partial B} = \tanh \beta(Jqm + B). \quad (5.94)$$

Equation (5.94) for m is a *self-consistent* transcendental equation whose solution yields m . That is, the mean-field that influences the mean value of m depends on the mean value of m .

From Figure 5.9 we see that nonzero solutions for m exist for $B = 0$ when $\beta qJ \geq 1$. Thus the critical temperature T_c is given by

$$kT_c = Jq. \quad (5.95)$$

That is, $m \neq 0$ for $T \leq T_c$ and $m = 0$ for $T > T_c$ for $B = 0$. Near T_c the magnetization is small, and we can expand $\tanh \beta Jqm$ to find

$$m = \beta Jqm - \frac{1}{3}(\beta Jqm)^3 + \dots \quad (5.96)$$

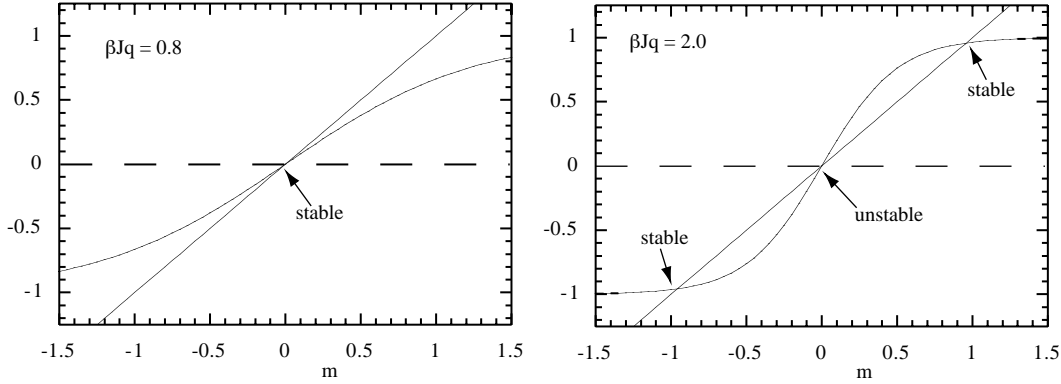


Figure 5.9: Graphical solution of the self-consistent equation (5.94). The solution $m = 0$ exists for all T , but the solution $m \neq 0$ exists only for T sufficiently small that the initial slope of $\tanh \beta q J$ is larger than one.

Equation (5.96) has two solutions:

$$m = 0, \quad (5.97a)$$

and

$$m = \frac{3^{1/2}}{(\beta J q)^{3/2}} (\beta J q - 1)^{1/2}. \quad (5.97b)$$

The first solution corresponds to the high temperature disordered paramagnetic state and the second solution to the low temperature ordered ferromagnetic state. How do we know which solution to choose? The answer can be found by calculating the free energies for both solutions and choosing the solution that gives the smaller free energy (see Problem 5.39).

If we set $kT_c = Jq$, it is easy to see that the spontaneous magnetization vanishes as

$$m(T) = 3^{1/2} \frac{T}{T_c} \left(\frac{T_c - T}{T_c} \right)^{1/2}. \quad (5.98)$$

We see from (5.98) that m approaches zero as T approaches from T_c from below. As mentioned, the quantity m is called the order parameter of the system, because $m \neq 0$ implies that the system is ordered and $m = 0$ implies that it is not.

In terms of the dimensionless temperature difference $\epsilon = (T_c - T)/T_c$, the exponent for the asymptotic power law behavior of the order parameter is given by

$$m(T) \sim \epsilon^\beta. \quad (5.99)$$

where we have introduced the critical exponent β (not to be confused with the inverse temperature). From (5.98) 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)?

Problem 5.17. Plot the numerical solution of (5.94) for m as a function of T/T_c for $B = 0$.

Problem 5.18. Determine $m(T)$ from the numerical solution of (5.94) for $B = 1$ and compare your values with the exact solution in one dimension (see (5.73)).

We next find the behavior of other important physical properties near T_c . The zero-field isothermal susceptibility (per spin) is given by

$$\chi = \lim_{B \rightarrow 0} \frac{\partial m}{\partial B} = \frac{\beta(1 - \tanh^2 \beta J q m)}{1 - \beta J q (1 - \tanh^2 \beta J q m)}. \quad (5.100)$$

Note that for very high temperatures, $\beta J \rightarrow 0$, and χ from (5.100) approaches the Curie law for noninteracting spins as expected. For T above and close to T_c , we find (see Problem 5.19)

$$\chi \sim \frac{T}{T - T_c}. \quad (5.101)$$

The result (5.101) for χ is known as the Curie-Weiss law. We characterize the divergence of the zero-field susceptibility as the critical point is approached from either the low or high temperature side as

$$\chi \sim |\epsilon|^{-\gamma}. \quad (T \text{ near } T_c) \quad (5.102)$$

The mean-field prediction for the critical exponent γ is $\gamma = 1$.

Problem 5.19. (a) Use the relation (5.100) to show that $\chi = (1/k)(T - T_c)^{-1}$ for $T \rightarrow T_c^+$. (b) It is more difficult to show that $\chi = (1/2k)(T_c - T)^{-1}$ for $T \rightarrow T_c^-$.

The magnetization at T_c as a function of B can be calculated by expanding (5.94) to third order in B with $\beta = \beta_c = 1/qJ$:

$$m = m + \beta_c B - \frac{1}{3}(m + \beta_c B)^3 + \dots \quad (5.103)$$

For m and B very small, we can assume that $\beta_c B \ll m$. This assumption yields

$$m = (3\beta_c B)^{1/3}, \quad (T = T_c) \quad (5.104)$$

which is consistent with this assumption. In general, we write

$$m \sim B^{1/\delta}. \quad (T = T_c) \quad (5.105)$$

The mean-field prediction is $\delta = 3$.

The energy per spin in the mean-field approximation is simply

$$E = -\frac{1}{2}Jqm^2, \quad (5.106)$$

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

$$E = -\frac{1}{2}Jq[\tanh(\beta(Jqm + B))]^2. \quad (5.107)$$

The specific heat can be calculated from (5.107) for $T < T_c$. As shown in Problem 5.20, $C \rightarrow 3k/2$ for $T \rightarrow T_c$ from below. Hence, mean-field theory predicts that there is a jump in the specific heat.

Problem 5.20. Show that according to mean-field theory, there is a jump of $3k/2$ in the specific heat at $T = T_c$.

Now let us 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 (5.95) 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 difficulty is that the mean 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.

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.

Mean-field theory predicts that near T_c , various thermodynamic properties exhibit power law behavior as defined in (5.99), (5.102), and (5.105). The mean-field prediction for the critical exponents are $\beta = 1/2$, $\gamma = 1$, and $\delta = 3$ respectively (see Table 5.1). Note that the mean-field results for the critical exponents are independent of dimension. These values of the critical exponents do not agree with the results of the Onsager solution of the two-dimensional Ising model. On the other hand, the mean-field predictions for the critical exponents are not terribly wrong. Another limitation of mean-field theory is that it 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 the unphysical case of 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. However, all mean-field theories predict the same (incorrect) values for the critical exponents.

Problem 5.21. From Table 5.1, we see that the predictions of mean-field theory increase in accuracy with increasing dimensionality. Why is this trend reasonable?

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. We will refer to this model as the infinite-range Ising model, although the interaction range becomes infinite only in the limit $N \rightarrow \infty$. We will leave it as a problem to show that for such a system of N spins, the energy is given by

$$E = \frac{J_N}{2}(N - M^2), \quad (5.108)$$

where M is the magnetization and J_N is the interaction between any two spins. Note that E depends only on M . We also leave it as a problem to show that the number of states with magnetization M is given by

$$g(M) = \frac{N!}{n!(N-n)!}, \quad (5.109)$$

where n is the number of up spins. As before, we have $n = N/2 + M/2$ and $N - n = N/2 - M/2$.

Problem 5.22. (a) Show that the energy of a system for which every spin interacts with every other spin is given by (5.108). 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 (5.109).

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

$$J_N = \frac{qJ}{N}, \quad (5.110)$$

so that $kT_c/J = q$ when $N \rightarrow \infty$.

Given the energy in (5.108) and the number of states in (5.109), we can write the partition function as

$$Z_N = \sum_M \frac{N!}{(\frac{N}{2} + \frac{M}{2})!(\frac{N}{2} - \frac{M}{2})!} e^{-\beta J_N(N-M^2)/2} e^{-\beta BM}, \quad (5.111)$$

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 very large we can convert the sum to an integral. We write

$$Z = \int_{-\infty}^{\infty} dM Z(M), \quad (5.112)$$

where

$$Z(M) = \frac{N!}{n!(N-n)!} e^{-\beta E} e^{-\beta BM}, \quad (5.113)$$

where $n = (M + N)/2$. A plot of $Z(M)$ shows that it is peaked about some value of M . So let us do our usual trick of expanding $\ln Z_M$ about its maximum. For simplicity, we will first find the value of M for which $Z(M)$ is a maximum. We write

$$\ln Z(M) = \ln N! - \ln n! - \ln(N-n)! - \beta E + \beta hM. \quad (5.114)$$

Then we use that the fact that $\frac{d}{dx}(\ln x!) = \ln x$, $dn/dM = 1/2$, and $d(N - n)/dM = -1/2$ and obtain

$$\frac{d \ln Z(M)}{dM} = -\frac{1}{2} \ln n + \frac{1}{2} \ln(N - n) + \beta J_N M + \beta B \quad (5.115a)$$

$$= -\frac{1}{2} \ln \frac{N}{2}(1 + m) + \frac{1}{2} \ln \frac{N}{2}(1 - m) + q\beta Jm + \beta B \quad (5.115b)$$

$$= -\frac{1}{2} \ln(1 + m) + \frac{1}{2} \ln(1 - m) + q\beta Jm + \beta B = 0. \quad (5.115c)$$

We set $d(\ln Z(M))/dM = 0$ because we wish to find the value of M that maximizes $Z(M)$. We have

$$\frac{1}{2} \ln \frac{1 - m}{1 + m} = -\beta(qJm + B), \quad (5.116)$$

so that

$$\frac{1 - m}{1 + m} = e^{-2\beta(qJm + B)} = x \quad (5.117)$$

Finally we solve (5.117) for m in terms of x and obtain

$$1 - m = x(1 + m) \quad (5.118a)$$

$$m(-1 - x) = -1 + x \quad (5.118b)$$

$$m = \frac{1 - x}{1 + x} = \frac{1 - e^{-2\beta(Jqm + B)}}{e^{-2\beta(Jqm + B)} + 1} \quad (5.119a)$$

$$= \frac{e^{\beta(Jqm + B)} - e^{-\beta(Jqm + B)}}{e^{-\beta(Jqm + B)} + e^{\beta(Jqm + B)}} \quad (5.119b)$$

$$= \tanh(\beta(Jqm + B)). \quad (5.119c)$$

Note that (5.119c) is identical to the previous mean-field result in (5.94).

***Problem 5.23.** Show that $Z(M)$ can be written as a Gaussian and then do the integral over M in (5.112) to find the mean-field form of Z . Then use this form of Z to find the mean-field result for the free energy F .

Appendix 5A. 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 the phenomena of diamagnetism does not exist in classical physics (see Problem 6.76). Hence, magnetism can be understood only by using quantum mechanics.

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

$$E = -\boldsymbol{\mu} \cdot \mathbf{B}. \quad (5.120)$$

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

$$\mathbf{B} = \mu_0(\mathbf{H} + \mathbf{m}). \quad (5.121)$$

The energy due to the external magnetic field \mathbf{H} coupled to \mathbf{M} is

$$E = -\mathbf{M} \cdot \mathbf{H}. \quad (5.122)$$

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

$$|\uparrow\uparrow\rangle, |\downarrow\downarrow\rangle, |\uparrow\downarrow\rangle, |\downarrow\uparrow\rangle, \quad (5.123)$$

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 (5.123) 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 (5.123) 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 (5.123) that satisfy this condition are

$$\frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle) \quad (5.124a)$$

$$|\uparrow\uparrow\rangle \quad (5.124b)$$

$$\frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle) \quad (5.124c)$$

$$|\downarrow\downarrow\rangle \quad (5.124d)$$

The state in (5.124a) 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

$$(\mathbf{S}_1 + \mathbf{S}_2)^2 = \mathbf{S}_1^2 + \mathbf{S}_2^2 + 2\mathbf{S}_1 \cdot \mathbf{S}_2. \quad (5.125)$$

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 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

$$E = \frac{1}{4}(E_{\text{singlet}} + 3E_{\text{triplet}}) - J\mathbf{S}_1 \cdot \mathbf{S}_2, \quad (5.126)$$

where $J = E_{\text{singlet}} - E_{\text{triplet}}$. The first part of (5.126) 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 (5.126) for the spin-spin interaction and is expressed as

$$\hat{H} = - \sum_{i < j=1}^N J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j - g\mu_0 \mathbf{H} \cdot \sum_{i=1}^N \mathbf{S}_i, \quad (\text{Heisenberg model}) \quad (5.127)$$

where $g\mu_0$ is the magnetic moment of the electron. The *exchange interaction* J_{ij} can be positive or negative. The form (5.127) 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 $S \rightarrow \infty$, 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.



Figure 5.10: The ground state of $N = 5$ Ising spins in an external magnetic field. For toroidal boundary conditions, the ground state energy is $E_0 = -5J - 5B$.



Figure 5.11: The flip of a single spin of $N = 5$ Ising spins. The corresponding energy cost is $4J + 2B$.

Appendix 5B. The Thermodynamics of Magnetism

[xx not written xx]

Appendix 5C: 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 B . 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 $1, 2, \dots, f$ 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 5.10. The energy cost of flipping a single spin is $4J + 2B$. (The energy of interaction of the flipped spin changes from $-2J$ to $+2J$.) A typical configuration is shown in Figure 5.11. Because the flipped spin can be at $N = 5$ different sites, we write

$$Z = [1 + 5e^{-\beta(4J+2B)} + \dots]e^{-\beta E_0}, \quad (5.128)$$

where $E_0 = -5(J + B)$.

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 5.12). We will leave it as an exercise (see Problem 5.24) to determine the corresponding energies and the number of different ways that this type of excitation occurs.



Figure 5.12: Configurations corresponding to two flipped spins. In (a) the flipped spins are not nearest neighbors and in (b) the flipped spins are neighbors.

Problem 5.24. Use the microstates that were enumerated in Problem 5.6 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

$$u = e^{-2\beta J}, \quad (5.129)$$

and

$$w = e^{-2\beta B}. \quad (5.130)$$

***Problem 5.25.** Generalize the low temperature expansion to find the order w^3 contributions to Z_N . If you have patience, go to higher order. An inspection of the series might convince you that the low temperature series can be summed exactly, (The low temperature series for the Ising can be summed exactly only in one dimension.)

Problem 5.26. Use (5.35 and (5.37) to find the low temperature behavior of F and S for a one-dimensional Ising chain in the absence of an external magnetic field. Compare your results with the above qualitative arguments.

Appendix D: High Temperature Expansion

At high temperatures for which $J/kT \ll 1$, the effects of the interaction 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

$$Z_N = \sum_s \prod_{i,j=\text{nn}(i)} e^{\beta J s_i s_j}, \quad (5.131)$$

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

$$\begin{aligned} e^{\beta J s_i s_j} &= \cosh \beta J + s_i s_j \sinh \beta J \\ &= \cosh \beta J (1 + v s_i s_j), \end{aligned} \quad (5.132)$$

where

$$v = \tanh \beta J. \quad (5.133)$$

The identity (5.132) can be demonstrated by considering the various cases $s_i, s_j = \pm 1$ (see Problem 5.34). The variable v approaches zero as $T \rightarrow \infty$ and will be used as an expansion parameter instead of J/kT for reasons that will become clear later. Equation (5.131) can now be written as

$$Z_N = (\cosh \beta J)^p \sum_s \prod_{\langle ij \rangle} (1 + v s_i s_j), \quad (5.134)$$

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

$$p = \frac{1}{2} N q, \quad (5.135)$$

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 (5.134): $(1 + v s_1 s_2)(1 + v s_2 s_3)(1 + v s_3 s_1)$. If we expand this product in powers of v , we obtain the $2^p = 8$ terms in the partition function:

$$\begin{aligned} Z_{N=3} = (\cosh \beta J)^3 \sum_{s_1=-1}^1 \sum_{s_2=-1}^1 \sum_{s_3=-1}^1 [1 + v(s_1 s_2 + s_2 s_3 + s_3 s_1) \\ + v^2(s_1 s_2 s_2 s_3 + s_1 s_2 s_3 s_1 + s_2 s_3 s_3 s_1) + v^3 s_1 s_2 s_2 s_3 s_3 s_1]. \end{aligned} \quad (5.136)$$

It is convenient to introduce a one-to-one correspondence between each of the eight terms in the bracket in (5.136) and a diagram on the lattice. The set of eight diagrams is shown in Figure 5.13. Because v enters into the product in (5.136) 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 (5.136). 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

$$\sum_{s_i=-1}^1 s_i^n = \begin{cases} 2 & n \text{ even} \\ 0 & n \text{ odd} \end{cases} \quad (5.137)$$

From (5.137) we see that only terms of order v^0 and v^3 contribute so that

$$Z_{N=3} = \cosh^3 \beta J [8 + 8v^3] = 2^3 (\cosh^3 \beta J + \sinh^3 \beta J). \quad (5.138)$$

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 (5.134). Hence, only diagrams with an even number of bonds from each vertex yield a nonzero contribution to Z_N .

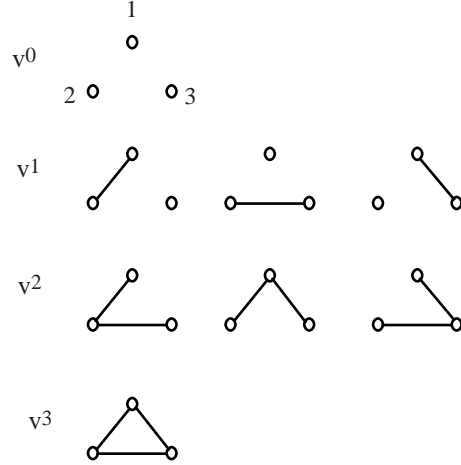


Figure 5.13: The eight diagrams that correspond to the eight terms in the Ising model partition function for the $N = 3$ Ising chain. The term $s_i s_j$ is represented by a line between the neighboring sites i and j .

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

$$Z_N = (\cosh \beta J)^N [2^N + 2^N v^N]. \quad (5.139)$$

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 (5.139) is not identical to the form of Z_N given in (5.28). Use the fact that $v < 1$ and take the thermodynamic limit $N \rightarrow \infty$ to explain the equivalence of the two results for Z_N .

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 $\alpha, \beta, \delta, \gamma, \nu, \eta$

exact enumeration, mean-field theory

low and high temperature expansions

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Table 5.3: Listing of inline problems.

Problem 5.29. *Thermodynamics of classical spins.* The energy of interaction of a classical magnetic dipole with an external magnetic field \mathbf{B} is given by

$$E = -\boldsymbol{\mu} \cdot \mathbf{B} = -\mu B \cos \theta, \quad (5.140)$$

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 $B \neq 0$, the mean magnetization is given by

$$M = \mu N \langle \cos \theta \rangle. \quad (5.141)$$

The direction of the magnetization is parallel to \mathbf{B} . Show that the partition function for one spin is given by

$$Z_1 = \int_0^{2\pi} \int_0^\pi e^{\beta \mu B \cos \theta} \sin \theta \, d\theta \, d\phi. \quad (5.142)$$

How is $\langle \cos \theta \rangle$ related to Z_1 ? Show that

$$M = N \mu L(\beta \mu B), \quad (5.143)$$

where the Langevin function $L(x)$ is given by

$$L(x) = \frac{e^x + e^{-x}}{e^x - e^{-x}} - \frac{1}{x} = \coth x - \frac{1}{x}. \quad (5.144)$$

For $|x| < \pi$, $L(x)$ can be expanded as

$$L(x) = \frac{x}{3} - \frac{x^3}{45} + \dots + \frac{2^{2n} B_{2n}}{(2n)!} + \dots, \quad (x \ll 1) \quad (5.145)$$

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

$$L(x) \approx 1 - \frac{1}{x} + 2e^{-2x}. \quad (x \gg 1) \quad (5.146)$$

What is the behavior of M in the limit of low T ?

Problem 5.30. 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 \mathbf{B} is restricted to $(2J+1)$ orientations. We write the energy of an individual atom as

$$E = -g\mu_0 \mathbf{J} \cdot \mathbf{B} = -g\mu_0 J_z B. \quad (5.147)$$

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 $-J, -J+1, -J+2, \dots, J-1, J$. Hence, the partition function for one atom contains $(2J+1)$ terms:

$$Z_1 = \sum_{m=-J}^J e^{-\beta(-g\mu_0 m B)}. \quad (5.148)$$

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:

$$Z_1 = \sum_{m=-J}^J e^{m\alpha}, \quad (5.149a)$$

$$= e^{-\alpha J} (1 + e^\alpha + e^{2\alpha} + \dots + e^{2J\alpha}). \quad (5.149b)$$

The sum of a finite geometrical series is given by

$$S_n = \sum_{p=0}^n x^p = \frac{x^{n+1} - 1}{x - 1}. \quad (5.150)$$

Given that there are $(2J+1)$ terms in (5.149b), show that

$$Z = e^{-\alpha J} \frac{e^{(2J+1)\alpha} - 1}{e^\alpha - 1} = e^{-\alpha J} \frac{[1 - e^{(2J+1)\alpha}]}{1 - e^\alpha}. \quad (5.151)$$

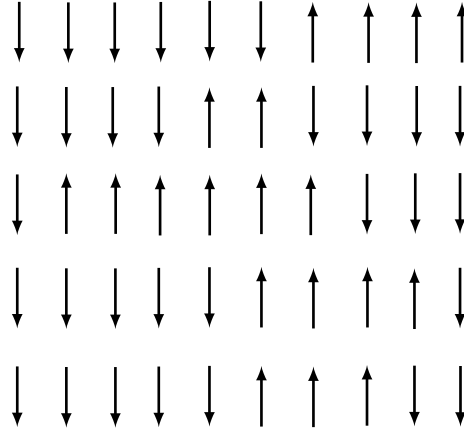


Figure 5.14: Five configurations of the $N = 10$ Ising chain with toroidal boundary conditions generated by the Metropolis algorithm at $\beta J = 1$ and $B = 0$.

Use the above relations to show that

$$M = Ng\mu_0 JB_J(\alpha), \quad (5.152)$$

where the Brillouin function $B_J(\alpha)$ is defined as

$$B_J(\alpha) = \frac{1}{J} \left[(J + 1/2) \coth(J + 1/2)\alpha - \frac{1}{2} \coth \alpha/2 \right]. \quad (5.153)$$

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 5.31. Suppose that the total energy of a system of spins can be written as

$$E = E_0 - MB, \quad (5.154)$$

where the first term does not depend explicitly on the magnetic field B , and M is the magnetization of the system (in the direction of \mathbf{B}). Show that the form of (5.154) implies that the zero-field susceptibility can be expressed as

$$\chi = \left(\frac{\partial M}{\partial B} \right)_{B=0} = \frac{1}{kT} [\langle M^2 \rangle - \langle M \rangle^2]. \quad (5.155)$$

Problem 5.32. The five configurations shown in Figure 5.14 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. However, better results

Problem 5.33. Use the applet at <http://stp.clarku.edu/simulations/ising/> 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?

Problem 5.34. Verify the validity of the identity (5.132) 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.** *Ising chain.* Write a program that uses the demon algorithm to generate a representative sample of microstates for the Ising chain at fixed energy. The energy for a particular configuration of spins is given by

$$E = -J \sum_{i=1}^N s_i s_{i+1}, \quad (5.156)$$

where $s_i = \pm 1$ and $s_{N+1} = s_1$. The easiest trial change is to flip a spin from $+1$ to -1 or vice versa. For such a flip the possible changes in energy are $\Delta E = E_{\text{trial}} - E_{\text{old}} = 0$ and $\pm 4J$. Confirm that the possible energies of the spins are $E = -NJ, -NJ + 4J, -NJ + 8J \dots + NJ$, and that the possible demon energies are $E_d = 4nJ$, where $n = 0, 1, 2, \dots$. The most difficult part of the simulation is choosing the initial state so that it has the desired energy. Choose $N = 20$ and $E_d = 0$ initially. Write a subroutine that begins with all spins down and randomly flips spins until the desired energy is reached. Choose J to be the unit of energy. Collect data for the mean energy of the system and the mean demon energy for about ten different energies and plot your results. 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. Increase the number of flips per spin until you obtain reasonable results. Compute the probability density, $P(E_d)$, and determine its dependence on E_d by making a semilog plot.

***Problem 5.37.** Consider a one-dimensional Ising-type model defined by the usual Hamiltonian with $B = 0$, 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. 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 thermal 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. It can be shown that the free energy per spin in the mean-field approximation is given by

$$f = -(q/2)Jm^2 - Bm + kTs(m), \quad (5.157)$$

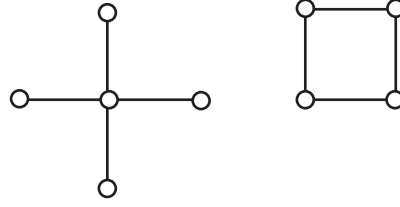


Figure 5.15: Two examples of possible diagrams on the square lattice. The only term that contributes to Z corresponds to the square.

where

$$s(m) = \frac{1}{2}(1+m) \ln \frac{1}{2}(1+m) + \frac{1}{2}(1-m) \ln \frac{1}{2}(1-m). \quad (5.158)$$

Show that $m = 0$ provides a lower free energy for $T > T_c$, and that $m \neq 0$ provides a lower free energy for $T < T_c$.

Problem 5.40. Write (5.94) in the form $\beta q J m = \tanh^{-1} m = (1/2) \ln[(1+m)/(1-m)]$ and show that

$$m \approx 1 - 2e^{-\beta q J} \quad \text{as } T \rightarrow 0 \quad (5.159)$$

***Problem 5.41.** The high temperature expansion we discussed for the Ising chain in Section 5.7 is very general and can be readily applied to the two and three-dimensional Ising model. We write

$$Z_N = (\cosh \beta J)^{Nq/2} 2^N \sum_{b=0}^{Nq/2} g(b) v^b, \quad (5.160)$$

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 (5.160) 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 5.15) and is given by

$$(\cosh \beta J)^{2N} 2^N g(4) v^4, \quad (5.161)$$

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. [xx need to expand later xx]

To make the high temperature expansion more explicit, work out the first several terms in (5.160) for a two-dimensional Ising model with $N = 4$ and $N = 9$.

Problem 5.42. Use the Metropolis algorithm to simulate the two-dimensional Ising model.

Suggestions for Further Reading

Stephen G. Brush, “History of the Lenz-Ising Model,” *Rev. Mod. Phys.* **39**, 883–893 (1967).

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Chapter 6

Noninteracting Particle Systems

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The goal of this chapter is to apply the general formalism of statistical mechanics to classical and quantum systems of noninteracting particles.

6.1 Introduction

Noninteracting systems are important for several reasons. For example, the interaction 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 thermal energy 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 Classical Ideal Gas

Consider an ideal gas of N identical particles of mass m confined within a cube of volume $V = L^3$.¹ If the gas is in thermal equilibrium with a heat bath at temperature T , it is natural to treat the ideal gas in the 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.

On the other hand, 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

¹An 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.

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 $\rho^{-1/3}$, the mean distance between particles (in three dimensions). Because we are interested in the thermodynamic limit for which $L \gg \lambda$, the semiclassical limit requires that

$$\lambda \ll \rho^{-1/3} \text{ or } \rho\lambda^3 \ll 1. \quad (\text{semiclassical limit}) \quad (6.1)$$

Problem 6.1. Mean distance between particles

- (a) Consider a system of N particles confined to a line of length L . What is the mean distance between the particles?
- (b) Consider a similar system of N particles confined to a square of linear dimension L . What is the mean distance between the particles?

To estimate the magnitude of λ , we need to know the typical value of the momentum of a particle. If the kinematics of the particles can be treated nonrelativistically, we know from (4.64) that $\overline{p^2}/2m = 3kT/2$. (We will rederive this result in Section 6.3.) Hence, we have $\overline{p^2} \sim mkT$ and $\lambda \sim h/\sqrt{mkT}$. We will find it is convenient to define the *thermal de Broglie wavelength* λ as

$$\lambda = \frac{h}{(2\pi mkT)^{1/2}} = \left(\frac{h^2}{2\pi mkT} \right)^{1/2} = \left(\frac{2\pi\hbar^2}{mkT} \right)^{1/2}. \quad (\text{thermal de Broglie wavelength}) \quad (6.2)$$

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 we now calculate Z_1 , the partition function for one particle, in the semiclassical limit. As we found in (4.41), the energy eigenvalues of a particle in a cube of side L are given by

$$\epsilon_n = \frac{h^2}{8mL^2}(n_x^2 + n_y^2 + n_z^2), \quad (6.3)$$

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

$$Z_1 = \sum_n e^{-\beta\epsilon_n} = \sum_{n_x=1}^{\infty} \sum_{n_y=1}^{\infty} \sum_{n_z=1}^{\infty} e^{-\beta h^2(n_x^2 + n_y^2 + n_z^2)/8mL^2}. \quad (6.4)$$

Because the sum over each quantum number is independent of the other two quantum numbers, we can rewrite (6.4) as

$$Z_1 = \left(\sum_{n_x=1}^{\infty} e^{-\alpha n_x^2} \right) \left(\sum_{n_y=1}^{\infty} e^{-\alpha n_y^2} \right) \left(\sum_{n_z=1}^{\infty} e^{-\alpha n_z^2} \right) \quad (6.5a)$$

$$= Z_x Z_y Z_z = Z_x^3, \quad (6.5b)$$

where

$$\alpha = \frac{\beta h^2}{8mL^2}, \quad (6.6)$$

and

$$Z_x = \sum_{n_x=1}^{\infty} e^{-\alpha n_x^2}. \quad (6.7)$$

The functions Z_y and Z_z have the same form as Z_x . Of course, we could have guessed beforehand that Z_1 in (6.5b) would factor into three terms. Why? Note that the magnitude of α in (6.7) is the order of $\lambda^2/L^2 \ll 1$.

We found in Problem 4.18 that the quantum numbers are order 10^{10} for a macroscopic system at room temperature. Thus we can convert the sum in (6.7) to an integral:

$$Z_x = \sum_{n_x=1}^{\infty} e^{-\alpha n_x^2} = \sum_{n_x=0}^{\infty} e^{-\alpha n_x^2} - 1 \rightarrow \int_0^{\infty} e^{-\alpha n_x^2} dn_x - 1. \quad (6.8)$$

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 make a change of variables and write $x^2 = \alpha n_x^2$. The Gaussian integral can be easily evaluated (see Appendix A), and we have that

$$Z_x = L \left(\frac{2^3 m}{\beta h^2} \right)^{1/2} \int_0^{\infty} e^{-x^2} dx - 1 = L \left(\frac{2\pi m}{\beta h^2} \right)^{1/2} - 1. \quad (6.9)$$

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

$$Z_1 = Z_x Z_y Z_z = V \left(\frac{2\pi m}{\beta h^2} \right)^{3/2}. \quad (6.10)$$

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

$$Z_1 = \frac{V}{\lambda^3}. \quad (6.11)$$

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

$$\ln Z_1 = \ln V - \frac{3}{2} \ln \beta + \frac{3}{2} \ln \frac{2\pi m}{h^2}. \quad (6.12)$$

Hence the mean pressure is given by

$$p_1 = \frac{1}{\beta} \frac{\partial \ln Z_1}{\partial V} \Big|_{T,N} = \frac{1}{\beta V} = \frac{kT}{V}, \quad (6.13)$$

and the mean energy is

$$e_1 = -\left.\frac{\partial \ln Z_1}{\partial \beta}\right|_{V,N} = \frac{3}{2\beta} = \frac{3}{2}kT. \quad (6.14)$$

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 gas² the equations of state

$$PV = NkT, \quad (6.15)$$

and

$$E = \frac{3}{2}NkT. \quad (6.16)$$

The heat capacity at constant volume of an ideal gas of N particles is

$$C_V = \left.\frac{\partial E}{\partial T}\right|_V = \frac{3}{2}Nk. \quad (6.17)$$

We have derived the mechanical and thermal equations of state for a classical ideal 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

$$Z_1 = \int \frac{dp dx}{h} e^{-\beta p^2/2m}. \quad (\text{one dimension}) \quad (6.18)$$

Remember that the integral over p in (6.18) extends from $-\infty$ to $+\infty$.

The entropy of a classical ideal gas of N particles. Although it is straightforward to calculate the mean energy and pressure of an ideal classical gas, 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: $E_s = \epsilon_1 + \epsilon_2 + \epsilon_3$, where ϵ_i is the energy of the i th particle. We write the partition function Z_3 as

$$Z_3 = \sum_{\text{all states}} e^{-\beta(\epsilon_1 + \epsilon_2 + \epsilon_3)}. \quad (6.19)$$

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

²If this section had a musical theme, the theme music for this section would be found at www.classicalgas.com/.

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

$$Z_3 = Z_1^3. \quad (\text{distinguishable particles}) \quad (6.20)$$

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

$$Z_1 = e^{-\beta\epsilon_1} + e^{-\beta\epsilon_2} + e^{-\beta\epsilon_3}. \quad (6.21)$$

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

$$\begin{aligned} Z_3 = & e^{-3\beta\epsilon_1} + e^{-3\beta\epsilon_2} + e^{-3\beta\epsilon_3} \\ & + 3[e^{-\beta(2\epsilon_1+\epsilon_2)} + e^{-\beta(\epsilon_1+2\epsilon_2)} + e^{-\beta(2\epsilon_1+\epsilon_3)} \\ & + e^{-\beta(2\epsilon_2+\epsilon_3)} + e^{-\beta(\epsilon_1+2\epsilon_3)} + e^{-\beta(\epsilon_2+2\epsilon_3)}] \\ & + 6e^{-\beta(\epsilon_1+\epsilon_2+\epsilon_3)}. \end{aligned} \quad (\text{three distinguishable particles}) \quad (6.22)$$

It is easy to see that Z_3 in (6.22) can be factored and expressed as

$$Z_3 = Z_1^3. \quad (6.23)$$

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 4.18). (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 simply given by

$$Z_3 = e^{-\beta(E_1+E_2+E_3)}. \quad (\text{indistinguishable, multiple occupancy ignored}) \quad (6.24)$$

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 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

$$Z_3 = \frac{Z_1^3}{3!}. \quad (\text{correction for overcounting}) \quad (6.25)$$

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

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 different states 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 .

that single particle states with multiple occupancy can be ignored, we can express Z_N , the partition function of N identical particles, as

$$Z_N = \frac{Z_1^N}{N!}. \quad (\text{semiclassical limit}) \quad (6.26)$$

If we substitute for Z_1 from (6.10), we obtain

$$Z_N = \frac{V^N}{N!} \left(\frac{2\pi mkT}{h^2} \right)^{3N/2}. \quad (6.27)$$

If we take the logarithm of both sides of (6.27) and use Stirling's approximation (3.89), we can write the free energy of a noninteracting classical gas as

$$F = -kT \ln Z_N = -kTN \left[\ln \frac{V}{N} + \frac{3}{2} \ln \left(\frac{2\pi mkT}{h^2} \right) + 1 \right]. \quad (6.28)$$

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 introducing the factor of $N!$ and assuming that the particles are distinguishable. That is, in the grand canonical ensemble we will be able to automatically satisfy the condition that the particles are indistinguishable.

Problem 6.4. 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

$$S(T, V, N) = Nk \left[\ln \frac{V}{N} + \frac{3}{2} \ln \left(\frac{2\pi mkT}{h^2} \right) + \frac{5}{2} \right]. \quad (6.29)$$

The form of S in (6.29) is known as the *Sackur-Tetrode equation* (see Problem 4.24). 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

$$S(E, V, N) = Nk \left[\ln \frac{V}{N} + \frac{3}{2} \ln \left(\frac{4\pi mE}{3Nh^2} \right) + \frac{5}{2} \right], \quad (6.30)$$

in agreement with the result (4.62) 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. Order of magnitude estimates

Calculate the entropy 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. 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

$$\mu = -kT \ln \left[\frac{V}{N} \left(\frac{2\pi mkT}{h^2} \right)^{3/2} \right]. \quad (6.31)$$

We will see in Problem 6.49 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?

Problem 6.8. 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

$$S = Nk \left[\ln V + \frac{3}{2} \ln \left(\frac{2\pi mkT}{h^2} \right) + \frac{3}{2} \right]. \quad (6.32)$$

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 (4.104))

$$dS/k = d(\ln Z + \beta E). \quad (6.33)$$

It is straightforward to integrate (6.33) and obtain

$$S = k(\ln Z + \beta E) + g(N), \quad (6.34)$$

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. Consider two identical ideal gases at the same temperature T in separate boxes each with the same density. What is the change in entropy of the combined system after the gases are allowed to mix? We can answer this question without doing any calculations. Because the particles in each gas are identical, there would be no change in the total entropy. Why? What if the gases were not identical? In this case, there would be a change in entropy because removing the partition between the two boxes is an irreversible process. (Reinserting the partition would not separate the two gases.) In the following we calculate the change in both cases.

Consider two ideal gases at the same temperature T with N_1 and N_2 particles in boxes of volume V_1 and V_2 , respectively. The gases are initially separated by a partition. If we use (6.29) for the entropy, we find

$$S_1 = N_1 k \left[\ln \frac{V_1}{N_1} + f(T) \right], \quad (6.35a)$$

$$S_2 = N_2 k \left[\ln \frac{V_2}{N_2} + f(T) \right], \quad (6.35b)$$

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 $V = V_1 + V_2$. If the particles are identical, the total entropy after the removal of the partition is given by

$$S = k(N_1 + N_2) \left[\ln \frac{V_1 + V_2}{N_1 + N_2} + f(T) \right], \quad (6.36)$$

and the change in the value of S , the *entropy of mixing*, is given by

$$\Delta S = k \left[(N_1 + N_2) \ln \frac{V_1 + V_2}{N_1 + N_2} - N_1 \ln \frac{V_1}{N_1} - N_2 \ln \frac{V_2}{N_2} \right]. \quad (\text{identical gases}) \quad (6.37)$$

Problem 6.9. For the special case of equal densities of the two gases before separation, use (6.37) to show that $\Delta S = 0$ as expected. (Use the fact that $N_1 = \rho V_1$ and $N_2 = \rho V_2$.) Why is the entropy of mixing nonzero for $N_1 \neq N_2$ and/or $V_1 \neq V_2$ even though the particles are identical?

If the two gases are not identical, the total entropy after mixing is

$$S = k \left[N_1 \ln \frac{V_1 + V_2}{N_1} + N_2 \ln \frac{V_1 + V_2}{N_2} + (N_1 + N_2) f(T) \right]. \quad (6.38)$$

Then the entropy of mixing becomes

$$\Delta S = k \left[N_1 \ln \frac{V_1 + V_2}{N_1} + N_2 \ln \frac{V_1 + V_2}{N_2} - N_1 \ln \frac{V_1}{N_1} - N_2 \ln \frac{V_2}{N_2} \right]. \quad (\text{non-identical gases}) \quad (6.39)$$

For the special case of $N_1 = N_2 = N$ and $V_1 = V_2 = V$, we find

$$\Delta S = 2Nk \ln 2. \quad (6.40)$$

Explain the result (6.40) in simple terms.

Problem 6.10. 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 $N_1 = N_2 = N$ and $V_1 = V_2 = V$.

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.

To derive the equipartition theorem, we consider the canonical ensemble and express the average of any physical quantity $f(\mathbf{r}, \mathbf{p})$ in a classical system by

$$\bar{f} = \frac{\int f(\mathbf{r}_1, \dots, \mathbf{r}_N, \mathbf{p}_1, \dots, \mathbf{p}_N) e^{-\beta E(\mathbf{r}_1, \dots, \mathbf{r}_N, \mathbf{p}_1, \dots, \mathbf{p}_N)} d\mathbf{r}_1 \dots d\mathbf{r}_N d\mathbf{p}_1 \dots d\mathbf{p}_N}{\int e^{-\beta E(\mathbf{r}_1, \dots, \mathbf{r}_N, \mathbf{p}_1, \dots, \mathbf{p}_N)} d\mathbf{r}_1 \dots d\mathbf{r}_N d\mathbf{p}_1 \dots d\mathbf{p}_N}, \quad (6.41)$$

where we have used the fact that the probability density of a particular microstate is proportional to $e^{-\beta E(\mathbf{r}_1, \dots, \mathbf{r}_N, \mathbf{p}_1, \dots, \mathbf{p}_N)}$. Remember that a microstate is defined by the positions and momenta of every particle. Classically, the sum over quantum states has been replaced by an integration over phase space.

Suppose that the total energy can be written as a sum of quadratic terms. The most common case is the kinetic energy in the nonrelativistic limit. For example, the kinetic energy of one particle

in three dimensions 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 for simplicity, and suppose that the energy of the system can be written as

$$E = \epsilon_1(p_1) + \tilde{E}(x_1, \dots, x_N, p_2, \dots, p_N), \quad (6.42)$$

where $\epsilon_1 = ap_1^2$. We have separated out the quadratic dependence of the energy of particle 1 on its momentum. We use (6.41) and express the mean value of ϵ_1 in one dimension as

$$\overline{\epsilon_1} = \frac{\int_{-\infty}^{\infty} \epsilon_1 e^{-\beta E(x_1, \dots, x_N, p_1, \dots, p_N)} dx_1 \dots dx_N dp_1 \dots dp_N}{\int_{-\infty}^{\infty} e^{-\beta E(x_1, \dots, x_N, p_1, \dots, p_N)} dx_1 \dots dx_N dp_1 \dots dp_N} \quad (6.43a)$$

$$= \frac{\int_{-\infty}^{\infty} \epsilon_1 e^{-\beta[\epsilon_1 + \tilde{E}(x_1, \dots, x_N, p_2, \dots, p_N)]} dx_1 \dots dx_N dp_1 \dots dp_N}{\int_{-\infty}^{\infty} e^{-\beta[\epsilon_1 + \tilde{E}(x_1, \dots, x_N, p_2, \dots, p_N)]} dx_1 \dots dx_N dp_1 \dots dp_N} \quad (6.43b)$$

$$= \frac{\int_{-\infty}^{\infty} \epsilon_1 e^{-\beta \epsilon_1} dp_1 \int e^{-\beta \tilde{E}} dx_1 \dots dx_N dp_2 \dots dp_N}{\int_{-\infty}^{\infty} e^{-\beta \epsilon_1} dp_1 \int e^{-\beta \tilde{E}} dx_1 \dots dx_N dp_2 \dots dp_N}. \quad (6.43c)$$

The integrals over all the coordinates except p_1 cancel, and we have

$$\overline{\epsilon_1} = \frac{\int_{-\infty}^{\infty} \epsilon_1 e^{-\beta \epsilon_1} dp_1}{\int_{-\infty}^{\infty} e^{-\beta \epsilon_1} dp_1}. \quad (6.44)$$

Note that we could have written $\overline{\epsilon_1}$ in the form (6.44) 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 all the other coordinates. As we have done in other contexts, we can write $\overline{\epsilon_1}$ as

$$\overline{\epsilon_1} = -\frac{\partial}{\partial \beta} \ln \left(\int_{-\infty}^{\infty} e^{-\beta \epsilon_1} dp_1 \right). \quad (6.45)$$

If we substitute $\epsilon_1 = ap_1^2$, the integral in (6.45) becomes

$$Z = \int_{-\infty}^{\infty} e^{-\beta \epsilon_1} dp_1 = \int_{-\infty}^{\infty} e^{-\beta ap_1^2} dp_1 \quad (6.46a)$$

$$= (\beta a)^{-1/2} \int_{-\infty}^{\infty} e^{-x^2} dx, \quad (6.46b)$$

where we have let $x^2 = \beta ap_1^2$. Note that the integral in (6.46b) is independent of β . Hence

$$\overline{\epsilon_1} = -\frac{\partial}{\partial \beta} \ln Z(\beta) = \frac{1}{2}kT. \quad (6.47)$$

Equation (6.47) is an example of the equipartition theorem of classical statistical mechanics.

Problem 6.11. Explain why we could have written (6.44) directly. What is the physical interpretation of the integrand in the numerator?

The equipartition theorem is not a theorem and is not a new result. It 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 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 terms in 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

$$C_V = 3Nk. \quad (\text{law of Dulong and Petit}) \quad (6.48)$$

The result (6.48) is known as the law of Dulong and Petit. This result was first discovered empirically, is not a law, 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 6.12.

The result (6.47) implies that the heat capacity of a monatomic classical ideal 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 6.51.

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 prefer to give the specific heat as the heat capacity per mole and experimental physicists frequently prefer to 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 $K(\mathbf{p}_1, \dots, \mathbf{p}_N)$ and the potential energy $U(\mathbf{r}_1, \dots, \mathbf{r}_N)$. The kinetic energy is a quadratic function of the momenta $\mathbf{p}_1, \dots, \mathbf{p}_N$ (or velocities), and the potential energy is a function of the positions $\mathbf{r}_1, \dots, \mathbf{r}_N$ of the particles. We write the total energy as $E = K + U$. The probability density of a configuration of N particles defined by $\mathbf{r}_1, \dots, \mathbf{r}_N, \mathbf{p}_1, \dots, \mathbf{p}_N$ is given in the canonical ensemble by

$$p(\mathbf{r}_1, \dots, \mathbf{r}_N; \mathbf{p}_1, \dots, \mathbf{p}_N) = A e^{-[K(\mathbf{p}_1, \mathbf{p}_2, \dots, \mathbf{p}_N) + U(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)]/kT} \quad (6.49a)$$

$$= A e^{-K(\mathbf{p}_1, \mathbf{p}_2, \dots, \mathbf{p}_N)/kT} e^{-U(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)/kT}, \quad (6.49b)$$

where A is a normalization constant. Note that 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. For example, 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

$$f(\mathbf{r}_1, \dots, \mathbf{r}_N) d\mathbf{r}_1 \dots d\mathbf{r}_N = B e^{-U(\mathbf{r}_1, \dots, \mathbf{r}_N)/kT} d\mathbf{r}_1 \dots d\mathbf{r}_N, \quad (6.50)$$

and the probability of the momenta is given by

$$f(\mathbf{p}_1, \dots, \mathbf{p}_N) d\mathbf{p}_1 \dots d\mathbf{p}_N = C e^{-K(\mathbf{p}_1, \dots, \mathbf{p}_N)/kT} d\mathbf{p}_1 \dots d\mathbf{p}_N. \quad (6.51)$$

For simplicity, we have denoted the two probability densities by f , even though their functional form is different in (6.50) and (6.51). The constants B and C in (6.51) and (6.50) 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 at first 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 are not true for quantum systems, because in this case the position and momentum operators do not commute. That is, $e^{-\beta(K+U)} \neq e^{-\beta K} e^{-\beta U}$ for quantum systems.

Because the total kinetic energy is a sum of the kinetic energy of each of the particles, the probability density $f(\mathbf{p}_1, \dots, \mathbf{p}_N)$ 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

$$f(p_x, p_y, p_z) dp_x dp_y dp_z = c e^{-(p_x^2 + p_y^2 + p_z^2)/2mkT} dp_x dp_y dp_z. \quad (6.52)$$

The constant c is given by the normalization condition

$$c \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} e^{-(p_x^2 + p_y^2 + p_z^2)/2mkT} dp_x dp_y dp_z = c \left[\int_{-\infty}^{\infty} e^{-p^2/2mkT} dp \right]^3 = 1. \quad (6.53)$$

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

$$f(p_x, p_y, p_z) dp_x dp_y dp_z = \frac{1}{(2\pi mkT)^{3/2}} e^{-(p_x^2 + p_y^2 + p_z^2)/2mkT} dp_x dp_y dp_z. \quad (6.54)$$

The corresponding velocity probability distribution is given by

$$f(v_x, v_y, v_z) dv_x dv_y dv_z = \left(\frac{m}{2\pi kT}\right)^{3/2} e^{-m(v_x^2 + v_y^2 + v_z^2)/2kT} dv_x dv_y dv_z. \quad (6.55)$$

Equation (6.55) is called the *Maxwell velocity distribution*. Note that it is a Gaussian. The probability distribution for the speed is derived in Problem 6.23.

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

$$f(v_x) dv_x = \left(\frac{m}{2\pi kT}\right)^{1/2} e^{-mv_x^2/2kT} dv_x. \quad (6.56)$$

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 6.12. 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 6.13. 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

$$f(v_x^2 + v_y^2 + v_z^2) = f(v_x^2)f(v_y^2)f(v_z^2). \quad (6.57)$$

(b) Show that the only mathematical function that satisfies the condition (6.57) is the exponential function

$$f(v^2) = c e^{-\alpha v^2}, \quad (6.58)$$

where c and α are independent of \mathbf{v} .

(c) Determine c in terms of α using the normalization condition $1 = \int_{-\infty}^{\infty} f(v) dv$ 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 (6.55).

6.5 Occupation Numbers and Bose and Fermi Statistics

We now develop the formalism 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

$$E_s = \sum_k n_k \epsilon_k. \quad (6.59)$$

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

$$Z(V, T, N) = \sum_{\{n_k\}} e^{-\beta \sum_k n_k \epsilon_k}, \quad (6.60)$$

where the occupation numbers n_k satisfy the condition

$$N = \sum_k n_k. \quad (6.61)$$

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 ${}^4\text{He}$ 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.³ For example, an atom of ${}^3\text{He}$ is composed of an odd number of particles: two electrons, two protons, and one neutron each of spin $\frac{1}{2}$. Hence, ${}^3\text{He}$ has half-integral spin making it a fermion. An atom of ${}^4\text{He}$ has one more neutron so there are an even number of fermions and ${}^4\text{He}$ 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.⁴

³You 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.

⁴In 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

$$n_k = 0 \text{ or } 1. \quad (\text{fermions}) \quad (6.62)$$

The restriction (6.62) 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:

$$n_k = 0, 1, 2, \dots \quad (\text{bosons}) \quad (6.63)$$

We will see in the following sections that the fermion or boson nature 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 with four single particle states. The spin of the fermions is neglected. Is it possible to reduce this problem to a one body problem as we did for a classical noninteracting system?

The partition function is given by

$$Z_3 = e^{-\beta(\epsilon_2+\epsilon_3+\epsilon_4)} + e^{-\beta(\epsilon_1+\epsilon_3+\epsilon_4)} + e^{-\beta(\epsilon_1+\epsilon_2+\epsilon_4)} + e^{-\beta(\epsilon_1+\epsilon_2+\epsilon_3)}. \quad (6.64)$$

Problem 6.14. Calculate \bar{n}_1 , the mean number of fermions in the state with energy ϵ_1 , for the system in Example 6.1.

Problem 6.15. 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 classical noninteracting system?

***Problem 6.16.** 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 6.17.** Calculate the mean energy and entropy in the four cases considered in Problem 6.16. Plot E and S as a function of T and compare the behavior of E and S in the limiting cases of $T \rightarrow 0$ and $T \rightarrow \infty$.

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 populated from a particle reservoir independently of the other single particle states.

Because we have not used the grand canonical ensemble until now, we briefly review its nature. The thermodynamic potential in the grand canonical ensemble is denoted by $\Omega(T, V, \mu)$ and is equal to $-PV$ (see (2.149)). 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

$$\mathcal{Z} = \sum_n e^{-\beta(E_n - \mu N_n)}. \quad (6.65)$$

In analogy to the procedure for the canonical ensemble, our 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

$$S = -\left(\frac{\partial \Omega}{\partial T}\right)_{V, \mu}, \quad (6.66)$$

and the mean number of particles from the relation

$$N = -\left(\frac{\partial \Omega}{\partial \mu}\right)_{T, V} \quad (6.67)$$

The probability of a particular microstate is given by

$$p_n = \frac{1}{\mathcal{Z}} e^{-\beta(E_n - \mu N_n)}. \quad (\text{Gibbs distribution}) \quad (6.68)$$

We will use all these relations in the following.

The first step in our application of the grand canonical ensemble is to calculate the grand partition function \mathcal{Z}_k for all particles in the k th single particle state. Because the energy of the n_k particles in the k th state is $n_k \epsilon_k$, we can write \mathcal{Z}_k as

$$\mathcal{Z}_k = \sum_{n_k} e^{-\beta n_k (\epsilon_k - \mu)}, \quad (6.69)$$

where the sum is over the possible values of n_k . For fermions this sum is straightforward because $n_k = 0$ and 1 (see (6.62)). Hence

$$\mathcal{Z}_k = 1 + e^{-\beta(\epsilon_k - \mu)}. \quad (6.70)$$

The corresponding thermodynamic or Landau potential, Ω_k , is given by

$$\Omega_k = -kT \ln \mathcal{Z}_k = -kT \ln[1 + e^{-\beta(\epsilon_k - \mu)}]. \quad (6.71)$$

We can use the relation $\bar{n}_k = -\partial\Omega_k/\partial\mu$ (see (6.67)) to find the mean number of particles in the k th quantum state. The result is

$$\bar{n}_k = -\frac{\partial\Omega_k}{\partial\mu} = \frac{e^{-\beta(\mu - \epsilon_k)}}{1 + e^{-\beta(\mu - \epsilon_k)}}, \quad (6.72)$$

or

$$\bar{n}_k = \frac{1}{e^{\beta(\epsilon_k - \mu)} + 1}. \quad (\text{Fermi-Dirac distribution}) \quad (6.73)$$

The result (6.73) for the mean number of particles in the k th state is known as the *Fermi-Dirac distribution*.

The integer values of n_k are unrestricted for bosons. We write (6.69) as

$$\mathcal{Z}_k = 1 + e^{-\beta(\epsilon_k - \mu)} + e^{-2\beta(\epsilon_k - \mu)} + \dots = \sum_{n_k=0}^{\infty} [e^{-\beta(\epsilon_k - \mu)}]^{n_k}. \quad (6.74)$$

The geometrical series in (6.74) 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

$$\mu < 0. \quad (\text{bosons}) \quad (6.75)$$

In contrast, the chemical potential may be either positive or negative for fermions. The summation of the geometrical series in (6.74) gives

$$\mathcal{Z}_k = \frac{1}{1 - e^{-\beta(\epsilon_k - \mu)}}, \quad (6.76)$$

and hence we obtain

$$\Omega_k = kT \ln [1 - e^{-\beta(\epsilon_k - \mu)}]. \quad (6.77)$$

The mean number of particles in the k th state is given by

$$\bar{n}_k = -\frac{\partial\Omega_k}{\partial\mu} = \frac{e^{-\beta(\epsilon_k - \mu)}}{1 - e^{-\beta(\epsilon_k - \mu)}} \quad (6.78)$$

or

$$\bar{n}_k = \frac{1}{e^{\beta(\epsilon_k - \mu)} - 1}. \quad (\text{Bose-Einstein distribution}) \quad (6.79)$$

The form (6.79) is known as the *Bose-Einstein distribution*.

It is frequently convenient to group the Fermi-Dirac and Bose-Einstein distributions together and to write

$$\bar{n}_k = \frac{1}{e^{\beta(\epsilon_k - \mu)} \pm 1}. \quad \begin{cases} + \text{ Fermi-Dirac distribution} \\ - \text{ Bose-Einstein distribution} \end{cases} \quad (6.80)$$

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 $\bar{n}_k \ll 1$ for all k , that is, the mean number of particles in any single particle state must be small. Hence $e^{\beta(\epsilon_k - \mu)} \gg 1$ and in this limit both the Fermi-Dirac and Bose-Einstein distributions reduce to

$$\bar{n}_k = e^{-\beta(\epsilon_k - \mu)} \quad (\text{Maxwell-Boltzmann distribution}) \quad (6.81)$$

This result (6.81) is known as the *Maxwell-Boltzmann distribution*.

6.7 Single Particle Density of States

If we sum (6.80) over all single particle states, we obtain the mean number of particles in the system:

$$\bar{N}(T, V, \mu) = \sum_k \bar{n}_k = \sum_k \frac{1}{e^{\beta(\epsilon_k - \mu)} \pm 1}. \quad (6.82)$$

For a given temperature T and volume V , (6.82) 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

$$\bar{E}(T, V, \mu) = \sum_k \epsilon_k \bar{n}_k. \quad (6.83)$$

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

$$\Omega(T, V, \mu) = \sum_k \Omega_k = \mp kT \sum_k \ln [1 \pm e^{-\beta(\epsilon_k - \mu)}]. \quad (6.84)$$

For a macroscopic system the number of particles and the energy are well defined, and we will usually replace \bar{n} and \bar{E} by N and E respectively.

Because we have described the microscopic states at the most fundamental level, that is, by using quantum mechanics, we see that the macroscopic averages of interest such as (6.82), (6.83) and (6.84) involve sums rather than integrals over the microscopic states. However, because our

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. Because it is easier to do integrals than to do sums over a very large number of states, we wish to replace the sums in (6.82)–(6.84) by integrals. For example, we wish to write for an arbitrary function $f(\epsilon)$

$$\sum_k f(\epsilon_k) \rightarrow \int_0^\infty f(\epsilon) g(\epsilon) d\epsilon, \quad (6.85)$$

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.

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 black body 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

$$\lambda = \frac{2L}{n} \quad n = 1, 2, \dots \quad (6.86)$$

where n is a nonzero positive integer. It is useful to define the *wave number* k as

$$k = \frac{2\pi}{\lambda}, \quad (6.87)$$

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

$$\mathbf{k} = (n_x, n_y, n_z) \frac{\pi}{L}, \quad (6.88)$$

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. These quantum numbers are usually very large for a macroscopic box, and hence the integers $\{n_x, n_y, n_z\}$ and k can be treated as continuous variables.

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

$$\Gamma(k) = \frac{1}{8} \frac{4\pi k^3/3}{(\pi/L)^3}. \quad (6.89)$$

If we use the relation

$$g(k) dk = \Gamma(k + dk) - \Gamma(k) = \frac{d\Gamma(k)}{dk} dk, \quad (6.90)$$

we obtain

$$g(k) dk = V \frac{k^2 dk}{2\pi^2}, \quad (6.91)$$

where the volume $V = L^3$. Equation (6.91) gives the density of states in k -space between k and $k + dk$.

Although we obtained the result (6.91) for a cube, the result is independent of the shape of the enclosure and the nature of the boundary conditions (see Problem 6.47). 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 6.18. Find the form of the density of states in k -space for standing waves in a two-dimensional and in a one-dimensional box.

6.7.1 Photons

The result (6.91) 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 . 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 form of $g(\epsilon)$ 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

$$\omega = ck. \quad (6.92)$$

The energy ϵ of a photon of frequency ω is

$$\epsilon = \hbar\omega = \hbar ck. \quad (6.93)$$

Because $k = \epsilon/\hbar c$, we find that

$$g(\epsilon) d\epsilon = V \frac{\epsilon^2}{2\pi^2 \hbar^3 c^3} d\epsilon. \quad (6.94)$$

The result (6.94) 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} .⁵ Thus the number of photon states in which the photon has a energy in the range ϵ to $\epsilon + d\epsilon$ is given by

$$g(\epsilon) d\epsilon = V \frac{\epsilon^2 d\epsilon}{\pi^2 \hbar^3 c^3}. \quad (\text{photons}) \quad (6.95)$$

⁵In 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 rather than $(2S + 1) = 3$ helicity states is a consequence of special relativity for massless particles.

6.7.2 Electrons

For a nonrelativistic particle of mass m , we know that

$$\epsilon = \frac{p^2}{2m}. \quad (6.96)$$

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

$$\epsilon = \frac{\hbar^2 k^2}{2m}, \quad (6.97)$$

and

$$d\epsilon = \frac{\hbar^2 k}{m} dk. \quad (6.98)$$

If we use the relations (6.97) and (6.98), we find that the number of states in the interval ϵ to $\epsilon + d\epsilon$ is given by

$$g(\epsilon) d\epsilon = n_s \frac{V}{4\pi^2 \hbar^3} (2m)^{3/2} \epsilon^{1/2} d\epsilon. \quad (6.99)$$

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 (6.99) as

$$g(\epsilon) d\epsilon = \frac{V}{2\pi^2 \hbar^3} (2m)^{3/2} \epsilon^{1/2} d\epsilon. \quad (\text{electrons}) \quad (6.100)$$

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 6.19. Calculate the energy density of states for a nonrelativistic particle of mass m in $d = 1$ and $d = 2$ spatial dimensions (see Problem 6.18). 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 6.20. 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 6.21. The relation between the energy and equation of state for an ideal gas

The mean energy E is given by

$$E = \int_0^\infty \epsilon \bar{n}(\epsilon) g(\epsilon) d\epsilon \quad (6.101a)$$

$$= n_s \frac{V}{4\pi^2 \hbar^3} (2m)^{3/2} \int_0^\infty \frac{\epsilon^{3/2} d\epsilon}{e^{\beta(\epsilon-\mu)} \pm 1}. \quad (6.101b)$$

Use (6.84) for the Landau potential and (6.99) for the density of states of nonrelativistic particles in three dimensions to show that Ω can be expressed as

$$\Omega = \mp kT \int_0^\infty g(\epsilon) \ln[1 \pm e^{-\beta(\epsilon-\mu)}] d\epsilon, \quad (6.102a)$$

$$= \mp kT \frac{n_s V}{4\pi^2 \hbar^3} (2m)^{3/2} \int_0^\infty \epsilon^{1/2} \ln[1 \pm e^{-\beta(\epsilon-\mu)}] d\epsilon. \quad (6.102b)$$

Integrate (6.102b) by parts with $u = \ln[1 \pm e^{-\beta(\epsilon-\mu)}]$ and $dv = \epsilon^{1/2} d\epsilon$ and show that

$$\Omega = -\frac{2}{3}n_s \frac{V}{4\pi^2\hbar^3} (2m)^{3/2} \int_0^\infty \frac{\epsilon^{3/2} d\epsilon}{e^{\beta(\epsilon-\mu)} \pm 1}. \quad (6.103)$$

The form (6.101b) for E is the same as the general result (6.103) for Ω except for the factor of $-\frac{2}{3}$. Because $\Omega = -PV$ (see (2.149)), we obtain

$$PV = \frac{2}{3}E. \quad (6.104)$$

The relation (6.104) 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 6.22. The relation between the energy and equation of state for photons

Use similar considerations as in Problem 6.21 to show that for photons:

$$PV = \frac{1}{3}E. \quad (6.105)$$

Equation (6.105) 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 $P = u(T)/3$.

The distribution of speeds in a classical system of particles can be found from (6.55). As we did previously, we need to know the number of states between v and $v + dv$. This number is simply $4\pi(v + \Delta v)^3/3 - 4\pi v^3/3 \rightarrow 4\pi v^2 \Delta v$ in the limit $\Delta v \rightarrow 0$. Hence, the probability that a particle has a speed between v and $v + dv$ is given by

$$f(v)dv = 4\pi A v^2 e^{-mv^2/2kT} dv, \quad (6.106)$$

where A is a normalization constant which we obtain in Problem 6.23.

Problem 6.23. Maxwell speed distribution

(a) Compare the form of (6.106) with (6.91).

(b) Use the fact that $\int_0^\infty f(v) dv = 1$ to calculate A and show that

$$f(v)dv = 4\pi v^2 \left(\frac{m}{2\pi kT}\right)^{3/2} e^{-mv^2/2kT} dv. \quad (\text{Maxwell speed distribution}) \quad (6.107)$$

(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.

Make the change of variables $u = v/\sqrt{(2kT/m)}$ and show that

$$f(v)dv = f(u)du = (4/\sqrt{\pi})u^2 e^{-u^2} du, \quad (6.108)$$

where again we have used same the same notation for two different, but physically related probability densities. The (dimensionless) speed probability density $f(u)$ is shown in Figure 6.1.

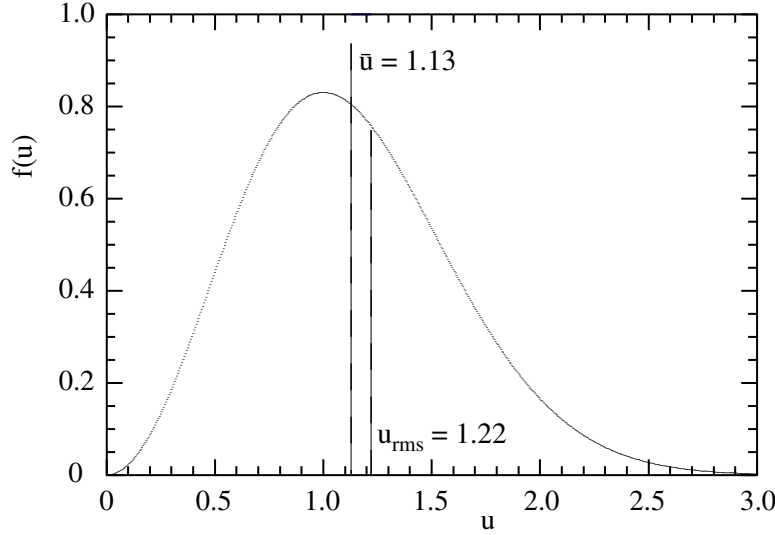


Figure 6.1: The probability density $f(u) = 4/\sqrt{\pi}u^2e^{-u^2}$ that a particle has a speed u . Note the difference between the most probable speed $\tilde{u} = 1$, the mean speed $\bar{u} \approx 1.13$, and the root-mean-square speed $u_{\text{rms}} \approx 1.22$ in units of $(2kT/m)^{1/2}$.

6.8 The Equation of State for a Noninteracting Classical Gas

We have already seen how to obtain the equation of state and other thermodynamic quantities for the classical ideal gas 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 \bar{N} . If we use the Maxwell-distribution distribution (6.81) and the density of states (6.100) for spinless particles of mass m , we obtain

$$\bar{N} = \sum_k \bar{n}_k \rightarrow \int_0^\infty \bar{n}(\epsilon) g(\epsilon) d\epsilon \quad (6.109a)$$

$$= \frac{V}{4\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} \int_0^\infty e^{-\beta(\epsilon-\mu)} \epsilon^{1/2} d\epsilon. \quad (6.109b)$$

We make the change of variables $x = \beta\epsilon$ and write (6.109b) as

$$\bar{N} = \frac{V}{4\pi^2} \left(\frac{2m}{\hbar^2\beta} \right)^{3/2} e^{\beta\mu} \int_0^\infty e^{-x} x^{1/2} dx. \quad (6.110)$$

The integral in (6.110) can be done analytically (make the change of variables $x = y^2$) and has the value $\pi^{1/2}/2$ (see Appendix A). Hence, the mean number of particles is given by

$$\bar{N}(T, V, \mu) = V \left(\frac{m}{2\pi\hbar^2\beta} \right)^{3/2} e^{\beta\mu}. \quad (6.111)$$

Because we cannot easily measure μ , we are not satisfied with knowing the function $\bar{N}(T, V, \mu)$. Instead, we can find the value of μ that yields the desired value of \bar{N} by solving (6.111) for the chemical potential:

$$\mu = kT \ln \left[\frac{\bar{N}}{V} \left(\frac{2\pi\hbar^2\beta}{m} \right)^{3/2} \right]. \quad (6.112)$$

What is the difference, if any, between (6.111) and the result (6.31) for μ found in the canonical ensemble?

Problem 6.24. Estimate the chemical potential of a monatomic ideal gas at room temperature.

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. On the other hand, because the particles do not interact, perhaps $\mu = 0$? So why is $\mu \ll 0$ for a classical ideal 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 $\bar{N}(T, V, \mu)$ leading to (6.111) 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 (6.84) 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

$$\Omega = \mp kT \sum_k \ln [1 \pm e^{-\beta(\epsilon_k - \mu)}] \quad (6.113a)$$

$$\rightarrow -kT \sum_k e^{-\beta(\epsilon_k - \mu)}. \quad (\text{semiclassical limit}) \quad (6.113b)$$

As expected, the form of Ω in (6.113b) 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

$$\Omega = -kT e^{\beta\mu} \int_0^\infty g(\epsilon) e^{-\beta\epsilon} d\epsilon \quad (6.114a)$$

$$= -kT \frac{V}{4\pi^2\hbar^3} \left(\frac{2m}{\beta} \right)^{3/2} e^{\beta\mu} \int_0^\infty x^{1/2} e^{-x} dx \quad (6.114b)$$

$$= -k \frac{V}{\beta^{5/2}} \left(\frac{m}{2\pi\hbar^2} \right)^{3/2} e^{\beta\mu}. \quad (6.114c)$$

If we substitute $\lambda = (2\pi\beta\hbar^2/m)^{1/2}$, we find

$$\Omega = -kT \frac{V}{\lambda^3} e^{\beta\mu}. \quad (6.115)$$

From the relation $\Omega = -PV$ (see (2.149)), we obtain

$$P = \frac{kT}{\lambda^3} e^{\beta\mu}. \quad (6.116)$$

If we use the thermodynamic relation (6.67), we obtain

$$\overline{N} = -\left.\frac{\partial\Omega}{\partial\mu}\right|_{V,T} = \frac{V}{\lambda^3} e^{\beta\mu}. \quad (6.117)$$

The usual classical equation of state, $PV = NkT$, is obtained by using (6.117) to eliminate μ . The simplest way of finding the energy is to use the relation (6.104).

We can find the entropy $S(T, V, \mu)$ using (6.115) and (6.66):

$$S(T, V, \mu) = -\left.\frac{\partial\Omega}{\partial T}\right|_{V,\mu} = k\beta^2 \frac{\partial\Omega}{\partial\beta} \quad (6.118a)$$

$$= Vk\beta^2 \left[\frac{5}{2\beta^{7/2}} - \frac{\mu}{\beta^{6/2}} \right] \left(\frac{m}{2\pi\hbar^2} \right)^{3/2} e^{\beta\mu}. \quad (6.118b)$$

If we eliminate μ from (6.118b), we obtain the Sackur-Tetrode expression for the entropy of an ideal gas:

$$S(T, V, N) = Nk \left[\frac{5}{2} - \ln \frac{N}{V} - \ln \left(\frac{2\pi\hbar^2}{mkT} \right)^{3/2} \right]. \quad (6.119)$$

We have written N rather than \overline{N} in (6.119). 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 6.25. Complete the missing steps and derive the ideal gas equations of state.

Problem 6.26. Show that \overline{N} can be expressed as

$$\overline{N} = \frac{V}{\lambda^3} e^{\beta\mu}, \quad (6.120)$$

and hence

$$\mu(T, V) = -kT \ln \frac{1}{\rho\lambda^3}, \quad (6.121)$$

where $\rho = \overline{N}/V$.

Problem 6.27. 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 (6.121) for μ and (6.81) for \overline{n}_k to show that the condition $\overline{n}_k \ll 1$ implies that $\lambda \ll \rho^{-1/3}$.

6.9 Black Body 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 black body. If a body in thermal equilibrium emits electromagnetic radiation, then this radiation is described as black body radiation and the object is said to be a black body. 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 (6.129)). 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.⁶ The observed cosmic microwave background spectrum fits the theoretical spectrum of a black body better than the best black body spectrum that we can make in a laboratory! In contrast, a piece of hot, glowing firewood, for example, is not really in thermal equilibrium, and the spectrum of glowing embers is only a crude approximation to black body spectrum. The existence of the cosmic microwave background spectrum and its fit to the black body 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 $E = n_1\epsilon_1 + n_2\epsilon_2 + \dots$, where n_k is the number of photons with energy ϵ_k . Because there is no

⁶The universe is filled with electromagnetic radiation with a distribution of frequencies given by (6.129) 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 black body 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.

constraint on the total number of photons, we can write the canonical partition function as

$$Z(T, V) = \sum_s e^{-\beta E_s} = \sum_{n_1, n_2, \dots=0}^{\infty} e^{-\beta(n_1 \epsilon_1 + n_2 \epsilon_2 + \dots)} \quad (6.122a)$$

$$= \sum_{n_1=0}^{\infty} e^{-\beta n_1 \epsilon_1} \sum_{n_2=0}^{\infty} e^{-\beta n_2 \epsilon_2} \dots \quad (6.122b)$$

$$= \prod_k \left[\sum_{n_k=0}^{\infty} e^{-\beta n_k \epsilon_k} \right]. \quad (6.122c)$$

The lack of a constraint means that we can do the sum over each occupation number separately. Because the term in brackets in (6.122c) is a geometrical series, we obtain

$$Z(T, V) = \prod_k \left[\frac{1}{1 - e^{-\beta \epsilon_k}} \right]. \quad (\text{photon gas}) \quad (6.123)$$

A quantity of particular interest is the mean number of photons in state k . In the canonical ensemble we have

$$\bar{n}_k = \frac{\sum_s n_k e^{-\beta E_s}}{\sum_s e^{-\beta E_s}} = \frac{\sum_{n_1, n_2, \dots} n_k e^{-\beta(n_1 \epsilon_1 + n_2 \epsilon_2 + \dots + n_k \epsilon_k + \dots)}}{Z} \quad (6.124a)$$

$$= \frac{1}{Z} \left[\frac{\partial}{\partial(-\beta \epsilon_k)} \sum_{n_1, n_2, \dots} e^{-\beta(n_1 \epsilon_1 + n_2 \epsilon_2 + \dots + n_k \epsilon_k + \dots)} \right] \quad (6.124b)$$

$$= \frac{\partial \ln Z}{\partial(-\beta \epsilon_k)}. \quad (6.124c)$$

Because the logarithm of a product of terms equals the sum of the logarithms of each term, we have from (6.123) and (6.124c)

$$\bar{n}_k = \frac{\partial}{\partial(-\beta \epsilon_k)} \left[\sum_{k'} -\ln(1 - e^{-\beta \epsilon_{k'}}) \right] \quad (6.125a)$$

$$= \frac{e^{-\beta \epsilon_k}}{1 - e^{-\beta \epsilon_k}}, \quad (6.125b)$$

or

$$\bar{n}_k = \frac{1}{e^{\beta \epsilon_k} - 1}. \quad (\text{Planck distribution}) \quad (6.125c)$$

If we compare the form of (6.125c) with the general Bose-Einstein distribution in (6.79), we see that the two expressions agree if we set $\mu = 0$. This result 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 (6.79) for noninteracting bosons, we find that the mean number of photons in state k is given by

$$\bar{n}_k = \frac{1}{e^{\beta h\nu} - 1}, \quad (6.126)$$

in agreement with (6.125c). 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. However, the chemical potential has no role to play for a system of photons in black body radiation. So we could have just started with (6.79) for \bar{n}_k in the grand canonical ensemble and set $\mu = 0$.

Planck's theory of black body radiation follows from the form of the density of states for photons found in (6.95). The number of photons with energy in the range ϵ to $\epsilon + d\epsilon$ is given by

$$N(\epsilon) d\epsilon = \bar{n}(\epsilon) g(\epsilon) d\epsilon = \frac{V}{\pi^2 \hbar^3 c^3} \frac{\epsilon^2 d\epsilon}{e^{\beta\epsilon} - 1}. \quad (6.127)$$

(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 (6.127), we find that the number of photons in the frequency range ν to $\nu + d\nu$ is given by

$$N(\nu) d\nu = \frac{8\pi V}{c^3} \frac{\nu^2 d\nu}{e^{\beta h\nu} - 1}. \quad (6.128)$$

The distribution of radiated energy is obtained by multiplying (6.128) by $h\nu$:

$$E(\nu) d\nu = h\nu N(\nu) d\nu = \frac{8\pi h V \nu^3}{c^3} \frac{d\nu}{e^{\beta h\nu} - 1}. \quad (6.129)$$

Equation (6.129) gives the energy radiated by a black body of volume V in the frequency range between ν and $\nu + d\nu$. The energy per unit volume $u(\nu)$ is given by

$$u(\nu) = \frac{8\pi h \nu^3}{c^3} \frac{1}{e^{\beta h\nu} - 1}. \quad (\text{Planck's radiation law}) \quad (6.130)$$

We can change variables to $\epsilon = h\nu$ and write the energy density as

$$u(\epsilon) = \frac{8\pi}{(hc)^3} \frac{\epsilon^3}{e^{\epsilon/kT} - 1}. \quad (6.131)$$

The temperature dependence of $u(\epsilon)$ is shown in Figure 6.2.

Problem 6.28. 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

$$(3 - x)e^x = 3, \quad (6.132)$$

where $x = \beta h\nu_{\max}$. Solve (6.132) numerically for x and show that

$$\frac{h\nu_{\max}}{kT} = 2.822. \quad (\text{Wien's displacement law}) \quad (6.133)$$

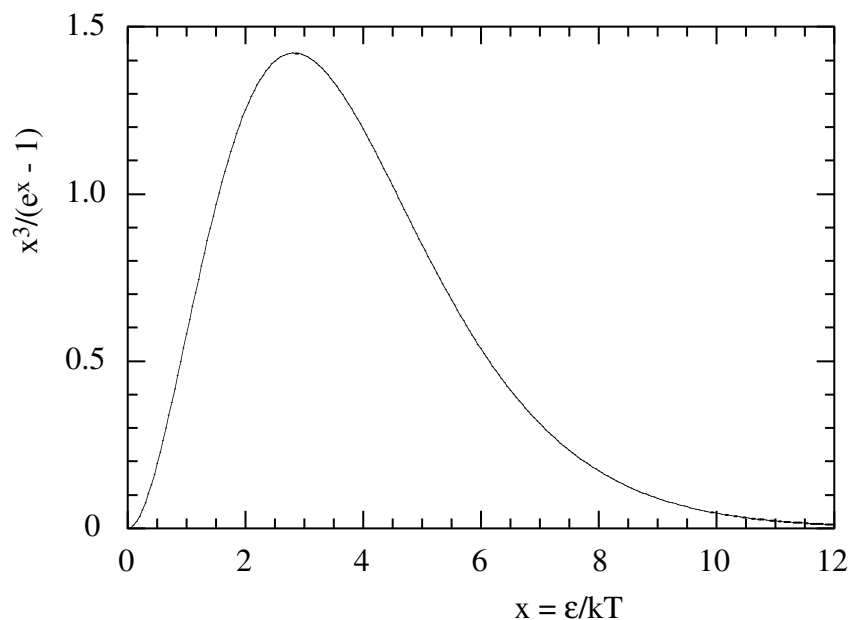


Figure 6.2: The Planck spectrum as a function of $x = \epsilon/kT$. The area under any portion of the curve multiplied by $8\pi(kT)^4/(hc)^3$ gives the energy of electromagnetic radiation within the corresponding energy or frequency range.

Problem 6.29. Derivation of the Rayleigh-Jeans and Wien's laws

- (a) Use (6.130) to find the energy emitted by a black body at a wavelength between λ and $\lambda + d\lambda$.
- (b) Determine the limiting behavior of your result for long wavelengths. This form is called the Rayleigh-Jeans law and is given by

$$u(\lambda)d\lambda = \frac{8\pi kT}{\lambda^4} d\lambda. \quad (6.134)$$

Does this form involve Planck's constant? The result in (6.134) was originally derived from purely classical considerations. 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 (6.134) would give an infinite result for the total energy that would be radiated.

- (c) Determine the limiting behavior for short wavelengths. This behavior is called Wien's law.

Problem 6.30. Thermodynamic functions of black body radiation

Use the various thermodynamic relations to show that

$$E = V \int_0^\infty u(\nu) d\nu = \frac{4\sigma}{c} VT^4. \quad (\text{Stefan-Boltzmann law}) \quad (6.135a)$$

$$F = -\frac{4\sigma}{3c} VT^4. \quad (6.135b)$$

$$S = \frac{16\sigma}{3c} VT^3. \quad (6.135c)$$

$$P = \frac{4\sigma}{3c} T^4 = \frac{1}{3} \frac{E}{V}. \quad (6.135d)$$

$$G = F + PV = 0. \quad (6.135e)$$

The free energy F in (6.135b) can be calculated from Z starting from (6.123) and using (6.95). The Stefan-Boltzmann constant σ is given by

$$\sigma = \frac{2\pi^5 k^4}{15h^3 c^2}. \quad (6.136)$$

The integral

$$\int_0^\infty \frac{x^3 dx}{e^x - 1} = \frac{\pi^4}{15}. \quad (6.137)$$

is evaluated in Appendix A.

The relation (6.135a) 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. What is the relation between E and PV ? Why is it not the same as (6.104)? Also 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?

Problem 6.31. Show that the total mean number of photons in black body radiation is given by

$$N = \frac{V}{\pi^2 c^3} \int_0^\infty \frac{\omega^2 d\omega}{e^{\hbar\omega/kT} - 1} = \frac{V(kT)^3}{\pi^2 c^3 \hbar^3} \int_0^\infty \frac{x^2 dx}{e^x - 1}. \quad (6.138)$$

The integral in (6.138) can be expressed in terms of known functions (see Appendix A). The result is

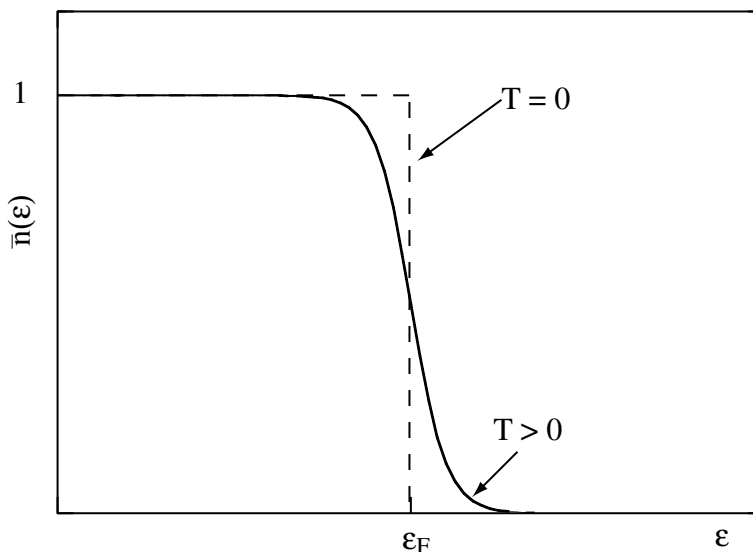
$$\int_0^\infty \frac{x^2 dx}{e^x - 1} = 2 \times 1.202. \quad (6.139)$$

Hence

$$N = 0.244V \left(\frac{kT}{\hbar c} \right)^3. \quad (6.140)$$

6.10 Noninteracting 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

Figure 6.3: The Fermi-Dirac distribution at $T = 0$ and for $T \ll T_F$.

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. 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 6.32, 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 (6.73) we see that the zero temperature limit ($\beta \rightarrow \infty$) of the Fermi-Dirac distribution is

$$\bar{n}(\epsilon) = \begin{cases} 1 & \text{for } \epsilon < \mu \\ 0 & \text{for } \epsilon > \mu. \end{cases} \quad (6.141)$$

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 6.3a.

The consequences of (6.141) 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 $\mu(T = 0) \equiv \epsilon_F$, we write

$$N = \int_0^\infty \bar{n}(\epsilon) g(\epsilon) d\epsilon \xrightarrow{T \rightarrow 0} \int_0^{\mu(T=0)} g(\epsilon) d\epsilon = V \int_0^{\epsilon_F} \frac{(2m)^{3/2}}{2\pi^2 \hbar^3} \epsilon^{1/2} d\epsilon. \quad (6.142)$$

We have substituted the electron density of states (6.100) in (6.142). The upper limit ϵ_F in (6.142) is equal to $\mu(T = 0)$ and is determined by requiring the integral to give the desired number of particles N . We find that

$$N = \frac{V}{3\pi^2} \left(\frac{2m\epsilon_F}{\hbar^2} \right)^{3/2}. \quad (6.143)$$

The energy of the highest occupied state is called the *Fermi energy* ϵ_F and the corresponding *Fermi momentum* is $p_F = \sqrt{2m\epsilon_F}$. From (6.143) we have that

$$\epsilon_F = \frac{\hbar^2}{2m} (3\pi^2 \rho)^{2/3}, \quad (6.144)$$

where the density $\rho = N/V$. It follows that the Fermi momentum is given by

$$p_F = (3\pi^2 \rho)^{1/3} \hbar. \quad (6.145)$$

At $T = 0$ all the states with momentum less than 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 . Note that the Fermi momentum can be estimated by assuming 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 box of order $\rho^{-1/3}$.

The chemical potential at $T = 0$ equals ϵ_F and is positive. On the other hand, in Section 6.8 we argued in that μ should be a negative quantity for a classical ideal 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

$$T_F = \epsilon_F/k. \quad (6.146)$$

The order of magnitude of T_F for typical metals is estimated in Problem 6.32.

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 is $3\epsilon_F/5$:

$$\frac{\bar{E}}{N} = \frac{\int_0^{\epsilon_F} \epsilon g(\epsilon) d\epsilon}{\int_0^{\epsilon_F} g(\epsilon) d\epsilon} = \frac{\int_0^{\epsilon_F} \epsilon^{3/2} d\epsilon}{\int_0^{\epsilon_F} \epsilon^{1/2} d\epsilon} \quad (6.147a)$$

$$= \frac{\frac{2}{5} \epsilon_F^{5/2}}{\frac{2}{3} \epsilon_F^{3/2}} = \frac{3}{5} \epsilon_F. \quad (6.147b)$$

The total energy is given by

$$E = \frac{3}{5}N\epsilon_F = \frac{3}{5}N(3\pi^2)^{2/3} \frac{\hbar^2}{2m} \rho^{2/3}. \quad (6.148)$$

The pressure can be immediately found from the general relation $PV = 2E/3$ (see (6.104)) for a noninteracting, nonrelativistic gas at any temperature. Alternatively, the pressure can be found either from the relation

$$P = -\frac{\partial F}{\partial V} = \frac{2}{3} \frac{E}{V}, \quad (6.149)$$

because the entropy is zero at $T = 0$, and the free energy is equal to the total energy, or from the Landau potential $\Omega = -PV$ as discussed in Problem 6.33. The result is that the pressure at $T = 0$ is given by

$$P = \frac{2}{5} \rho \epsilon_F. \quad (6.150)$$

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.

The nature of the result (6.150) can be understood simply by noting that the pressure is related to the rate of change of momentum at the walls of the system. We take $dp/dt \propto p_F/\tau$ with $\tau \propto L/(p_F/m)$. Hence, the pressure due to N particles is proportional to $Np_F^2/mV \propto \rho\epsilon_F$.

Problem 6.32. Order of magnitude estimates

- (a) Estimate the magnitude of the thermal de Broglie wavelength λ for an electron in a typical metal at room temperature. Compare your result for λ to the interparticle spacing, which you can estimate using the data in Table 6.3.
- (b) Use the same data to estimate the Fermi energy ϵ_F , the Fermi temperature T_F (see (6.146)), and the Fermi momentum p_F . Compare the values of T_F to room temperature.

Problem 6.33. The Landau potential for an ideal Fermi gas at arbitrary T can be expressed as

$$\Omega = -kT \int_0^\infty g(\epsilon) \ln[1 + e^{-\beta(\epsilon-\mu)}] d\epsilon. \quad (6.151)$$

To obtain the $T = 0$ limit of Ω , we have that $\epsilon < \mu$ in (6.151), $\beta \rightarrow \infty$, and hence $\ln[1 + e^{-\beta(\epsilon-\mu)}] \rightarrow \ln e^{-\beta(\epsilon-\mu)} = -\beta(\epsilon - \mu)$. Hence, show that

$$\Omega = \frac{(2m)^{3/2}V}{2\pi^2\hbar^2} \int_0^{\epsilon_F} d\epsilon \epsilon^{1/2} (\epsilon - \epsilon_F). \quad (6.152)$$

Calculate Ω and determine the pressure at $T = 0$.

Problem 6.34. Show that the limit (6.141) for $\bar{n}(\epsilon)$ at $T = 0$ follows only if $\mu > 0$.

element	Z	ρ ($10^{28}/\text{m}^3$)
Li ($T = 78$ K)	1	4.70
Cu	1	8.47
Fe	2	17.0

Table 6.3: Conduction electron densities for several metals at room temperature and atmospheric pressure unless otherwise noted. Data are taken from N. W. Ashcroft and N. D. Mermin, *Solid State Physics*, Holt, Rinehart and Winston (1976).

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 $\frac{3}{2}Nk$. 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 found in Problem 6.32b, 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 $T \ll T_F$. For example, we find $T_F \approx 8.2 \times 10^4$ K for copper, using $m_e = 9.1 \times 10^{-31}$ kg. 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 now 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 $C_V \sim \frac{3}{2}N_{\text{eff}}k$, 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

$$C_V \sim Nk \frac{T}{T_F}. \quad (T \ll T_F) \quad (6.153)$$

From (6.153) 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 $T < 1$ K is dominated by the contribution of the electrons and is given by $C_V/N = 0.8 \times 10^{-4} kT$.

We can understand why $\mu(T)$ remains unchanged as T is increased slightly from $T = 0$ by the

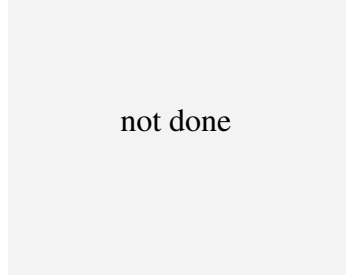


Figure 6.4: The area under the step function is approximately equal to the area under the continuous function, that is, the areas of the two cross-hatched areas are approximately equal.

following reasoning. The probability that a state is empty is

$$1 - \bar{n}(\epsilon) = 1 - \frac{1}{e^{\beta(\epsilon - \mu)} + 1} = \frac{1}{e^{\beta(\mu - \epsilon)} + 1}. \quad (6.154)$$

We see from (6.154) 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: $\bar{n}(\epsilon - \mu) = 1 - \bar{n}(\mu - \epsilon)$. This property implies that the area under the step function at $T = 0$ is nearly the same as the area under $\bar{n}(\epsilon)$ for $T \ll T_F$ (see Figure 6.4). That is, $\bar{n}(\epsilon)$ is symmetrical about $\epsilon = \mu$. If we make the additional assumption that the density of states changes very little in the region where \bar{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. We will show in the following that $\mu(T) - \mu(T = 0) \sim (T/T_F)^2$ and hence to first order in T/T_F , μ is unchanged. Note that the form of $\bar{n}(\epsilon)$ shown in Figure 6.3b is based on the assumption that $\mu(T) \approx \epsilon_F$ for $T \ll T_F$.

Problem 6.35. 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

$$N = \int_0^\infty \bar{n}(\epsilon) g(\epsilon) d\epsilon = \frac{V(2m)^{3/2}}{2\pi^2 \hbar^3} \int_0^\infty \frac{\epsilon^{1/2} d\epsilon}{e^{\beta(\epsilon - \mu)} + 1}, \quad (6.155)$$

where we have used (6.100) for $g(\epsilon)$. It is convenient to let $\epsilon = x\epsilon_F$, $\mu = \mu^*\epsilon_F$, and $T^* = kT/\epsilon_F$ and rewrite (6.155) as

$$\rho = \frac{N}{V} = \frac{(2m)^{3/2}}{2\pi^2 \hbar^3} \epsilon_F^{3/2} \int_0^\infty \frac{x^{1/2} dx}{e^{(x - \mu^*)/T^*} + 1}, \quad (6.156)$$

or

$$1 = \frac{3}{2} \int_0^\infty \frac{x^{1/2} dx}{e^{(x-\mu^*)/T^*} + 1}, \quad (6.157)$$

where we have substituted (6.144) for ϵ_F . To find the dependence of μ on T (or μ^* on T^*), use the application/applet **ComputeFermiIntegralApp** to evaluate (6.157). Start with $T^* = 0.2$ and find μ^* such that (6.157) is satisfied. Does μ^* initially increase or decrease as T is increased from zero? What is the sign of μ^* for $T^* \gg 1$? At what value of T^* is $\mu^* \approx 0$?

We now derive a quantitative expression for C_V valid for temperatures $T \ll T_F$.⁷ The increase $\Delta E = E(T) - E(0)$ in the total energy is given by

$$\Delta E = \int_0^\infty \epsilon \bar{n}(\epsilon) g(\epsilon) d\epsilon - \int_0^{\epsilon_F} \epsilon g(\epsilon) d\epsilon. \quad (6.158)$$

We multiply the identity

$$N = \int_0^\infty \bar{n}(\epsilon) g(\epsilon) d\epsilon = \int_0^{\epsilon_F} g(\epsilon) d\epsilon \quad (6.159)$$

by ϵ_F to obtain

$$\int_0^{\epsilon_F} \epsilon_F \bar{n}(\epsilon) g(\epsilon) d\epsilon + \int_{\epsilon_F}^\infty \epsilon_F \bar{n}(\epsilon) g(\epsilon) d\epsilon = \int_0^{\epsilon_F} \epsilon_F g(\epsilon) d\epsilon. \quad (6.160)$$

We can use (6.160) to rewrite as (6.158) as

$$\Delta E = \int_{\epsilon_F}^\infty (\epsilon - \epsilon_F) \bar{n}(\epsilon) g(\epsilon) d\epsilon + \int_0^{\epsilon_F} (\epsilon_F - \epsilon) [1 - \bar{n}(\epsilon)] g(\epsilon) d\epsilon. \quad (6.161)$$

The heat capacity is found by differentiating ΔE with respect to T . The only temperature-dependent term in (6.161) is $\bar{n}(\epsilon)$. Hence, we can write C_V as

$$C_V = \int_0^\infty (\epsilon - \epsilon_F) \frac{d\bar{n}(\epsilon)}{dT} g(\epsilon) d\epsilon. \quad (6.162)$$

For $kT \ll \epsilon_F$, the derivative $d\bar{n}/dT$ 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:

$$C_V = g(\epsilon_F) \int_0^\infty (\epsilon - \epsilon_F) \frac{d\bar{n}}{dT} d\epsilon. \quad (6.163)$$

We can also ignore the temperature-dependence of μ in $\bar{n}(\epsilon)$ and replace μ by ϵ_F . With this approximation we have

$$\frac{d\bar{n}}{dT} = \frac{d\bar{n}}{d\beta} \frac{d\beta}{dT} = \frac{1}{kT^2} \frac{(\epsilon - \epsilon_F) e^{\beta(\epsilon - \epsilon_F)}}{[e^{\beta(\epsilon - \mu)} + 1]^2}. \quad (6.164)$$

We next let $x = (\epsilon - \epsilon_F)/kT$ and use (6.163) and (6.164) to write C_V as

$$C_V = k^2 T g(\epsilon_F) \int_{-\beta\epsilon_F}^\infty x^2 \frac{e^x}{(e^x + 1)^2} dx. \quad (6.165)$$

⁷The following derivation is adapted from Kittel.

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

$$\int_{-\infty}^{\infty} x^2 \frac{e^x}{(e^x + 1)^2} dx = \frac{\pi^2}{3}, \quad (6.166)$$

we can write the heat capacity of an ideal Fermi gas as

$$C_V = \frac{1}{3} \pi^2 g(\epsilon_F) k^2 T. \quad (6.167)$$

It is straightforward to show that

$$g(\epsilon_F) = \frac{3N}{2\epsilon_F} = \frac{3N}{2kT_F}, \quad (6.168)$$

and we finally arrive at our desired result

$$C_V = \frac{\pi^2}{2} N k \frac{T}{T_F}. \quad (T \ll T_F) \quad (6.169)$$

A more detailed discussion of the low temperature properties of an ideal Fermi gas is given in Appendix 6A. For convenience, we summarize the main results here:

$$\Omega = -\frac{2}{3} \frac{2^{1/2} V m^{3/2}}{\pi^2 \hbar^3} \left[\frac{2}{5} \mu^{5/2} + \frac{\pi^2}{4} (kT)^2 \mu^{1/2} \right]. \quad (6.170)$$

$$\bar{N} = -\frac{\partial \Omega}{\partial \mu} = \frac{V(2m)^{3/2}}{3\pi^2 \hbar^3} \left[\mu^{3/2} + \frac{\pi^2}{8} (kT)^2 \mu^{-1/2} \right]. \quad (6.171)$$

The results (6.170) and (6.171) 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 \bar{N} fixed. To find this dependence we rewrite (6.171) as

$$\frac{3\pi^2 \hbar^3 \rho}{(2m)^{3/2}} = \mu^{3/2} \left[1 + \frac{\pi^2}{8} (kT)^2 \mu^{-2} \right], \quad (6.172)$$

where $\rho = \bar{N}/V$. If we raise both sides of (6.172) to the $2/3$ power and use (6.144), we have

$$\mu = \frac{3^{2/3} \pi^{4/3} \hbar^2 \rho^{2/3}}{2m} \left[1 + \frac{\pi^2}{8} (kT)^2 \mu^{-2} \right]^{-2/3}, \quad (6.173a)$$

$$= \epsilon_F \left[1 + \frac{\pi^2}{8} (kT)^2 \mu^{-2} \right]^{-2/3}. \quad (6.173b)$$

In the limit of $T \rightarrow 0$, $\mu = \epsilon_F$ as expected. From (6.173b) we see that the first correction for low temperatures is given by

$$\mu(T) = \epsilon_F \left[1 - \frac{2}{3} \frac{\pi^2}{8} \frac{(kT)^2}{\mu^2} \right] = \epsilon_F \left[1 - \frac{\pi^2}{12} \left(\frac{T}{T_F} \right)^2 \right], \quad (6.174)$$

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 (6.174), 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 low energy states below the Fermi energy to energy states above the Fermi energy as the temperature rises. Because the density of states increases with energy, it is necessary to decrease the chemical potential to keep the number of particles constant. In fact, as the temperature becomes larger than the Fermi temperature, the chemical potential changes sign and becomes negative.

Problem 6.36. Use (6.170) and (6.174) to show that the mean pressure for $T \ll T_F$ is given by

$$P = \frac{2}{5} \rho \epsilon_F \left[1 + \frac{5\pi^2}{12} \left(\frac{T}{T_F} \right)^2 + \dots \right]. \quad (6.175)$$

Use the general relation between E and PV to show that

$$E = \frac{3}{5} N \epsilon_F \left[1 + \frac{5\pi^2}{12} \left(\frac{T}{T_F} \right)^2 + \dots \right]. \quad (6.176)$$

Also show that the low temperature behavior of the heat capacity at constant volume is given by

$$C_V = \frac{\pi^2}{2} N k \frac{T}{T_F}. \quad (6.177)$$

For completeness, show that the low temperature behavior of the entropy is given by

$$S = \frac{\pi^2}{2} N k \frac{T}{T_F}. \quad (6.178)$$

Why is it not possible to calculate S by using the relations $\Omega = -PV$ and $S = -\partial\Omega/\partial T$, with P given by (6.175)?

We see from (6.177) that the conduction electrons of a metal contribute a linear term to the heat capacity. In Section 6.12 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 6.37. In Problem 6.32b we found that $T_F = 8.5 \times 10^4$ K for Copper. Use (6.177) 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 $1.3 m_e$, where m_e is the mass of an electron. What factors might account for the effective mass being greater than m_e ?

Problem 6.38. 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

$$\bar{N} = \frac{mA}{\pi\hbar^2} \int_0^\infty \frac{d\epsilon}{e^{\beta(\epsilon-\mu)} + 1}. \quad (6.179)$$

The integral in (6.179) can be evaluated in closed form using

$$\int \frac{dx}{1 + ae^{bx}} = \frac{1}{b} \ln \frac{e^{bx}}{1 + ae^{bx}} + \text{constant}. \quad (6.180)$$

Show that

$$\mu(T) = kT \ln [e^{\rho\pi\hbar^2/mkT} - 1], \quad (6.181)$$

where $\rho = \bar{N}/A$. 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 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 1930's 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.⁸

Although the form of the Landau potential for the ideal Bose gas and the ideal Fermi gas differs only superficially (see (6.84)), 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:

$$\epsilon_1 = \frac{\pi^2 \hbar^2}{2mL^2} (1^2 + 1^2 + 1^2) = 3 \frac{\pi^2 \hbar^2}{2mL^2}. \quad (6.182)$$

Note that ϵ_1 is a very small energy for a macroscopic system. 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 calculating $\bar{N}(T, V, \mu)$:

$$\bar{N} = \sum_k \frac{1}{e^{\beta(\epsilon_k - \mu)} - 1} \rightarrow \int_0^\infty \bar{n}(\epsilon) g(\epsilon) d\epsilon \quad (6.183)$$

$$= \frac{V}{4\pi^2 \hbar^3} (2m)^{3/2} \int_0^\infty \frac{\epsilon^{1/2} d\epsilon}{e^{\beta(\epsilon - \mu)} - 1} = \bar{g} V \int_0^\infty \frac{\epsilon^{1/2} d\epsilon}{e^{\beta(\epsilon - \mu)} - 1}. \quad (6.184)$$

For simplicity, we will assume that our gas of bosons has zero spin, the same value of the spin as the helium isotope ^4He .

⁸The 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.

To understand the nature of an ideal Bose gas at low temperatures, suppose 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 (6.185).

$$\rho = \frac{\overline{N}}{V} = \overline{g} \int_0^\infty \frac{\epsilon^{1/2} d\epsilon}{e^{\beta(\epsilon-\mu)} - 1}. \quad (6.185)$$

We study the behavior of μ as a function of the temperature in Problem 6.39.

Problem 6.39. We know that in the high temperature limit, the chemical potential μ must be given by its classical value given in (6.112). As we saw in Problem 6.24, μ is negative and large in magnitude. Let us investigate numerically how μ changes as we decrease the temperature. The application/applet `ComputeBoseIntegralApp` evaluates the integral on the right-hand side of (6.185) 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 .

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? Note that 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. 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 (6.185) with $\mu = 0$:

$$\rho = \overline{g} \int_0^\infty \frac{\epsilon^{1/2} d\epsilon}{e^{\beta\epsilon} - 1} = \overline{g}(kT_c)^{3/2} \int_0^\infty \frac{x^{1/2} dx}{e^x - 1}, \quad (6.186)$$

where T_c is the value of T at which $\mu = 0$. The definite integral in (6.186) can be written in terms of known functions (see Appendix A) and has the value:

$$\int_0^\infty \frac{x^{1/2} dx}{e^x - 1} = 2.612 \frac{\pi^{1/2}}{2} = C. \quad (6.187)$$

We have

$$kT_c = \left(\frac{\rho}{\overline{g}C} \right)^{2/3} = \left(\frac{4\pi}{C} \right)^{2/3} \frac{\hbar^2}{2ma^2}, \quad (6.188)$$

where $a = \rho^{-1/3}$ is the mean interparticle spacing. We thus obtain the temperature T_c that satisfies (6.186) for fixed density. Note that the energy $\hbar^2/2ma^2$ in (6.188) can be interpreted as the zero-point energy associated with localizing a particle of mass m in a volume a^3 .

Similarly we can find the maximum density for a given temperature:

$$\rho_c = \frac{2.612}{\lambda^3}. \quad (6.189)$$

Problem 6.40. Use `ComputeBoseIntegralApp` to find the numerical value of T at which $\mu = 0$ for $\rho^* = 1$. Confirm that your numerical value is consistent with (6.188).

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?

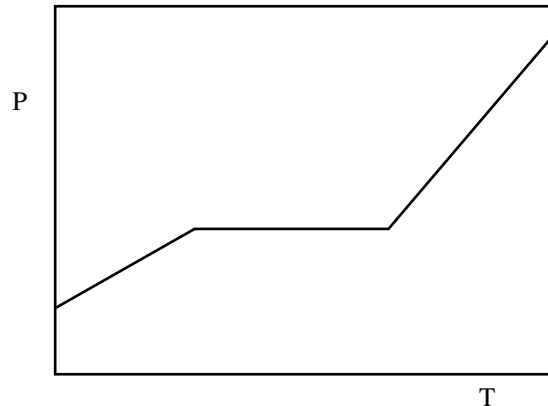


Figure 6.5: Sketch of the dependence of the pressure P on the temperature T for a typical gas and liquid.

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 measured pressure will decrease. However at some temperature, this dependence will abruptly break down, and the measured P will stop changing as indicated in Figure 6.5. We will not study this behavior of P until Chapter 9, but we 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 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 (6.184) 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 (6.99)). Because of this dependence on ϵ , $g(\epsilon = 0) = 0$, and our calculation of \bar{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 zero kinetic energy state. However, for the noninteracting Bose gas, the mean number of particles in the ground state is given by

$$\overline{N_0} = \frac{1}{e^{-\beta\mu} - 1}, \quad (6.190)$$

(Remember that we have set $\epsilon_0 = 0$.) When T is sufficiently low, N_0 will be very large. Hence, the denominator of (6.190) 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 $N_0 \gg 1$ becomes

$$N_0 = -\frac{kT}{\mu}. \quad (6.191)$$

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 (6.184) 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 $T < T_c$, N_0/N is nonzero in the limit of $N \rightarrow \infty$.

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 (6.184):

$$N_\epsilon = \frac{V}{4\pi^2\hbar^3} (2m)^{3/2} \int_0^\infty \frac{\epsilon^{1/2} d\epsilon}{e^{\beta\epsilon} - 1} = N \left(\frac{T}{T_c} \right)^{3/2}, \quad (T < T_c) \quad (6.192)$$

where T_c is defined by (6.188). All of the remaining particles, which we denote as N_0 , are in the ground state, that is, have energy $\epsilon = 0$. Another way of understanding (6.192) 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

$$N_0 = N - N_\epsilon = N \left[1 - \left(\frac{T}{T_c} \right)^{3/2} \right]. \quad (T < T_c) \quad (6.193)$$

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 $T < T_c$

$$E = \int_0^\infty \frac{\epsilon g(\epsilon) d\epsilon}{e^{\beta\epsilon} - 1} = \frac{V(mkT)^{3/2} kT}{2^{1/2}\pi^2\hbar^3} \int_0^\infty \frac{x^{3/2} dx}{e^x - 1}. \quad (6.194)$$

The definite integral in (6.194) is given in Appendix A:

$$\int_0^\infty \frac{x^{3/2} dx}{e^x - 1} = 1.341 \frac{3\pi^{1/2}}{4}. \quad (6.195)$$

If we substitute (6.195) into (6.194), we can write the energy as

$$E = 3 \frac{1.341}{2^{5/2}\pi^{3/2}} \frac{V(mkT)^{3/2} kT}{\hbar^3} = 0.1277 V \frac{m^{3/2} (kT)^{5/2}}{\hbar^3}. \quad (6.196)$$

Note that $E \propto T^{5/2}$ for $T < T_c$. The heat capacity at constant volume is

$$C_V = \frac{\partial E}{\partial T} = 3.2V \frac{(mkT)^{3/2}k}{\hbar^3}, \quad (6.197)$$

or

$$C_V = 1.9N_c k. \quad (6.198)$$

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 $PV = \frac{2}{3}E$ for a nonrelativistic ideal gas. From (6.196) we obtain

$$P = \frac{1.341}{2^{3/2}\pi^{3/2}} \frac{m^{3/2}(kT)^{5/2}}{\hbar^3} = 0.085 \frac{m^{3/2}(kT)^{5/2}}{\hbar^3}. \quad (6.199)$$

Note that the pressure is proportional to $T^{5/2}$ and is independent of the density. This behavior 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 the phase transition of an ideal Bose gas 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 $T \rightarrow T_c$ from below at fixed density.

What makes the Bose condensate particularly interesting 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 6.42. Show that the ground state contribution to the pressure is given by

$$P_0 = \frac{kT}{V} \ln(\overline{N}_0 + 1). \quad (6.200)$$

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 6.43. What is the approximate value of T_c for a noninteracting Bose gas at a density of $\rho = 0.14 \text{ gm cm}^{-3}$, the density of liquid ^4He ? Take $m = 6.65 \times 10^{-27} \text{ kg}$.

6.12 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, 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.

6.12.1 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

$$Z_1 = e^{-\beta\hbar\omega/2} \sum_{n=0}^{\infty} [e^{-\beta\hbar\omega}]^n \quad (6.201a)$$

$$= \frac{e^{-\beta\hbar\omega/2}}{1 - e^{-\beta\hbar\omega}}. \quad (6.201b)$$

(We considered this calculation in Example 4.4.) Other thermodynamic properties of one oscillator are given by

$$f = -kT \ln Z_1 = \frac{\hbar\omega}{2} + kT \ln[1 - e^{-\beta\hbar\omega}]. \quad (6.202)$$

$$s = -\frac{\partial f}{\partial T} = -k \ln[1 - e^{-\beta\hbar\omega}] + \beta\hbar\omega \frac{1}{e^{\beta\hbar\omega} - 1}. \quad (6.203)$$

$$e = f + Ts = (\bar{n} + \frac{1}{2})\hbar\omega, \quad (6.204)$$

where

$$\bar{n} = \frac{1}{e^{\beta\hbar\omega} - 1}. \quad (6.205)$$

Note the form of \bar{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

$$C_V = \left(\frac{\partial E}{\partial T}\right)_V = 3N \left(\frac{\partial e}{\partial T}\right)_V \quad (6.206)$$

$$= 3Nk(\beta\hbar\omega)^2 \frac{e^{\beta\hbar\omega}}{[e^{\beta\hbar\omega} - 1]^2}. \quad (6.207)$$

It is convenient to introduce the Einstein temperature

$$kT_E = \hbar\omega, \quad (6.208)$$

and rewrite C_V as

$$C_V = 3Nk \left(\frac{T_E}{T} \right)^2 \frac{e^{T_E/T}}{[e^{T_E/T} - 1]^2}. \quad (6.209)$$

The limiting behavior of C_V from (6.207) or (6.209) is

$$C_V \rightarrow 3Nk. \quad (T \gg T_E) \quad (6.210)$$

and

$$C_V \rightarrow 3Nk \left(\frac{\hbar\omega}{kT} \right)^2 e^{-\hbar\omega/kT}. \quad (T \ll T_E) \quad (6.211)$$

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:

$$C_V \propto T^3. \quad (6.212)$$

Problem 6.44. Explain the form of \bar{n} in (6.205). Why is the chemical potential zero in this case?

Problem 6.45. Derive the limiting behavior in (6.210) and (6.211).

6.12.2 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 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 (6.94), the density of states of the system is given by

$$g(\omega)d\omega = (2g_t + g_l)d\omega = \frac{V\omega^2 d\omega}{2\pi^2} \left(\frac{2}{c_t^3} + \frac{1}{c_l^3} \right). \quad (6.213)$$

It is convenient to define a mean speed of sound \bar{c} by the relation

$$\frac{3}{\bar{c}^3} = \frac{2}{c_t^3} + \frac{1}{c_l^3}. \quad (6.214)$$

Then the density of states can be written as

$$g(\omega) d\omega = \frac{3V\omega^2 d\omega}{2\pi^2 \bar{c}^3}. \quad (6.215)$$

The total energy is given by

$$E = \int \hbar\omega \bar{n}(\omega) g(\omega) d\omega, \quad (6.216a)$$

$$= \frac{3V\hbar}{2\pi^2\bar{c}^3} \int \frac{\omega^3 d\omega}{e^{\beta\hbar\omega} - 1}. \quad (6.216b)$$

Equation (6.216b) 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 (6.215), it follows that we can obtain a good approximation to the heat capacity by extending (6.215) 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

$$3N = \int_0^{\omega_D} g(\omega) d\omega. \quad (6.217)$$

If we substitute (6.215) into (6.217), we find that

$$\omega_D = 2\pi\bar{c} \left(\frac{3\rho}{4\pi} \right)^{1/3}. \quad (6.218)$$

It is convenient to relate the maximum frequency ω_D to a characteristic temperature, the Debye temperature T_D , by the relation

$$\hbar\omega_D = kT_D. \quad (6.219)$$

The thermal energy can now be expressed as

$$E = \frac{3V\hbar}{2\pi^2\bar{c}^3} \int_0^{kT_D/\hbar} \frac{\omega^3 d\omega}{e^{\beta\hbar\omega} - 1}, \quad (6.220a)$$

$$= 9NkT \left(\frac{T}{T_D} \right)^3 \int_0^{T_D/T} \frac{x^3 dx}{e^x - 1}. \quad (6.220b)$$

In the high temperature limit, $T_D/T \rightarrow 0$, and the important contribution to the integral in (6.220b) 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 $T_D/T \rightarrow \infty$, and the integral in (6.220b) is independent of temperature. Hence in the limit $T \rightarrow 0$, the energy is proportional to T^4 and the heat capacity is proportional to T^3 , consistent with experimental results at low temperature.

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

Appendix 6A: Low Temperature Expansion

For convenience, we repeat the formal expressions for the thermodynamic properties of a noninteracting Fermi gas at temperature T . The mean number of particles is given by

$$\bar{N} = \frac{2^{1/2} V m^{3/2}}{\pi^2 \hbar^3} \int_0^\infty \frac{\epsilon^{1/2} d\epsilon}{e^{\beta(\epsilon-\mu)} + 1}. \quad (6.221)$$

After an integration by parts, the Landau potential Ω is given by the expression (see (6.103))

$$\Omega = -\frac{2}{3} \frac{2^{1/2} V m^{3/2}}{\pi^2 \hbar^3} \int_0^\infty \frac{\epsilon^{3/2} d\epsilon}{e^{\beta(\epsilon-\mu)} + 1}. \quad (6.222)$$

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

$$I = \int_0^\infty \frac{f(\epsilon) d\epsilon}{e^{\beta(\epsilon-\mu)} + 1}, \quad (6.223)$$

where $f(\epsilon) = \epsilon^{1/2}$ and $\epsilon^{3/2}$, respectively.

The expansion procedure is based on the fact that the Fermi distribution function $\bar{n}(\epsilon)$ 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

$$I = kT \int_{-\beta\mu}^\infty \frac{f(\mu + kTx)}{e^x + 1} dx \quad (6.224)$$

$$= kT \int_{-\beta\mu}^0 \frac{f(\mu + kTx)}{e^x + 1} dx + kT \int_0^\infty \frac{f(\mu + kTx)}{e^x + 1} dx. \quad (6.225)$$

In the first integrand in (6.225) we let $x \rightarrow -x$ so that

$$I = kT \int_0^{\beta\mu} \frac{f(\mu - kTx)}{e^{-x} + 1} dx + kT \int_0^\infty \frac{f(\mu + kTx)}{e^x + 1} dx. \quad (6.226)$$

We next write $1/(e^{-x} + 1) = 1 - 1/(e^x + 1)$ in the first integrand in (6.226) and obtain

$$I = kT \int_0^{\beta\mu} f(\mu - kTx) dx - kT \int_0^{\beta\mu} \frac{f(\mu - kTx)}{e^x + 1} dx + kT \int_0^\infty \frac{f(\mu + kTx)}{e^x + 1} dx. \quad (6.227)$$

Equation (6.227) 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

$$I = \int_0^\mu f(\epsilon) d\epsilon + kT \int_0^\infty \frac{f(\mu + kTx) - f(\mu - kTx)}{e^x + 1} dx. \quad (6.228)$$

The values of x that contribute to the integrand in the second term in (6.228) 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

$$I = \int_0^\mu f(\epsilon) d\epsilon + 2(kT)^2 f'(\mu) \int_0^\infty \frac{x dx}{e^x + 1} + \frac{1}{3}(kT)^4 f'''(\mu) \int_0^\infty \frac{x^3 dx}{e^x + 1} + \dots \quad (6.229)$$

The definite integrals in (6.229) can be evaluated using analytical methods (see Appendix A). The results are

$$\int_0^\infty \frac{x dx}{e^x + 1} = \frac{\pi^2}{12} \quad (6.230)$$

$$\int_0^\infty \frac{x^3 dx}{e^x + 1} = \frac{7\pi^4}{120} \quad (6.231)$$

If we substitute (6.230) and (6.231) into (6.229), we obtain our desired result

$$I = \int_0^\mu f(\epsilon) d\epsilon + \frac{\pi^2}{6}(kT)^2 f'(\mu) + \frac{7\pi^4}{360}(kT)^4 f'''(\mu) + \dots \quad (6.232)$$

Note that although we expanded $f(\mu - kTx)$ in a power series in kTx , the expansion of I in (6.232) is not a power series expansion in $(kT)^2$. Instead (6.232) 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 (6.232). From (6.222) and (6.232) we find that in the limit of low temperatures

$$\Omega = -\frac{2}{3} \frac{2^{1/2} V m^{3/2}}{\pi^2 \hbar^3} \left[\frac{2}{5} \mu^{5/2} + \frac{\pi^2}{4} (kT)^2 \mu^{1/2} \right]. \quad (6.233)$$

$$\bar{N} = -\frac{\partial \Omega}{\partial \mu} = \frac{V(2m)^{3/2}}{3\pi^2 \hbar^3} \left[\mu^{3/2} + \frac{\pi^2}{8} (kT)^2 \mu^{-1/2} \right]. \quad (6.234)$$

Note that the expansions in (6.233) and (6.234) 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 is given by Weinstock.

Additional Problems

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Problem 6.46. We can write the total energy of a system of N particles in the form

$$E = \sum_{i=1}^N \frac{p_i^2}{2m} + \sum_{i=j+1}^N \sum_{j=1}^N u_{ij} \quad (6.235)$$

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

$$Z_N = \frac{1}{N! h^{3N}} \int d^{3N} \mathbf{p} d^{3N} \mathbf{r} e^{-\beta \sum_i p_i^2 / 2m} e^{-\beta \sum_{i < j} u_{ij}}. \quad (6.236)$$

***Problem 6.47.** Assume periodic boundary conditions so that the wave function ψ satisfies the condition (in one dimension)

$$\psi(x) = \psi(x + L). \quad (6.237)$$

The form of the one particle eigenfunction consistent with (6.237) is given by

$$\psi(x) \propto e^{ik_x x}. \quad (6.238)$$

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 (6.238) 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 (6.91) is obtained.

Problem 6.48. Estimate the chemical potential of one mole of helium gas at STP.

Problem 6.49. 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 6.50. 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 6.51. 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

$$\epsilon(j) = j(j+1) \frac{\hbar^2}{2I}, \quad (6.239)$$

where I is the moment of inertia and $j = 0, 1, 2, \dots$. 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 $C_{V,\text{rot}} = Nk$ 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)

$$\sum_{i=0}^{\infty} f(x) = \int_0^{\infty} f(x) dx + \frac{1}{2}f(0) - \frac{1}{12}f'(0) + \frac{1}{720}f'''(0) + \dots \quad (6.240)$$

Show that the corresponding result for $C_{V,\text{rot}}$ is

$$C_{V,\text{rot}} = Nk \left[1 + \frac{1}{45} \left(\frac{T_r}{T} \right)^2 + \dots \right]. \quad (6.241)$$

- (d) Show that the leading contribution to $C_{V,\text{rot}}$ for $T \ll T_r$ is

$$C_{V,\text{rot}} = 12Nk \left(\frac{T_r}{T} \right)^2 e^{-2T_r/T} + \dots \quad (6.242)$$

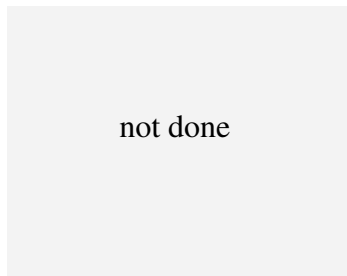


Figure 6.6: A schematic representation of a diatomic molecule.

Problem 6.52. 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

$$c_v = c_{\text{tr}} + c_{\text{rot}} + c_{\text{vib}}. \quad (6.243)$$

The last two terms in (6.243) 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 $10 \text{ K} \leq T \leq 10000 \text{ K}$.

Problem 6.53. What is the probability that a classical nonrelativistic particle has kinetic energy in the range ϵ to $\epsilon + d\epsilon$?

Problem 6.54. Consider a classical ideal 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 6.55. 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. (Think of the collision of two basketballs.) 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 (6.56)? 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 6.56.** In one of his experiments on gravitational sedimentation, Perrin observed the number of particles in water at $T = 293 \text{ K}$ and found that when the microscope was raised by

100 μm , the mean number of particles in the field of view decreased from 203 to 91. Assume that the particles have a mean volume of $9.78 \times 10^{-21} \text{ m}^3$ and a mass density of 1351 kg/m^3 . The density of water is 1000 kg/m^3 . Use this information to estimate the magnitude of Boltzmann's constant.

Problem 6.57.

- (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
- (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 $\overline{v_x v_y^2}$. Try to do a minimum of calculations.

Problem 6.58. Consider a classical one-dimensional oscillator whose energy is given by

$$\epsilon = \frac{p^2}{2m} + ax^4, \quad (6.244)$$

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 the mean kinetic energy, the mean potential energy, and the mean total energy of the oscillator.
- (b) Consider a classical one-dimensional oscillator whose energy is given by

$$\epsilon = \frac{p^2}{2m} + \frac{1}{2}kx^2 + ax^4. \quad (6.245)$$

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 6.59. 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 6.60. Show that the grand partition function \mathcal{Z} can be expressed as

$$\mathcal{Z} = \sum_{N=0}^{\infty} e^{\beta\mu N} Z_N \quad (6.246)$$

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 6.61. 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 6.62. Find general expressions for N , Ω , and E for a highly relativistic ideal gas and find a general relation between PV and E .

Problem 6.63. 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 6.38 and compare the qualitative behavior of $\mu(T)$ in one, two, and three dimensions.

Problem 6.64. Discuss the meaning of the Fermi temperature T_F . Why is it not the temperature of the Fermi gas?

Problem 6.65. High temperature limit for 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. 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 (6.103))

$$P = \frac{(2m)^{3/2}}{3\pi^2\hbar^3} \int_0^\infty \frac{\epsilon^{3/2} d\epsilon}{e^{\beta(x-\mu)} + 1}. \quad (6.247)$$

In the high temperature limit, $e^{\beta\mu} \ll 1$, and we can make the expansion

$$\frac{1}{e^{\beta(\epsilon-\mu)} + 1} = e^{\beta(\mu-\epsilon)} \frac{1}{1 + e^{-\beta(\epsilon-\mu)}} \quad (6.248a)$$

$$\approx e^{\beta(\mu-\epsilon)} [1 - e^{-\beta(\epsilon-\mu)}]. \quad (6.248b)$$

If we use (6.248b), we obtain

$$e^{\beta\mu} \int_0^\infty x^{3/2} e^{-x} (1 - e^{\beta\mu} e^{-x}) dx = \frac{3}{4} \pi^{1/2} e^{\beta\mu} [1 - \frac{1}{2^{5/2}} e^{\beta\mu}]. \quad (6.249)$$

Use (6.249) to show that P is given by

$$P = \frac{m^{3/2} (kT)^{5/2}}{2^{1/2} \pi^{3/2} \hbar^3} e^{\beta\mu} [1 - \frac{1}{2^{5/2}} e^{\beta\mu}]. \quad (6.250)$$

Find a similar expression for N . Eliminate μ and show that the leading order correction to the equation of state is given by

$$PV = NkT \left[1 + \frac{\pi^{3/2}}{4} \frac{\rho \hbar^3}{(mkT)^{3/2}} \right], \quad (6.251a)$$

$$= NkT \left[1 + \frac{1}{2^{7/2}} \rho \lambda^3 \right]. \quad (6.251b)$$

What is the condition for the correction term in (6.251b) 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 6.69)?

Mullin and Blaylock have emphasized that it is misleading to interpret the sign of the correction term in (6.251b) 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 6.66.** Numerical calculation of the chemical potential for the ideal Fermi gas

Although it is not possible to do integrals of the type (6.223) analytically for all T , we can perform these integrals numerically. From (6.227) show that we can express I in the form

$$I = \int_0^\mu f(\epsilon) d\epsilon + kT \int_0^\infty \frac{f(\mu + kTx) - f(\mu - kTx)}{e^x + 1} dx + kT \int_{\beta\mu}^\infty \frac{f(\mu - kTx)}{e^x + 1} dx. \quad (6.252)$$

To calculate \bar{N} we choose $f(\epsilon) = 2^{1/2} V m^{3/2} \epsilon^{1/2} / \pi^2 \hbar^3$ (see (6.221)). We also introduce the dimensionless variables u and t defined by the relations $\mu = u\epsilon_F$ and $T = tT_F$. As a result, show that we find the following implicit equation for u :

$$1 = u^{3/2} + \frac{3}{2}t \int_0^\infty \frac{(u+tx)^{1/2} - (u-tx)^{1/2}}{e^x + 1} dx + \frac{3}{2}t \int_{t^{-1}}^\infty \frac{(u+tx)^{1/2}}{e^x + 1} dx \quad (6.253)$$

Show that if the dimensionless “temperature” t is zero, then the dimensionless chemical potential $u = 1$. Use Simpson’s rule or a similar integration method to find u for $t = 0.1, 0.2, 0.5, 1.0, 1.2, 2$, and 4. Plot μ/ϵ_F versus T/T_F and discuss its qualitative T dependence. At approximately what temperature does $u = 0$?

Problem 6.67. 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 6.68.** Consider a system of N noninteracting fermions with single particle energies given by $\epsilon_n = n\Delta$, where $n = 1, 2, 3, \dots$. 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 6.69. High temperature limit for 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 (6.103))

$$P = \frac{2^{1/2} m^{3/2} (kT)^{5/2}}{3\pi^2 \hbar^3} \int_0^\infty \frac{x^{3/2} dx}{e^{x-\beta\mu} - 1}. \quad (6.254)$$

Follow the same procedure as in Problem 6.65 and show that

$$PV = NkT \left[1 - \frac{\pi^{3/2}}{2} \frac{\rho \hbar^3}{(mkT)^{3/2}} \right]. \quad (6.255)$$

We see that as the temperature is lowered at constant density, the pressure becomes less than its classical value. We can interpret this change due to an effective “attraction” between the particles due to the Bose statistics.

Problem 6.70. Does Bose condensation occur for a one and two-dimensional ideal Bose gas? If so, find the transition temperature. If not, explain.

Problem 6.71. Discuss why Bose condensation does not occur in a gas of photons in thermal equilibrium (black body radiation).

***Problem 6.72.** 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 6.73.** Bose-Einstein condensation in low-dimensional traps

As we found in Problem 6.70, 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

$$V(r) \sim r^n. \quad (6.256)$$

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

$$g(\epsilon) \sim L^d \epsilon^{\frac{1}{2}d-1} \sim \epsilon^{d/n} \epsilon^{\frac{1}{2}d-1} \sim \epsilon^\alpha, \quad (6.257)$$

where

$$\alpha = \frac{d}{n} + \frac{d}{2} - 1 \quad (6.258)$$

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 6.74.** Numerical evaluation of the chemical potential of an ideal Bose gas

Make the change of variables $\mu = kT u$ and $\beta\epsilon = x + u$ and show that (6.184) for $\rho = \bar{N}(T, V, \mu)/V$ can be written as

$$\rho = \frac{(2mkT)^{3/2}}{4\pi^2\hbar^3} \int_0^\infty \frac{dx (x+u)^{1/2}}{e^x - 1}. \quad (6.259)$$

Use the expression (6.188) for T_c to find the implicit equation for u :

$$2.31 = \left(\frac{T}{T_c}\right)^{3/2} \int_0^\infty \frac{dx (x+u)^{1/2}}{e^x - 1}. \quad (6.260)$$

Evaluate the integral in (6.260) numerically and find the value of u and hence μ for $T = 4T_c$, $T = 2T_c$, $T = 1.5T_c$, and $T = 1.1T_c$.

Problem 6.75. (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 (6.220b) numerically and plot the heat capacity versus T/T_D over the entire temperature range.

***Problem 6.76.** 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

$$P(N) = \frac{1}{\mathcal{Z}} e^{\beta N \mu} Z_N(V, T). \quad (6.261)$$

Use (6.261) to show that

$$\bar{N} = \sum_{N=0}^{\infty} N P(N) = \frac{z}{\mathcal{Z}} \frac{\partial \mathcal{Z}}{\partial z} = \frac{\partial \ln \mathcal{Z}}{\partial \beta \mu}, \quad (6.262)$$

where the *activity* z is defined as

$$z = e^{\beta \mu}. \quad (6.263)$$

Also show that the variance of the number of particles is given by

$$\overline{N^2} - \bar{N}^2 = kT \frac{\partial \bar{N}}{\partial \mu}. \quad (6.264)$$

***Problem 6.77.** Number fluctuations in a noninteracting classical gas

Show that the grand partition function of a noninteracting classical gas can be expressed as

$$\mathcal{Z} = \sum_{N=0}^{\infty} \frac{(z Z_1)^N}{N!} = e^{z Z_1}. \quad (6.265)$$

Show that the mean value of N is given by

$$\bar{N} = z Z_1, \quad (6.266)$$

and that the probability that there are N particles in the system is given by a Poisson distribution:

$$P_N = \frac{z^N Z_1^N}{\mathcal{Z}} = \frac{(z Z_1)^N}{N! \mathcal{Z}} = \frac{\bar{N}^N}{N!} e^{-\bar{N}}. \quad (6.267)$$

What is the variance, $\overline{(N - \bar{N})^2}$, and the N -dependence of the relative root mean square deviation, $[\langle N^2 \rangle - \bar{N}^2]^{1/2}/\bar{N}$?

***Problem 6.78.** Number fluctuations in a degenerate noninteracting Fermi gas

Use the relation

$$\overline{(N - \bar{N})^2} = kT \frac{\partial N}{\partial \mu} \quad (6.268)$$

to find the number fluctuations in the noninteracting Fermi gas for fixed T , V and μ . Show that

$$\overline{(N - \bar{N})^2} = \frac{kT}{2} \frac{V(2m)^{3/2}}{2\pi^2 \hbar^3} \int_0^\infty \frac{\epsilon^{-1/2} d\epsilon}{e^{\beta(\epsilon - \mu)} + 1}, \quad (6.269a)$$

$$\rightarrow \frac{3\bar{N}T}{2T_F}. \quad (T \ll T_F) \quad (6.269b)$$

Explain why the fluctuations in a degenerate Fermi system are much less than in the corresponding classical system.

***Problem 6.79.** 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 6.80.** 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 6.12, 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 $\kappa > 0$? The answer to this question is nontrivial and has interested physicists and mathematicians ever since. 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/>](http://jilawww.colorado.edu/bec/), [<bec.nist.gov/>](http://bec.nist.gov/), and [<cua.mit.edu/ketterle_group/>](http://cua.mit.edu/ketterle_group/).

Vanderlei Bagnato and Daniel Kleppner, “Bose-Einstein condensation in low-dimensional traps,” *Phys. Rev. A* **44**, 7439 (1991).

Ian Duck and E. C. G. Sudarshan, *Pauli and the Spin-Statistics Theorem*, World Scientific (1998). This graduate level book simplifies and clarifies the formal statements of the spin-statistics theorem, and corrects the flawed intuitive explanations that are frequently given.

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).

F. Herrmann and P. Würfel, “Light with nonzero chemical potential,” *Am. J. Phys.* **73**, 717–721 (2005). The authors discuss thermodynamic states and processes involving light in which the chemical potential of light is nonzero.

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.

W. J. Mullin and G. Blaylock, “Quantum statistics: Is there an effective fermion repulsion or boson attraction?,” *Am. J. Phys.* **71**, 1223–1231 (2003).

Jan Tobochnik, Harvey Gould, and Jonathan Machta, “Understanding temperature and chemical potential using computer simulations,” *Am. J. Phys.* **73**, 708–716 (2005).

Donald Rogers, *Einstein’s Other Theory: The Planck-Bose-Einstein of Heat Capacity*, Princeton University Press (2005).

Robert Weinstock, “Heat capacity of an ideal free electron gas: A rigorous derivation,” *Am. J. Phys.* **37**, 1273 (1969).

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Chapter 7

Thermodynamic Relations and Processes

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7.1 Introduction

All thermodynamic measurements can be expressed in terms of partial derivatives.¹ For example, the pressure P can be expressed as $P = -\partial F/\partial V$. Suppose that we make several thermodynamic measurements, for example, C_V , C_P , and K_T , the isothermal compressibility. The latter is defined as

$$K_T = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T. \quad (\text{isothermal compressibility}) \quad (7.1)$$

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

$$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T} \right)_P. \quad (\text{thermal expansion coefficient}) \quad (7.2)$$

(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, 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 reread [Appendix 2B](#) for a 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.

¹This point has been emphasized by [Styer](#).

Example 7.1. *The thermodynamics of black body radiation.* We can derive the relation $u(T) \propto T^4$ (see (6.135a)) for u , the energy per unit volume of blackbody radiation, by using thermodynamic arguments and two reasonable assumptions.

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

$$P = \frac{1}{3}u(T). \quad (7.3)$$

Equation (7.3) follows directly from Maxwell's electromagnetic theory and was obtained in Section 6.9 from first principles (see Problem 6.30).

We start from the fundamental thermodynamic relation $dE = TdS - PdV$, and write it as

$$dS = \frac{dE}{T} + \frac{P}{T}dV. \quad (7.4)$$

We let $E = Vu$, substitute $dE = Vdu + u dV$ and the relation (7.3) into (7.4), and write

$$dS = \frac{V}{T}du + \frac{u}{T}dV + \frac{1}{3}\frac{u}{T}dV = \frac{V}{T}\frac{du}{dT}dT + \frac{4}{3}\frac{u}{T}dV. \quad (7.5)$$

From (7.5) we have

$$\left(\frac{\partial S}{\partial V}\right)_T = \frac{4}{3}\frac{u}{T} \quad (7.6a)$$

$$\left(\frac{\partial S}{\partial T}\right)_V = \frac{V}{T}\frac{du}{dT}. \quad (7.6b)$$

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:

$$\frac{4}{3}\frac{\partial}{\partial T}\left(\frac{u}{T}\right) = \frac{\partial}{\partial V}\left(\frac{V}{T}\right)\frac{du}{dT}. \quad (7.7)$$

Next we assume that u depends only on T and perform the derivatives in (7.7) to find

$$\frac{4}{3}\left[\frac{1}{T}\frac{du}{dT} - \frac{u}{T^2}\right] = \frac{1}{T}\frac{du}{dT}, \quad (7.8)$$

which reduces to

$$\frac{du}{dT} = 4\frac{u}{T}. \quad (7.9)$$

If we substitute the form $u(T) = aT^n$ in (7.9), we find that this form is a solution for $n = 4$:

$$u(T) = aT^4. \quad (7.10)$$

The constant a in (7.10) cannot be determined by thermodynamic arguments.

We can obtain the entropy by using the first partial derivative in (7.6). The result is

$$S = \frac{4}{3T}Vu(T) + \text{constant}. \quad (7.11)$$

The constant of integration in (7.11) must be set equal to zero to make S proportional to V . Hence, we conclude that $S = 4aVT^3/3$. The above thermodynamic argument was first given by Boltzmann in 1884.

7.2 Maxwell Relations

Example 7.1 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 7.1 and relate the coefficient of thermal expansion to other thermodynamic derivatives.

We start with $E(S, V, N)$ and write

$$dE = TdS - PdV + \mu dN. \quad (7.12)$$

In the following we will assume that N is a constant. From (7.12) we have that

$$T = \left(\frac{\partial E}{\partial S} \right)_V. \quad (7.13)$$

and

$$P = - \left(\frac{\partial E}{\partial V} \right)_S. \quad (7.14)$$

Because the order of differentiation should be irrelevant, we obtain from (7.13) and (7.14)

$$\frac{\partial^2 E}{\partial V \partial S} = \frac{\partial^2 E}{\partial S \partial V}, \quad (7.15)$$

or

$$\left(\frac{\partial T}{\partial V} \right)_S = - \left(\frac{\partial P}{\partial S} \right)_V. \quad (7.16)$$

Equation (7.16) is our first Maxwell relation. The remaining Maxwell relations are obtained in Problem 7.1.

Problem 7.1. From the differentials of the thermodynamic potentials:

$$dF = -SdT - PdV, \quad (7.17)$$

$$dG = -SdT + VdP, \quad (7.18)$$

$$dH = TdS + VdP, \quad (7.19)$$

derive the Maxwell relations:

$$\left(\frac{\partial S}{\partial V} \right)_T = \left(\frac{\partial P}{\partial T} \right)_V, \quad (7.20)$$

$$\left(\frac{\partial S}{\partial P} \right)_T = - \left(\frac{\partial V}{\partial T} \right)_P, \quad (7.21)$$

$$\left(\frac{\partial T}{\partial P} \right)_S = \left(\frac{\partial V}{\partial S} \right)_P. \quad (7.22)$$

Also consider a variable number of particles to derive the Maxwell relations

$$\left(\frac{\partial V}{\partial N}\right)_P = \left(\frac{\partial \mu}{\partial P}\right)_N \quad (7.23)$$

and

$$\left(\frac{\partial \mu}{\partial V}\right)_N = -\left(\frac{\partial P}{\partial N}\right)_V. \quad (7.24)$$

7.3 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.

7.3.1 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 think of 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

$$\left(\frac{\partial E}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - P. \quad (7.25)$$

To show that E is a function of T only, we need to show that the right-hand side of (7.25) is zero. The term involving the entropy in (7.25) can be rewritten using the Maxwell relation (7.20):

$$\left(\frac{\partial E}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P. \quad (7.26)$$

Because $(\partial P/\partial T)_V = P/T$ for an ideal gas, we see that the right-hand side of (7.26) is zero.

Problem 7.2. Show that the enthalpy of an ideal gas is a function of T only.

7.3.2 Relation between the specific heats

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 . First recall that

$$C_V = \left(\frac{\partial E}{\partial T}\right)_V = T\left(\frac{\partial S}{\partial T}\right)_V \quad (7.27a)$$

and

$$C_P = \left(\frac{\partial H}{\partial T}\right)_P = T\left(\frac{\partial S}{\partial T}\right)_P. \quad (7.27b)$$

We consider S as a function of T and P and write

$$dS = \frac{\partial S}{\partial T}dT + \frac{\partial S}{\partial P}dP, \quad (7.28)$$

and take the partial derivative with respect to temperature at constant volume of both sides of (7.28):

$$\left(\frac{\partial S}{\partial T}\right)_V = \left(\frac{\partial S}{\partial T}\right)_P + \left(\frac{\partial S}{\partial P}\right)_T \left(\frac{\partial P}{\partial T}\right)_V. \quad (7.29)$$

We then use (7.27) to rewrite (7.29) as

$$\frac{C_V}{T} = \left(\frac{\partial S}{\partial P}\right)_T \left(\frac{\partial P}{\partial T}\right)_V + \frac{C_P}{T}. \quad (7.30)$$

Because we would like to express $C_P - C_V$ in terms of measurable quantities, we use the Maxwell relation (7.21) to eliminate $(\partial S/\partial P)$ and rewrite (7.30) as:

$$C_P - C_V = T\left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial P}{\partial T}\right)_V. \quad (7.31)$$

We next use the identity (see (2.162)),

$$\left(\frac{\partial V}{\partial T}\right)_P \left(\frac{\partial T}{\partial P}\right)_V \left(\frac{\partial P}{\partial V}\right)_T = -1, \quad (7.32)$$

to eliminate $(\partial P/\partial T)_V$ and write:

$$C_P - C_V = -T\left(\frac{\partial P}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P^2. \quad (7.33)$$

If we substitute the definitions (7.1) of the isothermal compressibility K_T and (7.2) for the thermal expansion coefficient α , we obtain the desired general relation:

$$C_P - C_V = V \frac{T}{K_T} \alpha^2. \quad (7.34)$$

Note that (7.34) is more general than the relation (2.36) which depends on only the first law.

For an ideal gas we have $K_T = 1/P$ and $\alpha = 1/T$ and (7.34) reduces to the familiar result (see (2.37))

$$C_P - C_V = Nk. \quad (7.35)$$

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 (7.34) that $C_P > C_V$ in general.

7.4 Applications to Irreversible Processes

Although the thermodynamic quantities of a system can be defined only when the system is in equilibrium, we found in Chapter 2 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.

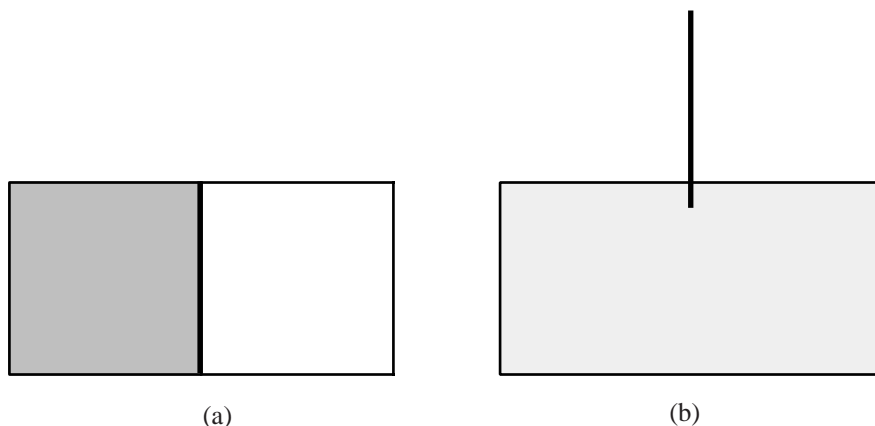


Figure 7.1: (a) A gas is kept in the left half of a box by a partition. The right half is evacuated. (b) The partition is removed and the gas expands irreversibly to fill the entire box.

7.4.1 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 7.1). The quantity of interest is the temperature change that is produced. Although this process is irreversible, it can be treated by thermodynamics as we learned in Section 2.14. Because $dQ = 0$ and $dW = 0$, the energy is a constant so that $dE(T, V) = 0$. This condition can be written as

$$dE = \frac{\partial E}{\partial T} dT + \frac{\partial E}{\partial V} dV = 0. \quad (7.36)$$

Hence, we obtain

$$\left(\frac{\partial T}{\partial V}\right)_E = -\frac{(\partial E/\partial V)_T}{(\partial E/\partial T)_V}, \quad (7.37)$$

$$= -\frac{1}{C_V} \left[T \left(\frac{\partial P}{\partial T}\right)_V - P \right]. \quad (7.38)$$

Equation (7.38) follows from the definition of C_V and from (7.26). 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 (7.38):

$$\Delta T = - \int_{V_1}^{V_2} \frac{1}{C_V} \left[T \left(\frac{\partial P}{\partial T}\right)_V - P \right] dV. \quad (7.39)$$

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 a simple modification of the ideal gas equation of state due to van der Waals (see (2.13):

$$(P + \frac{N^2}{V^2}a)(V - Nb) = NkT. \quad (\text{van der Waals equation of state}) \quad (7.40)$$

Problem 7.3. Calculate $(\partial T/\partial V)_E$ for the van der Waals equation of state (7.40) and show that a free expansion results in cooling.

The physical 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 $(\partial E/\partial V)_T$ increases. 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.

7.4.2 Joule-Thomson process

The Joule-Thomson (or Joule-Kelvin² 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 7.2). 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 work done on the gas is given by

$$W = -\int_{V_1}^0 PdV - \int_0^{V_2} PdV. \quad (7.41)$$

The pressure on each side of the porous plug is constant, and hence we obtain

$$W = P_1V_1 - P_2V_2. \quad (7.42)$$

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

$$\Delta E = E_2 - E_1 = W = P_1V_1 - P_2V_2. \quad (7.43)$$

Hence, we obtain

$$E_2 + P_2V_2 = E_1 + P_1V_1, \quad (7.44)$$

which can be written as

²William Thomson was later awarded a peerage and became Lord Kelvin.

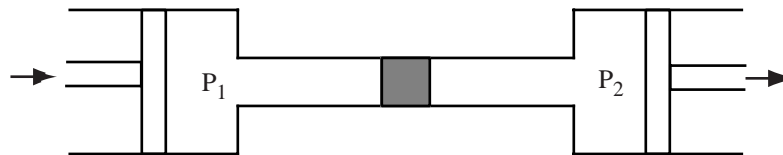


Figure 7.2: Schematic representation of the Joule-Thomson process. The two pistons ensure constant pressures on each side of the porous plug. The porous plug can be made by packing glass wool into a pipe. The process can be made continuous by using a pump to return the gas from the region of low pressure to the region of high pressure.

$$H_2 = H_1. \quad (7.45)$$

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

$$dH(T, P) = \frac{\partial H}{\partial T} dT + \frac{\partial H}{\partial P} dP = 0. \quad (7.46)$$

As before, we assume that the number of particles is a constant. From (7.46) we have

$$dT = -\frac{(\partial H / \partial P)_T}{(\partial H / \partial T)_P}. \quad (7.47)$$

From the relation, $dH = TdS + VdP$, we have $(\partial H / \partial P)_T = T(\partial S / \partial P)_T + V$. If we substitute this relation in (7.47), use the Maxwell relation (7.21), and the definition $C_P = (\partial H / \partial T)_P$, we obtain

$$\left(\frac{\partial T}{\partial P}\right)_H = \frac{V}{C_P}(T\alpha - 1), \quad (7.48)$$

where the thermal expansion coefficient α is defined by (7.2). 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 (7.48) and find

$$\Delta T = T_2 - T_1 = \int_{P_1}^{P_2} \frac{V}{C_P} (T\alpha - 1) dP. \quad (7.49)$$

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 (7.40). We write the latter in the form

$$P + a\rho^2 = \frac{\rho kT}{1 - b\rho}, \quad (7.50)$$

and take the derivative with respect to T at constant P :

$$2a\rho\left(\frac{\partial\rho}{\partial T}\right)_P = \frac{\rho k}{1-b\rho} + \left(\frac{\partial\rho}{\partial T}\right)_P \frac{kT}{(1-b\rho)^2}. \quad (7.51)$$

If we express α as

$$\alpha = -\frac{1}{\rho}\left(\frac{\partial\rho}{\partial T}\right)_P, \quad (7.52)$$

we can write (7.51) in the form:

$$\left[\frac{kT}{(1-b\rho)^2} - 2a\rho\right]\alpha = \frac{k}{(1-b\rho)}. \quad (7.53)$$

For simplicity, we consider only low densities in the following. In this limit we can write α as

$$\alpha = \frac{k(1-b\rho)}{kT - 2a\rho(1-b\rho)^2}, \quad (7.54a)$$

$$\approx \frac{1}{T}(1-b\rho)[1 + 2a\beta\rho(1-b\rho)^2], \quad (7.54b)$$

$$\approx \frac{1}{T}[1 - \rho(b - 2a\beta)]. \quad (7.54c)$$

From (7.54c) 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 (7.54) and (7.48), 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.

7.5 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.³ 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 solidifies eventually, and if heated about 373.15 K it vaporizes.⁴ 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

³All 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.

⁴If 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.

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.

7.5.1 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 ???. For example, the phases might be a solid and a liquid or a liquid and a gas. We know that as for any two bodies in thermodynamic equilibrium, the temperatures T_1 and T_2 of the two phases must be equal:

$$T_1 = T_2. \quad (7.55)$$

We also know that the pressure on the two phases must be equal,

$$P_1 = P_2, \quad (7.56)$$

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:

$$\mu_1 = \mu_2. \quad (7.57)$$

Because the temperatures and pressures are uniform, we can write (7.57) as

$$\mu_1(T, P) = \mu_2(T, P). \quad (7.58)$$

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 (7.58) as

$$g_1(T, P) = g_2(T, P). \quad (7.59)$$

We now derive the equilibrium condition (7.58) 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

$$G = N_1 g_1 + N_2 g_2. \quad (7.60)$$

Conservation of matter implies that the total number of particles remains constant:

$$N = N_1 + N_2 = \text{constant}. \quad (7.61)$$

Suppose we let N_1 vary. Because G is a minimum in equilibrium, we have

$$dG = 0 = g_1 dN_1 + g_2 dN_2 = (g_1 - g_2) dN_1, \quad (7.62)$$

with $dN_2 = -dN_1$. Hence, we find that a necessary condition for equilibrium is

$$g_1(T, P) = g_2(T, P). \quad (7.63)$$

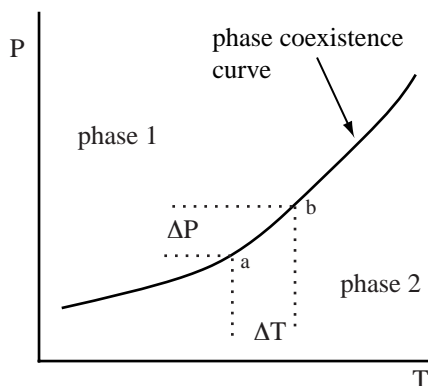


Figure 7.3: Derivation of the Clausius-Clapeyron equation.

7.5.2 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.

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 (7.59) 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 7.3). The equilibrium condition (7.59) 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

$$\Delta g_1 = \Delta g_2, \quad (7.64)$$

or using (2.139)

$$-s_1 \Delta T + v_1 \Delta P = -s_2 \Delta T + v_2 \Delta P. \quad (7.65)$$

Therefore,

$$\frac{\Delta P}{\Delta T} = \frac{s_2 - s_1}{v_2 - v_1} = \frac{\Delta s}{\Delta v}. \quad (\text{Clausius-Clapeyron equation}) \quad (7.66)$$

The relation (7.66) 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 (7.66) can be expressed as

$$\frac{dP}{dT} = \frac{\Delta S}{\Delta V}. \quad (7.67)$$

From the relation (7.25), we can write

$$T \frac{\partial S}{\partial V} = \frac{\partial E}{\partial V} + P. \quad (7.68)$$

At the phase coexistence curve for a given T and P , we can write

$$T \frac{S_2 - S_1}{V_2 - V_1} = \frac{E_2 - E_1}{V_2 - V_1} + P, \quad (7.69)$$

or

$$T(S_2 - S_1) = (E_2 - E_1) + P(V_2 - V_1). \quad (7.70)$$

Because the enthalpy $H = U + PV$, it follows that

$$L_{2 \rightarrow 1} = T(S_2 - S_1) = H_2 - H_1. \quad (7.71)$$

The energy L required to melt a given amount of a solid is called the *enthalpy of fusion*.⁵ The enthalpy of fusion is related to the difference in entropies of the liquid and the solid phase and is given by

$$L_{\text{fusion}} = H_{\text{liquid}} - H_{\text{solid}} = T(S_{\text{liquid}} - S_{\text{solid}}), \quad (7.72)$$

where T is the melting temperature at the given pressure. Similarly, the equilibrium of a vapor and liquid leads to the enthalpy of vaporization

$$\ell_{\text{vaporization}} = h_{\text{vapor}} - h_{\text{liquid}}. \quad (7.73)$$

where h is the specific enthalpy. The enthalpy of sublimation associated with the equilibrium of vapor and solid is given by

$$\ell_{\text{sublimation}} = h_{\text{vapor}} - h_{\text{solid}}. \quad (7.74)$$

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

$$\frac{dP}{dT} = \frac{L}{T\Delta V} = \frac{\ell}{T\Delta v}. \quad (7.75)$$

⁵The 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.

7.5.3 Simple phase diagrams

A typical phase diagram for a simple substance is shown in Figure 7.4a. 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 point *c* 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 directly to its vapor without passing through a liquid, a transformation known as *sublimation*. 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 7.4b).

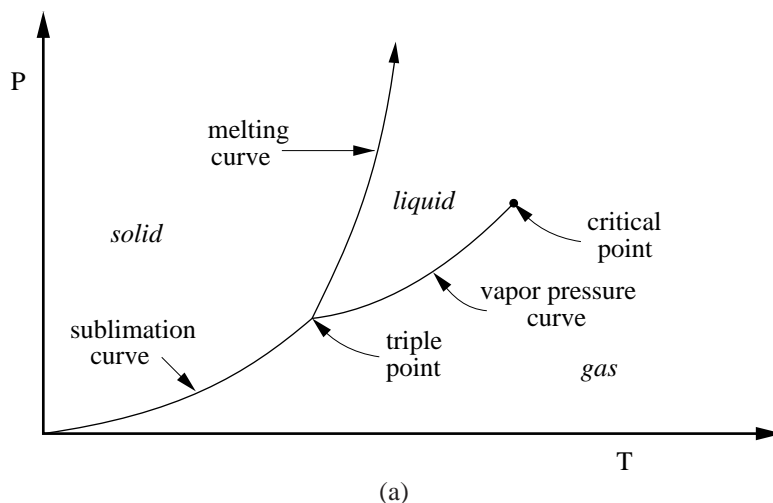


Figure 7.4: (a) Typical phase diagram of simple substances, for example, carbon dioxide. The triple point of CO_2 is at illustrates the more common forward slope of the melting point line. Notice that the triple point of carbon dioxide is well above one atmosphere. Notice also that at 1 atm carbon dioxide 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 7.2. Why is the triple-point temperature of water, $T_{\text{tp}} = 273.16\text{K}$ higher than the

ice-point temperature, $T_{\text{ice}} = 273.15 \text{ K}$, 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 (7.75), we have for liquid-solid equilibrium

$$\Delta T = \frac{T(v_{\text{solid}} - v_{\text{liquid}})}{\ell_{\text{fusion}}} \Delta P. \quad (7.76)$$

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 (7.76) from T_3 to T_{ice} and the right side from P_3 to atmospheric pressure P , we obtain

$$T_{\text{ice}} - T_3 = \frac{T(v_{\text{solid}} - v_{\text{liquid}})}{\ell_{\text{fusion}}} (P - P_3). \quad (7.77)$$

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 (7.77), we find $T_{\text{ice}} - T_3 = -0.0075 \text{ K}$. That is, the ice point temperature of pure water is 0.0075 K below the temperature of the triple point. Hence, the effect of the dissolved air is to lower the temperature by 0.0023 K at which the liquid phase is in equilibrium with pure ice at atmospheric pressure below the equilibrium temperature for pure water.

7.5.4 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

$$\ell_{\text{fusion}} = 3.35 \times 10^5 \text{ J/kg}. \quad (7.78)$$

The specific volumes in the solid and liquid phase are

$$v_{\text{solid}} = 1.09070 \times 10^{-3} \text{ m}^3/\text{kg}, \text{ and } v_{\text{liquid}} = 1.00013 \times 10^{-3} \text{ m}^3/\text{kg}, \quad (7.79)$$

so that $\Delta v = v_{\text{liquid}} - v_{\text{solid}} = -0.0906 \times 10^{-3} \text{ m}^3/\text{kg}$. If we substitute these values of ℓ and Δv in (7.75), we find

$$\frac{dP}{dT} = -\frac{3.35 \times 10^5}{273.2 \times 9.06 \times 10^{-5}} = -1.35 \times 10^7 \text{ Pa/K}. \quad (7.80)$$

From (7.80) 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} m^2 and the mass of the skater to be 100 kg. Then the pressure is given by

$$P = \frac{F}{A} = \frac{mg}{A} \approx 10^7 \text{ Pa} \approx 100 \text{ atm.} \quad (7.81)$$

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).

7.5.5 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

$$\ell_{\text{vaporization}} = 2.257 \times 10^6 \text{ J/kg.} \quad (7.82)$$

The specific volumes in the liquid and gas phase at $T = 373.15 \text{ K}$ and $P = 1 \text{ atm}$ are

$$v_{\text{liquid}} = 1.043 \times 10^{-3} \text{ m}^3/\text{kg} \text{ and } v_{\text{gas}} = 1.673 \text{ m}^3/\text{kg.} \quad (7.83)$$

Hence from (7.75) we have

$$\frac{dP}{dT} = \frac{2.257 \times 10^6}{373.15 \times 1.672} = 3.62 \times 10^3 \text{ Pa/K.} \quad (7.84)$$

7.5.6 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 (7.83) 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

$$\frac{dP}{P} = \ell \frac{dT}{RT^2}. \quad (7.85)$$

If we also assume that ℓ is approximately temperature independent, we can integrate (7.85) to find

$$\ln P(T) = -\frac{\ell}{RT} + \text{constant} \quad (7.86)$$

or

$$P(T) \approx P_0 e^{-\ell/RT}, \quad (7.87)$$

where P_0 is a constant.

Example 7.3. 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 Pa. The relation (7.86), $\ln P = -\ell/RT + \text{constant}$, 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, $\ell_{\text{fusion}} = (3.12 - 2.55) \times 10^4 = 5.74 \times 10^3 \text{ J/mol}$.

7.6 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	290
7.2	291
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Table 7.1: Listing of inline problems.

Problem 7.4. Show that the three enthalpy (differences) are not independent, but are related by

$$\ell_{\text{fusion}} + \ell_{\text{vaporization}} = \ell_{\text{sublimation}}. \quad (7.88)$$

Interpret this relation in physical terms.

Problem 7.5. Show that

$$\left(\frac{\partial C_P}{\partial P}\right)_T = -T\left(\frac{\partial^2 V}{\partial T^2}\right)_P, \quad (7.89)$$

and

$$\left(\frac{\partial C_V}{\partial V}\right)_T = T\left(\frac{\partial^2 P}{\partial T^2}\right)_V. \quad (7.90)$$

Problem 7.6. Show that

$$\frac{K_T}{K_S} = \frac{C_P}{C_V}, \quad (7.91)$$

where

$$K_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T \quad (7.92a)$$

$$K_S = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_S. \quad (7.92b)$$

K_S is the adiabatic compressibility. Use (7.92b) and (7.34) to obtain the relation

$$K_T - K_S = \frac{TV}{C_P}\alpha^2. \quad (7.93)$$

Problem 7.7. The inversion temperature for the Joule-Thomson effect is determined by the relation $(\partial T/\partial V)_P = T/V$ (see (7.48)). In Section 7.4.2 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

$$kT_{\text{inv}} = \frac{2a}{9b}(2 \pm \sqrt{1 - 3b^2P/a})^2. \quad (7.94)$$

Show that as $P \rightarrow 0$, $kT_{\text{inv}} = 2a/b$. 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 7.8. Use the result (7.84) to estimate the boiling temperature of water at the height of the highest mountain in your geographical region.

Problem 7.9. 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 7.10. 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

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.

Daniel F. Styer, “A thermodynamic derivative means an experiment,” *Am. J. Phys.* **67**, 1094–1095 (1999).

James D. White, “The role of surface melting in ice skating,” *Phys. Teacher* **30**, 495 (1992).

Chapter 8

Theories of Classical Gases and Liquids

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8.1 Introduction

Because there are few problems in statistical physics that can be solved exactly, we need to develop techniques for obtaining approximate solutions. In this chapter we introduce perturbation methods that are applicable whenever there is a small expansion parameter, for example, low density. As an introduction to the nature of many-body perturbation theory, we first consider the classical monatomic gas. The discussion in Section 8.4 involves many of the considerations and difficulties encountered in quantum field theory. For example, we will introduce diagrams that are analogous to Feynman diagrams and find divergences analogous to those found in quantum electrodynamics. We also will derive what is known as the *linked cluster expansion*, a derivation that is straightforward in comparison to its quantum counterpart.

8.2 The Free Energy of an Interacting System

Consider a gas of N identical particles of mass m at density $\rho = N/V$ and temperature T . If we make the assumption that the total potential energy U is a sum of two-body interactions $u(|\mathbf{r}_i - \mathbf{r}_j|) = u_{ij}$, we can write U as

$$U = \sum_{i < j}^N u_{ij}. \quad (8.1)$$

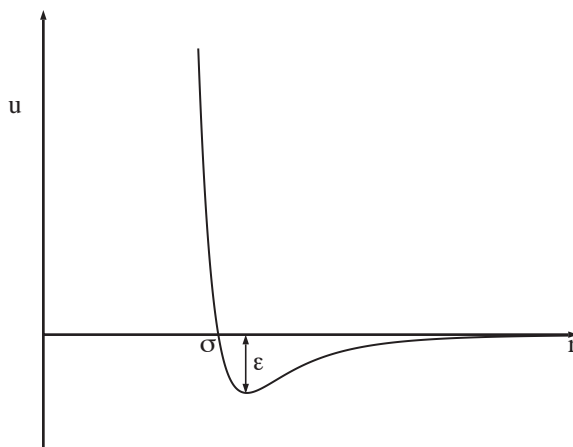


Figure 8.1: The Lennard-Jones potential $u(r)$. Note that $u(r) = 0$ for $r = \sigma$ and the depth of the well is $-\epsilon$.

The simplest interaction is the *hard sphere* interaction

$$u(r) = \begin{cases} \infty & r < \sigma \\ 0 & r > \sigma. \end{cases} \quad (8.2)$$

This interaction has no attractive part and is often used in model calculations of liquids. A more realistic interaction is the semiempirical *Lennard-Jones* potential (see Figure 8.1):¹

$$u(r) = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right]. \quad (8.3)$$

Both of the hard sphere interaction and Lennard-Jones potential are short-ranged, that is, $u(r) \approx 0$ for r greater than a separation r_0 .

The Lennard-Jones potential is the most common form of the interaction that is used to qualitatively represents the behavior of a typical intermolecular potential. The existence of many calculations and simulation results for the Lennard-Jones potential encourages us to use it even though there are more accurate forms of the interparticle potential for real fluids. The attractive $1/r^6$ contribution is well justified theoretically and is due to the induced dipole-dipole interaction of two atoms. Although each atom is electrically neutral, the instantaneous fluctuations in the charge distribution can have nonspherical symmetry. The resulting dipole in one atom can induce a dipole moment in the other atom. The cause of the repulsive interaction between atoms at small separations is much different. At small r , the electron distributions of the two atoms distort to avoid spatial overlap not allowed by the Pauli exclusion principle. The distortion of the electron distributions causes the energy of the atoms to increase thus leading to a repulsion between the atoms. However, the $1/r^{12}$ form of the repulsive potential is chosen only for convenience.

¹This form of the potential was first proposed by John Edward Lennard-Jones in 1924.

Problem 8.1. Show that the minimum of the Lennard-Jones potential is at $r_0 = 2^{1/6}\sigma$ and that $u(r_0) = -\epsilon$. At what value of r is $u(r)$ a minimum?

We assume that the condition $\lambda \ll n^{-1/3}$ is satisfied so that the system can be treated semiclassically. In this limit the partition function for N identical particles is given by

$$Z_N = \frac{1}{N! h^{3N}} \int d^{3N}\mathbf{p} d^{3N}\mathbf{r} e^{-\beta K} e^{-\beta U}, \quad (8.4)$$

where the kinetic energy $K = \sum_i p_i^2/2m$. The partition function for an ideal classical gas of N particles, Z_{ideal} , is given by

$$Z_{\text{ideal}} = \frac{1}{N! h^{3N}} V^N \int d^{3N}\mathbf{p} e^{-\beta K}. \quad (8.5)$$

We have already seen in Section 6.8 that Z_{ideal} can be evaluated exactly. The corresponding free energy of a classical ideal gas is $F_{\text{ideal}} = -kT \ln Z_{\text{ideal}}$.

Because the potential energy does not depend on the momenta of the particles, the kinetic energy part of the integrand in (8.4) can be integrated separately, and Z_N can be written in the form

$$\frac{Z_N}{Z_{\text{ideal}}} = \frac{1}{V^N} \int d^3\mathbf{r}_1 d^3\mathbf{r}_2 \dots d^3\mathbf{r}_N e^{-\beta U}, \quad (8.6)$$

We adopt the notation $\langle \dots \rangle_0$ to denote an average over the microstates of the ideal gas. That is, each particle in (8.6) has a probability d^3r/V of being in a volume d^3r . Using this notation we write

$$\frac{Z_N}{Z_{\text{ideal}}} = \langle e^{-\beta U} \rangle_0. \quad (8.7)$$

The contribution to the free energy from the correlations between the particles due to their interactions, F_c , has the form

$$F_c = -kT \ln \frac{Z}{Z_{\text{ideal}}} = -kT \ln \langle e^{-\beta U} \rangle_0. \quad (8.8)$$

We see that the calculation of the free energy of a classical system of interacting particles can be reduced to the evaluation of the ensemble average in (8.8). The evaluation of F_c for a classical system of interacting particles is the overall goal of this chapter.

Because we do not expect to be able to calculate F_c exactly for arbitrary densities, we first seek an approximation for F_c for low densities where we expect that the interactions between the particles are not too important. We know that the ideal gas equation of state, $PV/NkT = 1$, is a good approximation to a gas in the dilute limit where the intermolecular interactions can be ignored. If the interactions are short-range, we assume that we can make an expansion of the pressure in powers of the density. This expansion is known as the *virial expansion* and is written as

$$\frac{PV}{NkT} = 1 + \rho B_2(T) + \rho^2 B_3(T) + \dots \quad (8.9)$$

The quantities B_n are known as *virial coefficients* and involve the interaction of n particles. The first four virial coefficients are given by the integrals ($B_1 = 1$)

$$B_2(T) = -\frac{1}{2V} \int d^3\mathbf{r}_1 d^3\mathbf{r}_2 f_{12}, \quad (8.10a)$$

$$B_3(T) = -\frac{1}{3V} \int d^3\mathbf{r}_1 d^3\mathbf{r}_2 d^3\mathbf{r}_3 f_{12} f_{13} f_{23}, \quad (8.10b)$$

$$B_4(T) = -\frac{1}{8V} \int d^3\mathbf{r}_1 d^3\mathbf{r}_2 d^3\mathbf{r}_3 d^3\mathbf{r}_4 (3f_{12}f_{23}f_{34}f_{41} + 6f_{12}f_{23}f_{34}f_{41}f_{13} + f_{12}f_{23}f_{34}f_{41}f_{13}f_{24}), \quad (8.10c)$$

where $f_{ij} = f(|\mathbf{r}_i - \mathbf{r}_j|)$, and

$$f(r) = e^{-\beta u(r)} - 1. \quad (8.11)$$

The function $f(r)$ defined in (8.11) is known as the *Mayer f -function*.

Problem 8.2. The density expansion of the free energy F_c is usually written as

$$-\beta \frac{F_c}{N} = \sum_{p=1}^{\infty} \frac{b_p \rho^p}{p+1}, \quad (8.12)$$

where the b_p are known as *cluster integrals*. Use the thermodynamic relation between the pressure and the free energy to show that B_n and b_{n-1} are related by

$$B_n = -\frac{n-1}{n} b_{n-1} \quad (8.13)$$

Problem 8.3. Plot the Mayer function $f(r)$ for a hard sphere interaction and a Lennard-Jones potential. Does $f(r)$ depend on T for hard spheres?

8.3 Second Virial Coefficient

We can find the form of the second virial coefficient B_2 by simple considerations. For simplicity, we first consider the partition function for $N = 2$ particles:

$$\frac{Z_2}{Z_{\text{ideal}}} = \frac{1}{V^2} \int d^3\mathbf{r}_1 d^3\mathbf{r}_2 e^{-\beta u_{12}}. \quad (8.14)$$

We can simplify the integrals in (8.14) by choosing particle 1 as the origin and specifying particle 2 relative to particle 1. This choice of coordinates gives a factor of V because particle 1 can be anywhere in the box. Hence, we can write (8.26) as

$$\frac{Z_2}{Z_{\text{ideal}}} = \frac{1}{V} \int d^3\mathbf{r} e^{-\beta u(r)}, \quad (8.15)$$

where $\mathbf{r} = \mathbf{r}_2 - \mathbf{r}_1$ and $r = |\mathbf{r}|$. The function $e^{-\beta u(r)}$ that appears in the integrand for Z_2 has the undesirable property that it approaches unity rather than zero as $r \rightarrow \infty$. Because we want to

obtain an expansion in the density, we want to write the integrand in (8.15) in terms of a function of r which is significant only if two particles are close to each other. Such a function is the Mayer function $f(r)$ defined in (8.11). We write $e^{-\beta u(r)} = 1 + f(r)$ and express (8.15) as

$$\frac{Z_2}{Z_{\text{ideal}}} = \frac{1}{V} \int d^3 r [1 + f(r)]. \quad (8.16)$$

Note that $f(r) \rightarrow 0$ for sufficiently large r . The first term in the integrand in (8.16) corresponds to no interactions and the second term corresponds to the second virial coefficient B_2 defined in (8.10a). To see this correspondence, we choose particle 1 as the origin as before, and rewrite (8.10a) for B_2 as

$$B_2 = -\frac{1}{2} \int d^3 r f(r). \quad (8.17)$$

If we compare the form (8.16) and (8.17), we see that we can express Z_2/Z_{ideal} in terms of B_2 :

$$\frac{Z_2}{Z_{\text{ideal}}} = 1 - \frac{2}{V} B_2. \quad (8.18)$$

We next evaluate Z_N for $N = 3$ particles. We have

$$\frac{Z_3}{Z_{\text{ideal}}} = \frac{1}{V^3} \int d^3 \mathbf{r}_1 d^3 \mathbf{r}_2 d^3 \mathbf{r}_3 e^{-\beta \sum u_{ij}} \quad (8.19)$$

$$= \frac{1}{V^3} \int d^3 \mathbf{r}_1 d^3 \mathbf{r}_2 d^3 \mathbf{r}_3 \prod_{i < j} (1 + f_{ij}), \quad (8.20)$$

$$= \frac{1}{V^3} \int d^3 \mathbf{r}_1 d^3 \mathbf{r}_2 d^3 \mathbf{r}_3 [(1 + f_{12})(1 + f_{13})(1 + f_{23})] \quad (8.21)$$

$$= \frac{1}{V^3} \int d^3 \mathbf{r}_1 d^3 \mathbf{r}_2 d^3 \mathbf{r}_3 [1 + (f_{12} + f_{13} + f_{23}) + (f_{12}f_{13} + f_{12}f_{23} + f_{13}f_{23}) + f_{12}f_{13}f_{23}] \quad (8.22)$$

We see that we can group terms of products of f 's. If we neglect all but the first term in the expansion (8.22), we recover the ideal gas result $Z/Z_{\text{ideal}} = 1$. It is plausible that in the limit of low density, only the second sum in (8.22) involving pairs of particles is important, and we can ignore the remaining terms involving products of two and three f 's. Because the three terms f_{12} , f_{13} , and f_{23} give the same contribution, we have

$$\frac{Z_3}{Z_{\text{ideal}}} \approx 1 + \frac{3}{V} \int d^3 r f(r) = 1 - \frac{6}{V} B_2 \quad (8.23)$$

We will see in Section 8.5 that the term in (8.22) involving a product of three f 's is related to the third virial coefficient.

For arbitrary N we write

$$\begin{aligned} \frac{Z_N}{Z_{\text{ideal}}} &= \frac{1}{V^N} \int d^3 \mathbf{r}_1 d^3 \mathbf{r}_2 \dots d^3 \mathbf{r}_N e^{-\beta \sum u_{ij}} \\ &= \frac{1}{V^N} \int d^3 \mathbf{r}_1 d^3 \mathbf{r}_2 \dots d^3 \mathbf{r}_N \prod_{i < j} (1 + f_{ij}). \end{aligned} \quad (8.24)$$

We have

$$\prod_{i < j} (1 + f_{ij}) = 1 + \sum_{k < l} f_{kl} + \sum_{k < l, m < n} f_{kl} f_{mn} + \dots \quad (8.25)$$

We keep only the ideal gas contribution and the terms involving pairs of particles, and we ignore the remaining terms involving products of two or more f 's. There are a total of $\frac{1}{2}N(N-1)$ terms in the sum $\sum f_{kl}$ corresponding to the number of ways of choosing pairs of particles. These terms are all equal because they differ only in the way the variables of integration are labeled. Hence, we can write the integral of the first sum in (8.25) as

$$\frac{1}{V^N} \int d^3r_1 \dots d^3r_N \sum_{k < l} f_{kl} = \frac{1}{V^N} \frac{N(N-1)}{2} \int d^3r_1 \dots d^3r_N f(r_{12}). \quad (8.26)$$

The integration with respect to $\mathbf{r}_3 \dots \mathbf{r}_N$ over the volume of the system gives a factor of V^{N-2} .

As before, we can simplify the remaining integration over \mathbf{r}_1 and \mathbf{r}_2 by choosing particle 1 as the origin and specifying particle 2 relative to particle 1. Hence, we can write the right-hand side of (8.26) as

$$\frac{N(N-1)}{2V} \int d^3r f(r) \rightarrow \frac{N^2}{2V} \int d^3r f(r), \quad (8.27)$$

where we have replaced $N-1$ by N because $N \gg 1$. If we identify the integral in (8.27) with B_2 , we see that we can write

$$\frac{Z_N}{Z_{\text{ideal}}} \approx 1 - N\rho B_2. \quad (8.28)$$

If the interparticle potential $u(r) \approx 0$ for $r > r_0$, then $f(r)$ differs from zero only for $r < r_0$ and the integral B_2 is bounded and is order r_0^3 in three dimensions (see Problem 8.4). Hence B_2 is independent of V and is an intensive quantity. However, this well-behaved nature of B_2 implies that the second term in (8.28) is proportional to N and in the limit $N \rightarrow \infty$, this term is larger than the first — not a good omen for a perturbation theory.

The reason we have obtained this apparent divergence in Z_N/Z_{ideal} is that we have calculated the wrong quantity. The quantity of physical interest is F rather than Z . Because F is proportional to N , it follows from the relation $F \propto \ln Z$ that Z_N must depend on the N th power of an intensive quantity. Thus Z must have the form

$$\frac{Z_N}{Z_{\text{ideal}}} = (1 - \rho B_2 + \dots)^N, \quad (8.29)$$

so that F will be proportional to N . Hence, the leading contribution to Z/Z_{ideal} should be written as

$$\frac{Z_N}{Z_{\text{ideal}}} = 1 - N\rho B_2 \rightarrow (1 - \rho B_2)^N. \quad (8.30)$$

The corresponding free energy is given by

$$\begin{aligned} F &= F_{\text{ideal}} - NkT \ln(1 - \rho B_2), \\ &\approx F_{\text{ideal}} + NkT \rho B_2, \end{aligned} \quad (8.31)$$

where we have used the fact that $\ln(1+x) \approx x$ for $x \ll 1$. The corresponding equation of state is given by

$$\frac{PV}{NkT} = 1 + \rho B_2. \quad (8.32)$$

The second term in (8.32) represents the first density correction to the ideal gas equation of state. The properties of B_2 and the approximate equation of state (8.32) are explored in Problems 8.4–8.7.

Problem 8.4. To calculate B_2 we need to first perform the angular integrations in (8.17). Show that because $u(r)$ depends only on r , B_2 can be written as

$$B_2(T) = -\frac{1}{2} \int d^3r f(r) = 2\pi \int_0^\infty dr r^2 (1 - e^{-\beta u(r)}). \quad (8.33)$$

Show that $B_2 = 2\pi\sigma^3/3$ for a system of hard spheres of diameter σ .

Problem 8.5. *Qualitative temperature behavior of $B_2(T)$.* Suppose that $u(r)$ has the qualitative behavior shown in Figure 8.1. Take r_0 to be the value of r at which $u(r)$ is a minimum (see Problem 8.1). Interpret r_0 in terms of the effective diameter of the atoms.

For high temperatures ($kT \gg \epsilon$), $u(r)/kT \ll 1$ for $r > r_0$. Explain why the value of the integral in (8.33) is determined by the contributions from the integrand for $r < r_0$ where $u(r)/kT$ is large and positive. Show that in this limit $B_2(T) \approx b$, where $b = 2\pi r_0^3/3$. What is the interpretation of the parameter b ?

For low temperatures ($kT \ll \epsilon$), the dominant contributions to the integral are determined by the contributions from the integrand for $r > r_0$. What is the sign of $u(r)$ for $r > r_0$? What is the sign of $B_2(T)$ at low T ? Show that in this limit $B_2 \approx -a/kT$, where

$$a = -2\pi \int_{r_0}^\infty u(r) r^2 dr. \quad (8.34)$$

Show that this reasoning implies that B_2 can be written in the approximate form

$$B_2 = b - \frac{a}{kT}, \quad (8.35)$$

where $b = 2\pi r_0^3/3$ and a is given by (8.34). Why does $B_2(T)$ pass through zero at some intermediate temperature? The temperature at which $B_2(T) = 0$ is known as the Boyle temperature.

Problem 8.6. Use a simple numerical method such as Simpson's rule (see Appendix Bxx) to determine the T -dependence of B_2 for the Lennard-Jones potential. At what temperature does B_2 vanish? How does this temperature compare with that predicted by (8.35)? Compare your numerical result with the approximate result found in Problem 8.5.

Problem 8.7. *Inversion temperature of Argon.* In Section 7.4.2 we discussed the porous plug or Joule-Thomson process in which a gas is forced from a high pressure chamber through a porous plug into a lower pressure chamber. The process occurs at constant enthalpy and the change in temperature of the gas is given by $dT = (\partial T/\partial P)_H dP$ for small changes in pressure. We know that (see (7.48))

$$\left(\frac{\partial T}{\partial P}\right)_H = \frac{1}{C_P} \left[T \left(\frac{\partial V}{\partial T}\right)_{P,N} - V \right]. \quad (8.36)$$

The locus of points $(\partial T/\partial P)_H = 0$ is called the Joule-Thompson inversion curve. Assume the approximate equation of state $V = NkT/P + NB_2$ and use your numerical results for B_2 from Problem 8.6 for the Lennard-Jones potential to compute the inversion temperature at which the inversion curve is a maximum. Use $\sigma = 3.4 \text{ \AA}$ and $\epsilon/k = 120 \text{ K}$ and compare your result with the experimental value of 780 K.

Problem 8.8. Assume that $u(r)$ has the form $u(r) \sim r^{-n}$ for large r . What is the condition on n such that the integral in (8.33) for B_2 exists? Why is it plausible that the density expansion (8.8) is not applicable to a system of particles with an interaction proportional to $1/r$ (a Coulomb system)?

***Problem 8.9.** Show that if the last term in (8.22) is neglected, $Z_3/Z_{\text{ideal}} = 1 - 6B_2/V + 12B_2^2/V^2 \approx (1 - 2\rho B_2)^3$, where $\rho = 3/V$. Also show that the last term in (8.22) is related to B_3 .

In Problem 8.5 we found that B_2 can be written in the approximate form (8.35). This approximate form of B_2 allows us to write the equation of state as (see (8.32))

$$PV = NkT \left[1 + \rho b - \frac{\rho a}{kT} \right]$$

or

$$\begin{aligned} P &\approx \rho kT \left[\frac{1}{1 - \rho b} - \frac{\rho a}{kT} \right] \\ &= \frac{\rho kT}{1 - \rho b} - \rho^2 a^2. \end{aligned} \tag{8.37}$$

Note that we have made the approximation $1 + \rho b \approx 1/(1 - \rho b)$, which is consistent with our assumption that $\rho b \ll 1$. The approximate equation of state in (8.37) is known as the *van der Waals equation of state* as discussed on page 33. Note that the parameter a takes into account the long-range attraction of the molecules and the parameter b takes into account their short-range repulsion. A more systematic derivation of the van der Waals equation of state will be given in Section 8.9.1.

8.4 Cumulant Expansion

In Section 8.2 we had to make some awkward assumptions to obtain the form of B_2 from an expansion of Z/Z_{ideal} . To find the form of the higher order virial coefficients, we introduce what is known as the cumulant expansion. In Section 8.5 we apply this formalism to obtain an expansion of $\ln Z/Z_{\text{ideal}}$ in powers of β . Finally, we rearrange this expansion so that it becomes an expansion of $\ln Z/Z_{\text{ideal}}$ in powers of ρ .

The form (8.8) for F_c is similar to that frequently encountered in probability theory. We introduce the function $\phi(t)$ defined as

$$\phi(t) \equiv \langle e^{tx} \rangle, \tag{8.38}$$

where the random variable x occurs according to the probability distribution $p(x)$, that is, the average denoted by $\langle \dots \rangle$ is over $p(x)$. The function $\phi(t)$ is an example of a *moment generating*

function because a power series expansion in t yields

$$\phi(t) = \langle [1 + tx + \frac{1}{2!}t^2x^2 + \dots] \rangle, \quad (8.39)$$

$$\begin{aligned} &= 1 + t\langle x \rangle + \frac{t^2}{2!}\langle x^2 \rangle + \dots, \\ &= \sum_{n=0}^{\infty} \frac{t^n \langle x^n \rangle}{n!}. \end{aligned} \quad (8.40)$$

In the present case the physical quantity of interest is proportional to $\ln Z$, so we will want to consider the series expansion of $\ln \phi$ rather than ϕ . (The correspondence is $t \rightarrow -\beta$ and $x \rightarrow U$.) The series expansion of $\ln \phi(t)$ can be written in the form

$$\ln \phi = \ln \langle e^{tx} \rangle = \sum_{n=1}^{\infty} \frac{t^n M_n(x)}{n!}, \quad (8.41)$$

where the coefficients M_n are known as *cumulants* or *semi-invariants*. The first four cumulants are

$$M_1 = \langle x \rangle, \quad (8.42a)$$

$$M_2 = \langle x^2 \rangle - \langle x \rangle^2, \quad (8.42b)$$

$$M_3 = \langle x^3 \rangle - 3\langle x^2 \rangle \langle x \rangle + 2\langle x \rangle^3, \quad (8.42c)$$

$$M_4 = \langle x^4 \rangle - 4\langle x^3 \rangle \langle x \rangle - 3\langle x^2 \rangle^2 + 12\langle x^2 \rangle \langle x \rangle^2 - 6\langle x \rangle^4. \quad (8.42d)$$

Problem 8.10. Use the first few terms in the Taylor expansion of $\ln(1+x)$ (see Appendix A) to obtain the expressions for M_n given in (8.42).

Because $\ln \phi(x)$ is an extensive or additive quantity, the independent random variables x and y satisfy the condition that

$$\ln \langle e^{t(x+y)} \rangle = \ln \langle e^{tx} \rangle \langle e^{ty} \rangle = \ln \langle e^{tx} \rangle + \ln \langle e^{ty} \rangle. \quad (8.43)$$

Because

$$\ln \langle e^{t(x+y)} \rangle = \sum_{n=0}^{\infty} \frac{t^n}{n!} M_n(x+y), \quad (8.44)$$

we have the result

$$M_n(x+y) = M_n(x) + M_n(y). \quad (8.45)$$

The relation (8.45) implies that all cross terms in M_n involving independent variables vanish.

Problem 8.11. As an example of the cancellation of cross terms, consider $M_3(x+y)$. From (8.42c) we know that $M_3(x+y)$ is given by

$$M_3(x+y) = \overline{(x+y)^3} - 3\overline{(x+y)^2}\overline{(x+y)} + 2\overline{(x+y)}^3 \quad (8.46)$$

Show explicitly that all cross terms cancel and that $M_3(x+y) = M_3(x) + M_3(y)$.

8.5 High Temperature Expansion

Now that we have discussed the formal properties of the cumulants, we can use these properties to evaluate F_c . According to (8.8) and (8.41) we can write F_c as

$$-\beta F_c = \ln \langle e^{-\beta U} \rangle_0 = \sum_{n=1}^{\infty} \frac{(-\beta)^n}{n!} M_n. \quad (8.47)$$

The expansion (8.47) in powers of β is known as a *high temperature expansion*. Such an expansion is very natural because $\beta = 1/kT$ is the only parameter that appears explicitly in (8.47). So an obvious strategy is to assume that the inverse temperature is small and expand F_c in powers of β . However, β enters in the combination βu_0 , where u_0 is a measure of the strength of the interaction. Although we can choose β to be as small as we wish, the potential energy of interaction between the particles in a gas is strongly repulsive at short distances (see Figure 8.1), and hence u_0 is not well defined. Hence, a strategy based on expanding in the parameter β is not physically reasonable.

The difficulty of generating an appropriate perturbation theory for a dilute gas is typical of the difficulties of doing perturbation theory for a system with many degrees of freedom. Our strategy is to begin with what we can do and then try to do what we want. What we want is to generate an expansion in powers of ρ for a dilute gas, even though the parameter ρ does not appear in (8.47). Our strategy will be to formally do a high temperature expansion and find the high temperature expansion coefficients M_n . Then we will find that we can reorder the high temperature expansion to obtain a power series expansion in the density.

The first expansion coefficient in (8.47) is the average of the total potential energy:

$$M_1 = \langle U \rangle = \frac{1}{V^N} \int d\mathbf{r}_1 d\mathbf{r}_2 \dots d\mathbf{r}_N \sum_{i < j} u_{ij}. \quad (8.48)$$

Because every term in the sum gives the same contribution, we have

$$\begin{aligned} M_1 &= \frac{1}{2} N(N-1) \frac{1}{V^N} \int d\mathbf{r}_1 d\mathbf{r}_2 \dots d\mathbf{r}_N u_{12} \\ &= \frac{1}{2} N(N-1) \frac{1}{V^N} V^{N-2} \int d\mathbf{r}_1 d\mathbf{r}_2 u_{12} \\ &= \frac{1}{2} N(N-1) \frac{1}{V^2} \int d\mathbf{r}_1 d\mathbf{r}_2 u_{12}. \end{aligned} \quad (8.49)$$

The combinatorial factor $\frac{1}{2} N(N-1)$ is the number of terms in the sum. Because we are interested in the limit $N \rightarrow \infty$, we replace $N-1$ by N . We can simplify (8.49) further by measuring the position of particle 2 from particle 1, and write

$$M_1 = \frac{N^2}{2V^2} V \int d\mathbf{r} u(r),$$

or

$$\frac{M_1}{N} = \frac{\rho}{2} \int d\mathbf{r} u(r). \quad (8.50)$$

Note that M_1 is an extensive quantity as is the free energy.

Before we proceed further, we note that we have implicitly assumed that the integral in (8.50) converges. However, the integral diverges for small r for a system of hard spheres or the Lennard-Jones potential. So what can we do? The answer might seem strange at first, but we will let our intuition rather than mathematical rigor guide us. So let us assume that we can overcome these problems later. Or if this assumption seems unacceptable, we can equally well assume that the potential energy of interaction is not strongly repulsive at small separations and is short-range. Examples of such potentials include the step potential $u(r) = u_0$ for $r < a$ and $u(r) = 0$ for $r > a$, and the Gaussian potential $u(r) = u_0 e^{-r^2/a^2}$.

We next consider M_2 which is given by

$$M_2 = \langle U^2 \rangle - \langle U \rangle^2, \quad (8.51)$$

where

$$\langle U \rangle = \sum_{i < j} \sum_j \langle u_{ij} \rangle. \quad (8.52)$$

and

$$\langle U^2 \rangle = \sum_{i < j} \sum_j \sum_{k < l} \sum_l \langle u_{ij} u_{kl} \rangle, \quad (8.53)$$

The various terms in (8.53) and (8.52) may be classified according to the number of subscripts in common. As an example, suppose that $N = 4$. We have

$$U = \sum_{i < j=1}^4 u_{ij} = u_{12} + u_{13} + u_{14} + u_{23} + u_{24} + u_{34}, \quad (8.54)$$

and

$$\begin{aligned} U^2 = & [u_{12}^2 + u_{13}^2 + u_{14}^2 + u_{23}^2 + u_{24}^2 + u_{34}^2] \\ & + 2[u_{12}u_{13} + u_{12}u_{14} + u_{12}u_{23} + u_{12}u_{24} + u_{13}u_{14} + u_{13}u_{23} \\ & + u_{13}u_{34} + u_{14}u_{24} + u_{14}u_{34} + u_{23}u_{24} + u_{23}u_{34} + u_{24}u_{34}] \\ & + 2[u_{12}u_{34} + u_{13}u_{24} + u_{14}u_{23}] \end{aligned} \quad (8.55)$$

An inspection of (8.55) shows that the 36 terms in (8.55) can be grouped into three classes:

No indices in common (disconnected terms). A typical disconnected term is $\langle u_{12}u_{34} \rangle$. Because the variables \mathbf{r}_{12} and \mathbf{r}_{34} are independent, u_{12} and u_{34} are independent, and we can write

$$\langle u_{12}u_{34} \rangle = \langle u_{12} \rangle \langle u_{34} \rangle. \quad (8.56)$$

From (8.45) we know that every disconnected term such as the one in (8.56) is a cross term that is canceled if all terms in M_2 are included.

One index in common (reducible terms). An example of a reducible term is $\langle u_{12}u_{23} \rangle$. We can see that such a term also factorizes because of the homogeneity of space. Suppose we choose

particle 2 as the origin and integrate over \mathbf{r}_1 and \mathbf{r}_3 . We have

$$\langle u_{12}u_{23} \rangle = \frac{1}{V^3} \int d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 u_{12} u_{23} \quad (8.57)$$

$$\begin{aligned} &= \frac{1}{V^2} \int d\mathbf{r}_{12} d\mathbf{r}_{23} u_{12} u_{23} \\ &= \langle u_{12} \rangle \langle u_{23} \rangle. \end{aligned} \quad (8.58)$$

A factor of V was obtained because particle 2 can be anywhere in the box of volume V . Again we find that the variables $u_{ij}u_{jk}$ are independent and hence are canceled by other terms in M_2 .

Both pairs of indices in common (irreducible terms). An example of an irreducible term is $\langle u_{12}^2 \rangle$. Such a term is not canceled, and we find that the corresponding contribution to M_2 is

$$M_2 = \sum_{i < j=1}^N [\langle u_{ij}^2 \rangle - \langle u_{ij} \rangle^2]. \quad (8.59)$$

We can simplify (8.59) further by comparing the magnitude of the two types of terms in the limit $N \rightarrow \infty$. We have that

$$\langle u_{ij}^2 \rangle = \frac{1}{V} \int u_{ij}^2 d\mathbf{r}_{ij} \propto \frac{1}{V} \propto O\left(\frac{1}{N}\right). \quad (8.60a)$$

$$\langle u_{ij} \rangle^2 = \left(\frac{1}{V} \int u_{ij} d\mathbf{r}_{ij} \right)^2 \propto O\left(\frac{1}{N^2}\right). \quad (8.60b)$$

From (8.60) we see that we can ignore the second term in comparison to the first (assuming that the above integrals converge.)

The above considerations lead us to the desired form of M_2 . Because there are $N(N-1)/2$ identical contributions such as (8.60a) to M_2 in (8.59), we obtain in the limit $N \rightarrow \infty, V \rightarrow \infty$

$$\frac{M_2}{N} = \frac{\rho}{2} \int u^2(\mathbf{r}) d\mathbf{r}. \quad (8.61)$$

The most important result of our evaluation of M_1 and M_2 is that the disconnected and reducible contributions are canceled. This cancellation is due to the statistical independence of the variables that appear. According to (8.45) their contribution must necessarily vanish. The vanishing of the disconnected contributions is essential for M_n and thus for F_c to be an extensive quantity proportional to N . For example, consider the contribution $\sum_{i < j, k < l} \langle u_{ij} \rangle \langle u_{kl} \rangle$ for $i \neq j \neq k \neq l$. As we saw in (8.60b), each $\langle u_{ij} \rangle$ is order $1/V$. Because each index is different, the number of terms is $\sim N^4$ and hence the order of magnitude of this type of contribution is $N^4/V^2 \sim N^2$. (Recall that $N/V = \rho$ is fixed.) Because the presence of the disconnected terms in M_2 would imply that F_c would be proportional to N^2 rather than N , it is fortunate that this spurious N dependence cancels exactly. The fact that the disconnected terms do not contribute to F_c was first shown for a classical gas by Mayer in 1937. The corresponding result was not established for a quantum gas until 1957.

The reducible terms also vanish but do not lead to a spurious N -dependence. As an example, consider the term $\langle u_{ij}u_{jk}u_{kl} \rangle$ with all four indices distinct. We can choose relative coordinates and

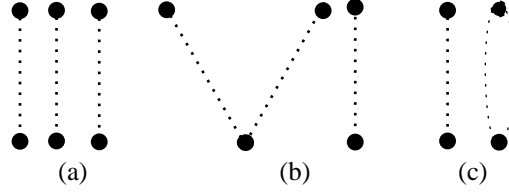


Figure 8.2: Examples of disconnected diagrams with three bonds. For (a) the volume dependence is V^{-3} , the number of terms in the sum is $O(N^6)$ and the magnitude of the contribution is $O(N^3)$. For (b) the volume dependence is V^{-3} , the number of terms in the sum is $O(N^5)$, and the magnitude of the contribution is $O(N^2)$. For (c) the volume dependence is V^{-2} , the number of terms is $O(N^4)$, and magnitude is $O(N^2)$.

show that this term factorizes, $\langle u_{ij}u_{jk}u_{kl} \rangle = \langle u_{ij} \rangle \langle u_{jk} \rangle \langle u_{kl} \rangle$, and hence is canceled for a classical gas. However, the N -dependence of this term is $N^4/V^3 \sim N$. This fact that the reducible terms are proportional to N is fortunate because the reducible terms do not cancel for a quantum gas.

Problem 8.12. Consider a system of $N = 4$ particles and obtain the explicit form of the first three cumulants. Show that the disconnected and reducible contributions cancel.

To consider the higher-order cumulants, we introduce a graphical notation that corresponds to the various contributions to M_n . As we have seen, we do not need to consider products of expectation values because they either cancel or are $O(1/N)$ relative to the irreducible terms arising from the first term in M_n . The rules for the calculation of M_n are

- For each particle (subscript on u) draw a vertex (a point).
- Draw a bond (dotted line) between two vertices. There is a total of n bonds among p vertices, where $2 \leq p \leq n$.
- If the diagram contains two or more pieces not joined by a bond, then the diagram is *disconnected*; If the diagram can be separated into two disconnected pieces by removing one vertex, then the diagram is *reducible*. The remaining diagrams are *irreducible* and are the only ones that need to be considered.

Examples of the various types of disconnected and reducible diagrams are shown in Figs. 8.2–8.4 corresponding to $M_{n=3}$. What are the corresponding contributions to M_3 ?

It is straightforward to find the contributions to M_3 corresponding to the two types of irreducible diagrams shown in Figure 8.4. There are $\frac{1}{2}N(N-1)$ identical contributions of type (a) and $N(N-1)(N-2)$ of the type shown in (b). Hence, the form of M_3 in the limit $N \rightarrow \infty$ is

$$\frac{M_3}{N} = \frac{\rho}{2} \int u^3(\mathbf{r}) d\mathbf{r} + \rho^2 \int u_{12} u_{23} u_{31} d\mathbf{r}_{12} d\mathbf{r}_{23}. \quad (8.62)$$

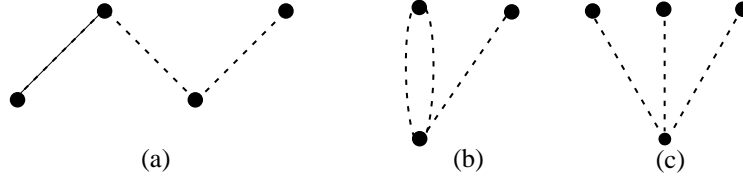


Figure 8.3: Examples of reducible diagrams with three (potential) bonds. The u bonds are represented by dotted lines and the vertices are represented by filled circles. For (a) the volume dependence is V^{-3} , the number of terms is $O(N^4)$, and the magnitude is $O(N)$. For (b) the volume dependence is V^{-2} , the number of terms is $O(N^3)$, and the magnitude is $O(N)$. For (c) the volume dependence is V^{-3} , the number of terms is $O(N^4)$, and the magnitude is $O(N)$.

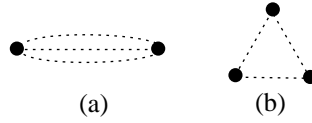


Figure 8.4: Examples of irreducible diagrams with three (potential) bonds. For (a) the volume dependence is V^{-1} , the number of terms is $O(N^2)$, and the magnitude is $O(N)$. For (b) the volume dependence is V^{-2} , the number of terms is $O(N^3)$, and the magnitude is N .

8.6 Density Expansion

We saw in Section 8.5 that we have reduced the problem of calculating M_n to enumerating all irreducible diagrams containing n -bonds among p vertices, where $2 \leq p \leq n$. The expansion (8.47) is an expansion in β or in the number of bonds n . We now show how this expansion can be reordered so that we can obtain an expansion in the density ρ or in the number of vertices p .

Consider an irreducible diagram of n bonds and p vertices. An example is shown in Figure 8.4 for $p = 2$ and $n = 3$. Because there are p particles, there is a factor of N^p . For such a diagram all but $p - 1$ integrations can be performed leaving a factor of $1/V^{p-1}$. We conclude that an irreducible diagram with p vertices contributes a term that is order N^p/V^{p-1} , leading to an order ρ^{p-1} contribution to F_c/N . Hence, a classification of the diagrams according to the number of bonds corresponds to a high temperature expansion while a classification according to the number of vertices is equivalent to a density expansion. That is, by summing all diagrams with a given number of vertices, the expansion (8.47) can be converted to a power series in the density. The result is traditionally written in the form (see (8.12))

$$-\beta \frac{F_c}{N} = \sum_{p=1}^{\infty} \frac{b_p \rho^p}{p+1}. \quad (8.63)$$

Our goal in the following is to find the form of the first few cluster integrals b_p .

We first add the contribution of all the two-vertex diagrams to find b_1 (see Figure 8.5). From (8.47) we see that a factor of $-\beta$ is associated with each bond. The contribution to $-\beta F_c$ from all

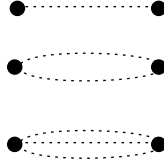


Figure 8.5: The first several irreducible diagrams with two vertices.

Figure 8.6: The single diagram contributing to b_1 . The solid line represents a f bond.

two vertex diagrams is

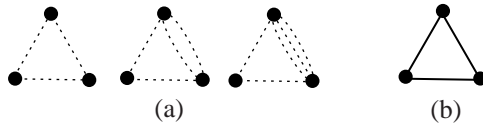
$$\begin{aligned} & \sum_{n=1}^{\infty} \frac{(-\beta)^n}{n!} M_n \text{ (contribution from irreducible diagrams with two vertices)} \\ &= N \frac{\rho}{2} \sum_{n=1}^{\infty} \frac{(-\beta)^n}{n!} \int u^n(\mathbf{r}) d\mathbf{r} = N \frac{\rho}{2} \int (e^{-\beta u(\mathbf{r})} - 1) d\mathbf{r}. \end{aligned} \quad (8.64)$$

Because $B_2 = -\frac{1}{2}b_1$, we recover the result (8.33) that we found in Section 8.2 by a plausibility argument. Note the appearance of the Mayer f function in (8.64).

We can now simplify the diagrammatic expansion by replacing the infinite sum of u (potential) bonds between any two particles by f . For example, b_2 corresponds to the single diagram shown in Figure 8.6.

To find b_2 we consider the set of all irreducible diagrams containing $n = 3$ vertices. Some of the diagrams with u bonds are shown in Figure 8.7a. By considering all the possible combinations of the u bonds, we can add up all the irreducible diagrams containing three vertices with l_{12} , l_{23} , l_{31} bonds. Instead, we will use our intuition and simply replace the various combinations of u bonds by a single f bond between any two vertices as shown in Figure 8.7b. The corresponding contribution to b_2 is

$$b_2 = \frac{1}{2!} \int f_{12} f_{23} f_{31} d\mathbf{r}_{12} d\mathbf{r}_{23}. \quad (8.65)$$

Figure 8.7: (a) The first several irreducible diagrams with three vertices and various numbers of u bonds (dotted lines). (b) The corresponding diagram with f -bonds (solid lines).

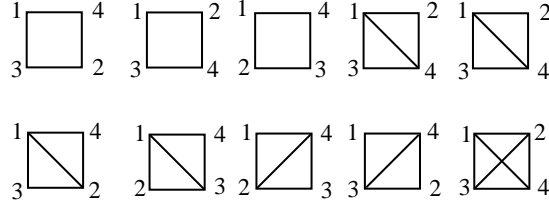


Figure 8.8: The four-vertex diagrams with all the possible different labelings. Note that the bonds are f bonds.

In general, it can be shown that

$$b_p = \frac{1}{p!} \sum \int \prod f_{ij} d\mathbf{r}_1 \dots d\mathbf{r}_p, \quad (8.66)$$

where the sum is over all irreducible topologically distinct diagrams among $p + 1$ vertices. For example, b_3 corresponds to the four-vertex diagrams shown in Figure 8.8. The corresponding result for b_3 is

$$b_3 = \frac{1}{3!} \int (3f_{12}f_{23}f_{34}f_{41} + 6f_{12}f_{23}f_{34}f_{41}f_{13} + f_{12}f_{23}f_{34}f_{41}f_{13}f_{24}) d\mathbf{r}_2 d\mathbf{r}_3 d\mathbf{r}_4. \quad (8.67)$$

We see that we have converted the original high temperature expansion to a density expansion by summing what are known as *ladder diagrams*. These diagrams correspond to all the possible u bonds between any two particles (vertices). The result of this sum is the Mayer f function. The resultant density expansion for the free energy and the pressure equation of state is one of the few expansions known in physics that is convergent for sufficiently small densities. In contrast, most expansions in physics are asymptotic.

The procedure for finding higher order terms in the density expansion of the free energy is straightforward in principle. To find the contribution of order ρ^{p-1} , we enumerate all the diagrams with p vertices and various numbers of f bonds such that the diagrams are irreducible. There is only one f bond between any two vertices. However, the enumeration of the cluster integrals b_p becomes more and more difficult for larger p . Even more difficult is the calculation of the cluster integrals even for hard spheres.

The results for the known virial coefficients for hard spheres are summarized in Table 8.1 in terms of the parameter

$$\eta = \pi\rho\sigma^3/6, \quad (8.68)$$

where σ is the diameter of the spheres. The parameter η can be expressed as

$$\eta = \rho(4\pi/3)(\sigma/2)^3. \quad (8.69)$$

The form of (8.69) shows that η is the fraction of the space occupied by N spheres. For this reason η is often called the *packing fraction*.

virial coefficient	magnitude
ρB_2	$\frac{2}{3}\pi\rho\sigma^3 = 4\eta$
$\rho^2 B_3$	$\frac{5}{18}\pi^2\rho^2\sigma^6 = 10\eta^2$
$\rho^3 B_4$	$18.365\eta^3$
$\rho^4 B_5$	$28.24\eta^4$
$\rho^5 B_6$	$39.5\eta^5$
$\rho^6 B_7$	$56.5\eta^6$

Table 8.1: The values of the known virial coefficients for hard spheres.

Problem 8.13. The results shown in Table 8.1 imply that the equation of state of a system of hard spheres can be written as

$$\begin{aligned}\frac{PV}{NkT} &= 1 + \sum_{s=1}^6 C_s \eta^s \\ &= 1 + 4\eta + 10\eta^2 + 18.365\eta^3 + 28.24\eta^4 + 39.5\eta^5 + 56.5\eta^6,\end{aligned}\quad (8.70)$$

where the dimensionless parameter $\eta = \pi\rho\sigma^3/6$. It is clear from the form (8.70) that the convergence is not very rapid.

Show that the coefficients C_s can be written in the approximate form $C_s = 3s + s^2$ and this form of C_s implies that

$$\frac{PV}{NkT} = 1 + \sum_{s=1}^{\infty} (3s + s^2) \eta^s. \quad (8.71)$$

Do the sum in (8.71) and show that

$$\frac{PV}{NkT} = \frac{1 + \eta + \eta^2 - \eta^3}{(1 - \eta)^3}. \quad (8.72)$$

The form (8.72) is known as the Carnahan-Starling equation of state.

Problem 8.14. Show that the close-packed volume of a system of hard spheres is equal to $N\sigma^3/\sqrt{2}$. What is the corresponding maximum value of η ? Do you expect the Carnahan-Starling equation of state to be applicable at densities close to the fluid-solid transition?

Problem 8.15. The applet at [xx](#) simulates a system of hard disks. Choose $N = xx$ and start at density of $\rho = xx$. Run long enough to obtain meaningful estimates of the pressure. Then gradually increase the density. What happens to the pressure at $\rho \approx xx$? Evidence for the existence of a fluid-solid transition was first hypothesized on the basis of similar computer simulations. Computer simulation studies suggest that for $\rho\sigma^2$ is between approximately 0.91 and $\rho\sigma^2 = 2/3^{1/2} \approx 1.1547$, the thermodynamically stable phase is the triangular crystal with increased mean neighbor spacing that allows restricted local motion. The equilibrium concentration of defects, especially defects, appears to be very small in this density range and to vanish exponentially as ρ approaches the density of maximum packing.

Problem 8.16. Use the Carnahan-Starling equation of state (8.72) to derive analytical expressions for the excess entropy S_{ex} , excess energy ES_{ex} , excess Helmholtz free energy for a hard-sphere fluid. The excess entropy S_{ex} is defined by $S - -NK \ln P - Nk \ln \beta \lambda^3 + 5Nk/2 + S_{\text{ex}}$ and the excess energy is defined by $E = 3NkT + E_{\text{ex}}$.

Problem 8.17. Consider a one-dimensional gas of particles confined to a box of length L . Suppose that the interparticle interaction is given by

$$u(x) = \begin{cases} \infty & x < a \\ 0 & x \geq a \end{cases} \quad (8.73)$$

Such a system of *hard rods* is known as a Tonks gas. (a) Evaluate the virial coefficients B_2 and B_3 . It is possible to do the integrals analytically. (b) Note that the form of the interaction (8.73) prevents particles from exchanging places, that is, from changing their order. What is the available “volume” in which the particles can move? Use this consideration to guess the form of the equation of state. (c*) Calculate the partition function and the equation of state exactly and show that your results are consistent with part (a).

8.7 Radial Distribution Function

Now that we know how to include the interactions between particles to obtain the equation of state, we can consider how these interactions lead to correlations between the particles. We know that if the interactions are neglected, the positions of the particles are uncorrelated and the probability of finding a particle a distance r away from a particular particle is proportional to ρ . In the following, we define a quantity that is a measure of the correlations between particles and determine its dependence on r in the limit of low density.

The probability of a configuration of N particles in a volume V is given in the canonical ensemble by

$$\begin{aligned} P_N(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) d\mathbf{r}_1 d\mathbf{r}_2 \dots d\mathbf{r}_N &= \frac{e^{-\beta U} d\mathbf{r}_1 d\mathbf{r}_2 \dots d\mathbf{r}_N}{\int e^{-\beta U} d\mathbf{r}_1 d\mathbf{r}_2 \dots d\mathbf{r}_N} \\ &= \frac{e^{-\beta U} d\mathbf{r}_1 d\mathbf{r}_2 \dots d\mathbf{r}_N}{Q_N}, \end{aligned} \quad (8.74)$$

where U is the total potential energy of the configuration. The quantity $P_N d\mathbf{r}_1 d\mathbf{r}_2 \dots d\mathbf{r}_N$ is the probability that particle 1 is in the range $d\mathbf{r}_1$ about \mathbf{r}_1 , particle 2 is in the range $d\mathbf{r}_2$ about \mathbf{r}_2 , etc.

The *configurational integral* Q_N is defined as

$$Q_N = \int d\mathbf{r}_1 d\mathbf{r}_2 \dots d\mathbf{r}_N e^{-\beta U}. \quad (8.75)$$

Note that Q_N is related to the partition function Z_N for a classical system by $Q_N = Z_N / (N! \lambda^{3N})$. Q_N is defined so that $Q_N = V^N$ for an ideal gas.

The probability that particle 1 is in the range $d\mathbf{r}_1$ about \mathbf{r}_1 and particle 2 is in the range $d\mathbf{r}_2$ about \mathbf{r}_2 is obtained by integrating (8.74) over the positions of particles 3 through N :

$$P_2(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 = \frac{\int e^{-\beta U} d\mathbf{r}_3 \dots d\mathbf{r}_N}{Q_N} d\mathbf{r}_1 d\mathbf{r}_2. \quad (8.76)$$

The probability that *any* particle is in the range $d\mathbf{r}_1$ about \mathbf{r}_1 and any other particle is in the range $d\mathbf{r}_2$ about \mathbf{r}_2 is $N(N-1)P_2$. In general, we define the n -particle density function for a system of N particles as

$$\rho_n(\mathbf{r}_1, \dots, \mathbf{r}_n) = \frac{N!}{(N-n)!} \frac{\int e^{-\beta U} d\mathbf{r}_{N-n} \dots d\mathbf{r}_N}{Q_N}. \quad (8.77)$$

It is easy to see that $\rho_2 = N(N-1)P_2$. The normalization condition for ρ_n is

$$\int \rho_n(\mathbf{r}_1, \dots, \mathbf{r}_n) d\mathbf{r}_1 \dots d\mathbf{r}_n = \frac{N!}{(N-n)!}. \quad (8.78)$$

For $n = 1$, we have

$$\int \rho_1(\mathbf{r}) d\mathbf{r} = N. \quad (8.79)$$

If the system is homogeneous, then $\rho_1(\mathbf{r})$ is independent of \mathbf{r} , and it follows from (8.79) that

$$\rho_1(\mathbf{r}) = \frac{N}{V} = \rho. \quad (8.80)$$

We define the *pair distribution function* $g(\mathbf{r}_1, \mathbf{r}_2)$ as

$$\rho^2 g(\mathbf{r}_1, \mathbf{r}_2) = \rho_2 = N(N-1)P_2 = N(N-1) \frac{\int e^{-\beta U} d\mathbf{r}_3 \dots d\mathbf{r}_N}{Q_N}, \quad (8.81)$$

or

$$g(\mathbf{r}_1, \mathbf{r}_2) = \left(1 - \frac{1}{N}\right) \frac{V^2 \int e^{-\beta U} d\mathbf{r}_3 \dots d\mathbf{r}_N}{Q_N}. \quad (8.82)$$

If the interparticle interaction is spherically symmetric and the system is a liquid, then $g(\mathbf{r}_1, \mathbf{r}_2)$ depends only on the relative separation $r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|$ between particles 1 and 2. We adopt the notation $g(r) = g(r_{12})$ in the following; $g(r)$ is called the *radial distribution function*.

Note that $g(r)$ is defined so that $g(r) = 1$ for an ideal gas. (Actually $g(r) = 1 - 1/N$, but we can ignore the $1/N$ correction in the thermodynamic limit.) The quantity $\rho g(r) d\mathbf{r}$ is related to the probability of observing a second particle in the range $d\mathbf{r}$ a distance r away from a particle at the origin. The normalization for $\rho g(r)$ is given by

$$\rho \int g(r) 4\pi r^2 dr = \rho \left(1 - \frac{1}{N}\right) V^2 \frac{1}{V} = N - 1. \quad (8.83)$$

From (8.83) we see that $\rho g(r) 4\pi r^2 dr$ is the number of particles between r and $r + dr$ about a particular particle, that is, the product $\rho g(r)$ can be interpreted as the local density about a particular particle.

The qualitative features of $g(r)$ for a Lennard-Jones fluid are shown in Figure 8.9. We see that $g \rightarrow 0$ as $r \rightarrow 0$ because the interaction between the particles does not allow the particles to become too close. Similarly at large r the other particles are not correlated with the fixed particle and $g(r) \rightarrow 1$ as $r \rightarrow \infty$.

It is easy to find the form of $g(r)$ in the limit of low densities. In the limit $N \rightarrow \infty$, $g(r)$ is given by (see (8.82))

$$g(r) = \frac{V^2 \int e^{-\beta U} d\mathbf{r}_3 \dots d\mathbf{r}_N}{Q_N}. \quad (8.84)$$

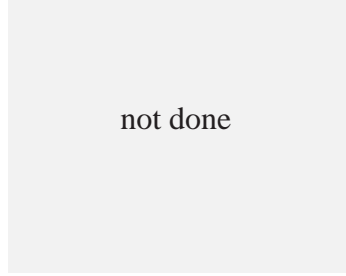


Figure 8.9: Dependence of $g(r)$ on r for a three-dimensional Lennard-Jones liquid at $kT/\epsilon = xx$ and $\rho\sigma^3 = xx$.

At low densities, we may integrate over particles 3, 4, ..., N , assuming that these particles are distant from particles 1 and 2 and also distant from each other. Also for almost all configurations, we can replace U by u_{12} in the numerator. Similarly, the denominator can be approximated by V^N . Hence we have

$$g(r) \approx \frac{V^2 e^{-\beta u_{12}} V^{N-2}}{V^N} = e^{-\beta u(r)}. \quad (8.85)$$

Another way of defining $g(r)$ is in terms of the local particle density. Consider the sum $\sum_{i=1}^N \delta(\mathbf{r} - \mathbf{r}_i)$. Given the properties of the delta function, we know that the integral of this sum about \mathbf{r} over the volume element d^3r yields the number of particles in the volume element. Hence, we can define the *local particle density* as

$$\rho(\mathbf{r}) = \sum_{i=1}^N \delta(\mathbf{r} - \mathbf{r}_i). \quad (8.86)$$

We have

$$\rho_1(\mathbf{r}) = \left\langle \sum_{i=1}^N \delta(\mathbf{r} - \mathbf{r}_i) \right\rangle, \quad (8.87)$$

where $\langle \delta(\mathbf{r} - \mathbf{r}_i) \rangle$ is given by

$$\langle \delta(\mathbf{r} - \mathbf{r}_i) \rangle = \frac{1}{Q_N} \int \delta(\mathbf{r} - \mathbf{r}_1) e^{-\beta U(\mathbf{r}_1, \dots, \mathbf{r}_N)} d\mathbf{r}_1 \dots d\mathbf{r}_N \quad (8.88)$$

$$= \frac{1}{Q_N} \int e^{-\beta U(\mathbf{r}, \mathbf{r}_2, \dots, \mathbf{r}_N)} d\mathbf{r}_2 \dots d\mathbf{r}_N. \quad (8.89)$$

For a homogeneous system $\rho_1(\mathbf{r}_1) = \rho$.

Problem 8.18. Use (8.89) and the definition (8.87) to show that $\rho_1(\mathbf{r}_1) = \rho$ for a homogeneous system.

We can define $\rho_2(\mathbf{r}_1, \mathbf{r}_2)$ as

$$\rho_2(\mathbf{r}_1, \mathbf{r}_2) = \sum_{i \neq j} \langle \delta(\mathbf{r}_1 - \mathbf{r}_i) \delta(\mathbf{r}_2 - \mathbf{r}_j) \rangle \quad (8.90)$$

We can use the same reasoning as in (8.89) to show that

$$\rho_2(\mathbf{r}_1, \mathbf{r}_2) = N(N-1) \frac{\int d^3r_3 d^3r_4 \dots d^3r_N e^{-\beta U(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \dots, \mathbf{r}_N)}}{\int d^3r_1 d^3r_2 d^3r_3 d^3r_4 \dots d^3r_N e^{-\beta U(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3, \dots, \mathbf{r}_N)}} \quad (8.91)$$

If we compare (8.91) and (8.81), we see that we can also define $g(\mathbf{r}_1, \mathbf{r}_2)$ as

$$\rho^2 g(\mathbf{r}_1, \mathbf{r}_2) = \sum_{i \neq j} \langle \delta(\mathbf{r}_1 - \mathbf{r}_i) \delta(\mathbf{r}_2 - \mathbf{r}_j) \rangle \quad (8.92)$$

Hence, we see that $g(r)$ is related to the spatial correlation of the density fluctuations in the system.

8.7.1 Relation of thermodynamic functions to $g(r)$

We first derive a relation for the mean energy E in terms of $g(r)$. We write

$$E = \frac{3}{2} N k T + \bar{U}, \quad (8.93)$$

where

$$\bar{U} = \frac{1}{Q_N} \int \dots \int U e^{-\beta U} d\mathbf{r}_1 d\mathbf{r}_2 \dots d\mathbf{r}_N. \quad (8.94)$$

The two terms in (8.93) are the mean kinetic energy and the mean potential energy \bar{U} , respectively. If we assume that U is given by (8.1), we can write \bar{U} as

$$\bar{U} = \frac{N(N-1)}{2} \frac{1}{Q_N} \int e^{-\beta U} u(r_{12}) d\mathbf{r}_1 \dots d\mathbf{r}_N, \quad (8.95)$$

$$\begin{aligned} &= \frac{N(N-1)}{2} \int u(r_{12}) \left[\frac{\int e^{-\beta U} d\mathbf{r}_3 \dots d\mathbf{r}_N}{Q_N} \right] d\mathbf{r}_1 d\mathbf{r}_2, \\ &= \frac{1}{2} \int u(r_{12}) \rho^2 g(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2. \end{aligned} \quad (8.96)$$

Hence

$$\bar{U} = \frac{N^2}{2V} \int u(r) g(r) d^3r = N \frac{\rho}{2} \int u(r) g(r) 4\pi r^2 dr, \quad (8.97)$$

and the total energy E per particle is given by

$$\frac{E}{N} = \frac{3}{2} k T + \frac{\rho}{2} \int_0^\infty u(r) g(r) 4\pi r^2 dr. \quad (8.98)$$

The form of the second term in (8.98) for the mean potential energy is clear from physical considerations. The potential energy of interaction between a particular particle and all the other particles between r and $r + dr$ is $u(r) \rho g(r) 4\pi r^2 dr$, where we have interpreted $\rho g(r)$ as the local density. The total potential energy is found by integrating over all values of r and multiplying by $N/2$. The factor of N is included because any of the N particles can be chosen as the particle at the origin; the factor of $1/2$ is included so that each pair interaction is counted only once.

We can derive a similar relation between the mean pressure and an integral over the product of $g(r)$ and the force $-du(r)/dr$. The pressure is related to the configurational part of the partition function by

$$P = -\frac{\partial F}{\partial V} = kT \frac{\partial \ln Q_N}{\partial V}. \quad (8.99)$$

For large V the pressure is independent of the shape of the container. For convenience, we assume that the container is a cube of linear dimension L , and we write the configuration integral Q_N as

$$Q_N = \int_0^L \cdots \int_0^L e^{-\beta U} dx_1 dy_1 dz_1 \cdots dx_N dy_N dz_N. \quad (8.100)$$

We first change variables so that the limits of integration are independent of L and let $\tilde{x}_i = x_i/L$, etc. Then

$$Q_N = V^N \int_0^1 \cdots \int_0^1 e^{-\beta U} d\tilde{x}_1 d\tilde{y}_1 d\tilde{z}_1 \cdots d\tilde{x}_N d\tilde{y}_N d\tilde{z}_N, \quad (8.101)$$

where U depends on the separation $r_{ij} = L[(\tilde{x}_i - \tilde{x}_j)^2 + (\tilde{y}_i - \tilde{y}_j)^2 + (\tilde{z}_i - \tilde{z}_j)^2]^{1/2}$. This change of variables allows us to take the derivative of Q_N with respect to V . We have

$$\begin{aligned} \frac{\partial Q_N}{\partial V} &= NV^{N-1} \int_0^1 \cdots \int_0^1 e^{-\beta U} d\tilde{x}_1 \cdots d\tilde{z}_N \\ &\quad - \frac{V^N}{kT} \int_0^1 \cdots \int_0^1 e^{-\beta U} \frac{\partial U}{\partial V} d\tilde{x}_1 \cdots d\tilde{z}_N, \end{aligned} \quad (8.102)$$

where

$$\frac{\partial U}{\partial V} = \sum_{i < j} \frac{du(r_{ij})}{dr_{ij}} \frac{dr_{ij}}{dL} \frac{dL}{dV} = \sum_{i < j} \frac{du(r_{ij})}{dr_{ij}} \frac{r_{ij}}{L} \frac{1}{3L^2}. \quad (8.103)$$

Now that we have differentiated Q_N with respect to V , we transform back to the original variables x_1, \dots, z_N . In the second term of (8.103) we also can use the fact that there are $N(N-1)/2$ identical contributions. We obtain

$$\frac{\partial \ln Q_N}{\partial V} = \frac{1}{Q_N} \frac{\partial Q_N}{\partial V} = \frac{N}{V} - \frac{\rho^2}{6VkT} \int r_{12} \frac{du(r_{12})}{dr_{12}} g(r_{12}) d\mathbf{r}_1 d\mathbf{r}_2, \quad (8.104)$$

and hence

$$\frac{PV}{NkT} = 1 - \frac{\rho}{6kT} \int_0^\infty r \frac{du(r)}{dr} g(r) 4\pi r^2 dr. \quad (\text{virial equation of state}) \quad (8.105)$$

The integrand in (8.105) is related to the virial in classical mechanics and is the mean value of the product $\mathbf{r} \cdot \mathbf{F}$ (cf. Goldstein).

8.7.2 Relation of $g(r)$ to static structure function $S(k)$

A measurement of the radial distribution function $g(r)$ probes distances on the order of the mean interparticle spacing, which is the order of Angstroms or 10^{-10} m. Such wavelengths can be obtained with neutrons or x-rays. To understand how an elastic scattering experiment can probe the

structure, we consider x-ray scattering. A typical x-ray wavelength is 1 Å, and the corresponding energy per photon is $\hbar\omega = hc/\lambda \approx 10^4$ eV. This energy is very large in comparison to the thermal energy of the particles in a liquid that is the order of kT or approximately 0.1 eV at room temperatures. Hence, collisions with the particles in a liquid will leave the photon energies almost unaltered and to a good approximation, the scattering can be treated as elastic.

In [Appendix 8A](#), we show that the scattered intensity of the x-rays is given by

$$I(\theta) = NI_1 S(k), \quad (8.106)$$

where the wave vector k is related to the scattering angle θ . The *static structure function* $S(k)$ is given by

$$S(k) = \frac{1}{N} \left\langle \sum_{i,j=1}^N e^{i\mathbf{k} \cdot (\mathbf{r}_i - \mathbf{r}_j)} \right\rangle. \quad (8.107)$$

It is easy to show that $S(k)$ is N if the particles are not correlated because in this case the only contribution to the sum in (8.107) is for $i = j$.

The static structure function $S(k)$ is a measure of the correlations between the positions of the atoms in the liquid and is related to the Fourier transform of $g(r)$ as we show in the following. We first divide the sum over i and j in (8.107) into self, $i = j$, and distinct, $i \neq j$, contributions. There are N of the former and $N(N-1)$ of the latter. We write

$$S(k) = 1 + \frac{1}{N} N(N-1) \langle e^{i\mathbf{k} \cdot (\mathbf{r}_1 - \mathbf{r}_2)} \rangle \quad (8.108)$$

$$= 1 + \frac{N(N-1)}{N} \frac{\int d\mathbf{r}_1 \dots d\mathbf{r}_N e^{i\mathbf{k} \cdot (\mathbf{r}_1 - \mathbf{r}_2)} e^{-\beta U}}{\int d\mathbf{r}_1 \dots d\mathbf{r}_N e^{-\beta U}}. \quad (8.109)$$

If we use the definition (8.81) of $g(\mathbf{r}_1, \mathbf{r}_2)$, we can write (8.109) as

$$S(k) = 1 + \frac{1}{N} \int d\mathbf{r}_1 d\mathbf{r}_2 \rho^2 g(\mathbf{r}_1, \mathbf{r}_2) e^{i\mathbf{k} \cdot (\mathbf{r}_1 - \mathbf{r}_2)}. \quad (8.110)$$

For a homogeneous liquid, $g(\mathbf{r}_1, \mathbf{r}_2)$ depends only on $|\mathbf{r}_1 - \mathbf{r}_2|$, and we obtain

$$S(k) = 1 + \rho \int d\mathbf{r} g(r) e^{i\mathbf{k} \cdot \mathbf{r}}. \quad (8.111)$$

It is customary to rewrite (8.111) as

$$\begin{aligned} S(k) - 1 &= \rho \int d\mathbf{r} [g(r) - 1] e^{i\mathbf{k} \cdot \mathbf{r}} + \rho \int d\mathbf{r} e^{i\mathbf{k} \cdot \mathbf{r}} \\ &= \rho \int d\mathbf{r} [g(r) - 1] e^{i\mathbf{k} \cdot \mathbf{r}} + \rho (2\pi)^3 \delta(\mathbf{k}). \end{aligned} \quad (8.112)$$

The contribution of the $\delta(\mathbf{k})$ term in (8.112) is unimportant because it is identically zero except when $\mathbf{k} = 0$, that is, for radiation not scattered by the atoms in the fluid. Hence, we can rewrite (8.112) in the desired form:

$$S(k) - 1 = \rho \int d\mathbf{r} [g(r) - 1] e^{i\mathbf{k} \cdot \mathbf{r}}. \quad (8.113)$$

From (8.113) we see that $S(k) - 1$ is the Fourier transform of $g(r) - 1$, and a measurement of the intensity of elastically scattered radiation yields the Fourier transform of the radial correlation function.

8.7.3 Variable number of particles

In a scattering experiment the beam samples a subset of the total volume. Because the number of particles in the subset fluctuates, we need to use the grand canonical ensemble to describe the measured value of $S(k)$. The energy and pressure equations (8.98) and (8.105) are identical in both ensembles, but the *compressibility equation*, which we derive in the following, can only be derived in the grand canonical ensemble because it relates the integral of $g(r) - 1$ and hence $S(k = 0)$ to fluctuations in the density.

The compressibility K_T is defined as (see (7.1))

$$K_T = -\frac{1}{V} \frac{\partial V}{\partial P} = \frac{1}{\rho} \frac{\partial \rho}{\partial P}. \quad (8.114)$$

We will use thermodynamic arguments in the following to show that

$$\rho K_T = \frac{1}{N} \left(\frac{\partial N}{\partial \mu} \right)_{T,V}. \quad (8.115)$$

If we combine (8.115) with (6.262), we see that the compressibility is related to the density fluctuations:

$$\rho K_T = \frac{1}{kT} \frac{\langle N^2 \rangle - \langle N \rangle^2}{\langle N \rangle}. \quad (8.116)$$

The thermodynamic argument proceeds as follows. We have that

$$d\Omega = -PdV - SdT - Nd\mu = -PdV - VdP. \quad (8.117)$$

We cancel the PdV term on both sides of (8.117) and solve for $d\mu$:

$$d\mu = \frac{V}{N} dP - \frac{S}{N} dT. \quad (8.118)$$

We let $v = V/N$; v is the volume per particle or specific volume. Because μ is an intensive quantity, we can express μ as $\mu(v, T)$ and obtain

$$\left(\frac{\partial \mu}{\partial v} \right)_T = v \left(\frac{\partial P}{\partial v} \right)_T. \quad (8.119)$$

We can change v by changing either V or N :

$$\left(\frac{\partial \mu}{\partial v} \right)_{T,V} = \frac{\partial N}{\partial v} \frac{\partial \mu}{\partial N} = -\frac{N^2}{V} \frac{\partial \mu}{\partial N} \quad (8.120)$$

$$\left(\frac{\partial \mu}{\partial v} \right)_{T,N} = \frac{\partial V}{\partial v} \frac{\partial \mu}{\partial V} = -N \frac{\partial \mu}{\partial V}. \quad (8.121)$$

However, the way in which v is changed cannot affect (8.119). Hence,

$$-\frac{N^2}{V}\left(\frac{\partial\mu}{\partial N}\right)_{T,V} = V\left(\frac{\partial P}{\partial V}\right)_{T,N}. \quad (8.122)$$

We leave it as an exercise to the reader to use (8.122) and (8.114) to obtain the desired relation (8.115).

We now relate the integral over $g(r)$ to the density fluctuations. In the grand canonical ensemble the probability density of finding n particular particles with positions $\mathbf{r}_1, \dots, \mathbf{r}_n$ in the range $d\mathbf{r}_1, \dots, d\mathbf{r}_n$ is given by

$$P_n(\mathbf{r}_1, \dots, \mathbf{r}_n) = \sum_{N=0}^{\infty} \frac{z^N}{N! \mathcal{Z}} \int e^{-\beta U_N} d\mathbf{r}_{n+1} \dots d\mathbf{r}_N, \quad (8.123)$$

where $z = e^{\beta\mu}$. There are $N(N-1)\dots(N-n+1) = N!/(N-n)!$ different sets of particles which can correspond to the n particles. Hence, the total probability that any n particles occupy these volume elements is given by

$$P_n(\mathbf{r}_1, \dots, \mathbf{r}_n) \equiv \rho^n g(\mathbf{r}_1, \dots, \mathbf{r}_n), \quad (8.124a)$$

$$= \sum_{N=0}^{\infty} \frac{z^N}{N-n)! \mathcal{Z}} \int \dots \int e^{-\beta U_N} d\mathbf{r}_{N+1}, \dots, d\mathbf{r}_N. \quad (8.124b)$$

As before, the main quantity of interest is $g(\mathbf{r}_1, \mathbf{r}_2)$.

From the definition of P_1 and P_2 , it follows that

$$\int P_1(\mathbf{r}_1) d\mathbf{r}_1 = \langle N \rangle, \quad (8.125)$$

and

$$\iint P_2(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2 = \langle N(N-1) \rangle. \quad (8.126)$$

We can use (8.126) and (8.125) to obtain

$$\iint [P_2(\mathbf{r}_1, \mathbf{r}_2) - P_1(\mathbf{r}_1)P_1(\mathbf{r}_2)] d\mathbf{r}_1 d\mathbf{r}_2 = \langle N^2 \rangle - \langle N \rangle^2 - \langle N \rangle. \quad (8.127)$$

The left-hand side of (8.127) is equal to $V\rho^2 \int [g(r) - 1] d^3r$ for a homogeneous system. Hence we obtain

$$N\rho \int [g(r) - 1] d^3r = \langle N^2 \rangle - \langle N \rangle^2 - \langle N \rangle, \quad (8.128)$$

or

$$1 + \rho \int [g(r) - 1] d^3r = \frac{\langle N^2 \rangle - \langle N \rangle^2}{\langle N \rangle}. \quad (8.129)$$

If we use the relation (8.115), we find the desired relation

$$1 + \rho \int [g(r) - 1] d^3r = \rho k T K_T. \quad (\text{compressibility equation}) \quad (8.130)$$

The relation (8.130), known as the *compressibility equation*, expresses K_T as an integral over $g(r)$ and holds only in the grand canonical ensemble. From the relation (8.113), we have

$$S(k=0) - 1 = \rho \int [g(r) - 1] d^3r,$$

and hence

$$S(k=0) = \rho k T K_T. \quad (8.131)$$

As mentioned, the condition (8.131) on $S(k=0)$ only applies in the grand canonical ensemble. What is $S(k=0)$ in the canonical ensemble? Why is the value of $S(k=0)$ different in these two ensembles?

8.7.4 Density expansion of $g(r)$

The density expansion of $g(r)$ is closely related to the density expansion of the free energy. Instead of deriving the relation here, we show the first few diagrams corresponding to the first two density contributions. We write

$$g(r) = e^{-\beta u(r)} y(r), \quad (8.132)$$

and

$$y(r) = \sum_{n=0}^{\infty} \rho^n y_n(r). \quad (8.133)$$

The function $y(r)$ has the convenient property that $y(r) \rightarrow 1$ in the limit of low density. The diagrams for $y(r)$ have two fixed points represented by open circles corresponding to particles 1 and 2. The other particles are integrated over the volume of the system. The diagrams for $y_1(r)$ and $y_2(r)$ are shown in Figure 8.10. The corresponding integrals are

$$y_1(r) = \int f(r_{13}) f(r_{23}) d\mathbf{r}_3, \quad (8.134)$$

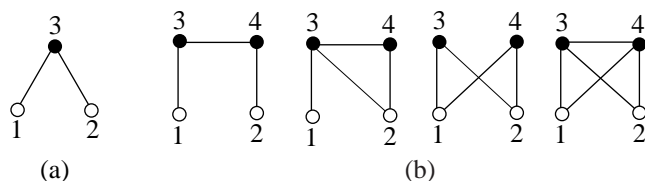
and

$$y_2(r) = \frac{1}{2} \int [2f_{13}f_{34}f_{42} + 4f_{13}f_{34}f_{42}f_{32} + f_{13}f_{42}f_{32}f_{14} + f_{13}f_{34}f_{42}f_{32}f_{14}] d\mathbf{r}_3 d\mathbf{r}_4. \quad (8.135)$$

Note that the diagrams in Figure 8.10 and hence the integrals in (8.134) and (8.135) are closely related to the diagrams for the virial coefficients.

8.8 Computer Simulation of Liquids

We have already discussed several models that can be solved analytically and be used to increase our understanding of gases and crystalline solids. For example, the ideal gas can be used as the starting point for a density expansion, and the harmonic model provides an idealized model of a solid. For liquids no simple model exists. The closest candidate is the hard sphere model, the

Figure 8.10: The diagrams contributing to (a) $y_1(r)$ and (b) $y_2(r)$.

properties of which can be calculated approximately using the various methods described in the following sections.

The development of a microscopic theory of liquids was hampered for many years by the lack of a convenient small expansion parameter. One of the first successes of the computer simulations of simple liquids is that they lead to the development of a microscopic theory of liquids based on the realization that the details of the weak attractive part of the interparticle interaction are unimportant. The implication of this realization is that $g(r)$ does not depend strongly on the temperature. As we will find in Problem 8.19, simulations have also taught us that the behavior of $g(r)$ is also insensitive to the details of the repulsive part of the interaction. Hence $g(r)$ for a system of system of hard spheres is a good approximation to $g(r)$ for Lennard-Jones systems at the same density. Moreover, we can simulate hard sphere systems and obtain essentially exact solutions for $g(r)$ and the equation of state.

In the Monte Carlo implementation of the canonical ensemble, a particle is chosen at random and is moved randomly to a new position, and the change in energy of the system, ΔE , is calculated. Why are the velocities of the particles irrelevant? As discussed in Section 4.11, we can do a Monte Carlo simulation of the equilibrium properties of a system of particles by using the Metropolis algorithm. In this algorithm, a particle is chosen at random and randomly displaced. The move is accepted if the change in energy $\Delta E < 0$; otherwise a random number r between 0 and 1 is generated and the move is accepted if $r \leq e^{-\beta \Delta E}$. Otherwise, the move is rejected, and the new configuration is identical to the old configuration.

For a system of hard spheres, the rules are even simpler. If the trial position of a particle does not overlap another sphere, the trial position is accepted; otherwise it is rejected.

Problem 8.19. Use the applet at [xx](#) to determine the behavior of $g(r)$ by doing Monte Carlo simulations for different interactions, densities, and temperatures. (a) For a given interaction, describe qualitatively how $g(r)$ changes with the density ρ at a given temperature T . (b) How does $g(r)$ change with T for a given ρ ? (c) Consider the Lennard-Jones and hard sphere interactions and confirm that the form of $g(r)$ depends more on the repulsive part of the interaction and only weakly on the attractive part. (d) Confirm that the function $y(r)$ introduced in (8.132) depends less sensitively on the interaction than does $g(r)$ itself.

8.9 Perturbation Theory of Liquids

The physical picture of a liquid that we developed in Section 8.8 from several computer simulations suggests that the repulsive part of the interaction dominates the structure of a liquid, and the attractive part of the interaction can be treated as a perturbation. In the following we develop a perturbation theory of liquids in which the unperturbed or reference system is taken to be a system of hard spheres rather than an ideal gas. The idea is that the effect of the difference between the hard sphere interaction and the real interaction should be small. We will see that if we choose the effective diameter of the hard spheres in a clever way, the difference can be minimized.

We begin by writing the potential energy as

$$U = U_{\text{ref}} + U_1, \quad (8.136)$$

where U_{ref} is the potential energy of the reference system, and U_1 will be treated as a perturbation. The configurational integral Q_N can be written as

$$Q_N = \int \cdots \int e^{-\beta(U_{\text{ref}} + U_1)} d\mathbf{r}_1 \cdots d\mathbf{r}_N. \quad (8.137)$$

We multiply and divide the right-hand side of (8.137) by

$$Q_{\text{ref}} = \int \cdots \int e^{-\beta U_{\text{ref}}} d\mathbf{r}_1 \cdots d\mathbf{r}_N, \quad (8.138)$$

and write

$$\begin{aligned} Q_N &= \int \cdots \int e^{-\beta U_{\text{ref}}} d\mathbf{r}_1 \cdots d\mathbf{r}_N \frac{\int \cdots \int e^{-\beta(U_{\text{ref}} + U_1)} d\mathbf{r}_1 \cdots d\mathbf{r}_N}{Q_{\text{ref}}}, \\ &= Q_{\text{ref}} \int \cdots \int P_{\text{ref}} e^{-\beta U_1} d\mathbf{r}_1 \cdots d\mathbf{r}_N, \end{aligned} \quad (8.139)$$

where

$$P_{\text{ref}} = \frac{e^{-\beta U_{\text{ref}}}}{Q_{\text{ref}}}. \quad (8.140)$$

We see that we have expressed Q_N in (8.139) as the average of $\exp(-\beta U_1)$ over the reference system. We write

$$Q_N = Q_{\text{ref}} \langle e^{-\beta U_1} \rangle_{\text{ref}}, \quad (8.141)$$

and

$$-\beta F_1 = \ln \langle e^{-\beta U_1} \rangle_{\text{ref}}, \quad (8.142)$$

$$= \sum_{n=1}^{\infty} \frac{(-\beta)^n M_n}{n!}. \quad (8.143)$$

The brackets $\langle \dots \rangle_{\text{ref}}$ denote an average over the microstates of the reference system. That is, the microstates are weighted by the probability P_{ref} . Note that in Section 8.2, the brackets $\langle \dots \rangle$ included a factor $1/V$ with each integral over \mathbf{r} . This factor is omitted in this section and in the following.

Problem 8.20. Show that if we choose the reference system to be an ideal gas, the above expressions reduce to formal expressions similar to those considered in Section 8.2.

The leading term in (8.143) is

$$\begin{aligned} M_1 &= \langle U_1 \rangle_{\text{ref}} = \sum_{i < j=1}^N \langle u_1(r_{ij}) \rangle_{\text{ref}}, \\ &= \frac{N(N-1)}{2} \frac{1}{Q_{\text{ref}}} \int \dots \int e^{-\beta U_{\text{ref}}} u_1(r_{12}) d\mathbf{r}_1 \dots d\mathbf{r}_N. \end{aligned} \quad (8.144)$$

The radial distribution function of the reference system is given by

$$\rho^2 g_{\text{ref}}(r_{12}) = N(N-1) \frac{\int e^{-\beta U_{\text{ref}}} d\mathbf{r}_3 \dots d\mathbf{r}_N}{Q_{\text{ref}}}. \quad (8.145)$$

Hence

$$\begin{aligned} M_1 &= \frac{\rho^2}{2} \int u_1(r_{12}) g_{\text{ref}}(r_{12}) d\mathbf{r}_1 d\mathbf{r}_2 \\ &= \frac{\rho N}{2} \int u_1(r) g_{\text{ref}}(r) d^3r, \end{aligned} \quad (8.146)$$

and

$$F = F_{\text{ref}} + \frac{\rho N}{2} \int u_1(r) g_{\text{ref}}(r) d^3r. \quad (8.147)$$

Note that F_{ref} in (8.147) is the free energy of the reference system. We evaluate (8.147) with increasing sophistication in the following two subsections.

8.9.1 The van der Waals Equation

As we have mentioned, the reason for the success of the reference theory of liquids is that the structure of a simple liquid is determined primarily by the repulsive part of the potential. The main effect of the remaining part of the potential is to provide a uniform potential in which the particles move. This idea is not new and is the basis of the van der Waals equation of state. We now show how the van der Waals equation of state can be derived from the perturbation theory developed in Section 8.9 about the hard sphere reference potential.

If we assume that $g_{\text{ref}}(r)$ has the simple form

$$g_{\text{ref}}(r) = \begin{cases} 0 & r < \sigma \\ 1 & r \geq \sigma, \end{cases} \quad (8.148)$$

then M_1 in (8.146) can be written as

$$M_1 = 2\pi\rho N \int_{\sigma}^{\infty} u_1(r) r^2 dr = -\rho a N, \quad (8.149)$$

where

$$a = -2\pi \int_{\sigma}^{\infty} u_1(r) r^2 dr. \quad (8.150)$$

Our next job is to approximate F_{ref} . Until recently, the equation of state of hard spheres was not known very accurately. A simple way of approximating F_{ref} is based on the assumption that the effective volume available to a particle in a fluid is smaller than the volume available in an ideal gas. In this spirit we assume that F_{ref} has the same form as it does for an ideal gas (see (6.28)), but with V replaced by V_{eff} . We write

$$\frac{F_{\text{ref}}}{NkT} = 3 \ln \lambda - 1 - \ln V_{\text{eff}} + \ln N, \quad (8.151)$$

where

$$V_{\text{eff}} = V - V_0, \quad (8.152)$$

and

$$V_0 = Nb = \frac{1}{2} N \frac{4\pi\sigma^3}{3}. \quad (8.153)$$

In (8.153) we have accounted for the fact that only half of the volume of a sphere can be assigned to a given particle. The corresponding equation of state with the above approximations for M_1 , F_{ref} , and V_{eff} is given by

$$\frac{PV}{NkT} = \frac{1}{1 - b\rho} - \frac{a\rho}{kT}. \quad (\text{van der Waals equation}) \quad (8.154)$$

Equation (8.154) is the familiar van der Waals equation of state and gives results that are in poor agreement with experimental data, especially if a is calculated using (8.150). Better results can be obtained by regarding a and b as free parameters chosen to fit a measured equation of state. However, agreement with experimental data is only qualitative. Nevertheless, the van der Waals equation of state predicts a liquid-gas transition as we will discuss in Section xx.

8.9.2 Chandler-Weeks-Andersen theory

We now develop a more systematic way of choosing the reference potential. The most appropriate way of dividing the interparticle potential into a reference part and a perturbative part is not obvious. One way is to separate the potential into positive and negative contributions. This choice implies that we should separate the Lennard-Jones potential at $r = \sigma$. Another way is to separate the potential into a part containing all the repulsive forces and a part containing all the attractive forces. This choice is the one adopted by the Chandler-Weeks-Andersen theory. We write the Lennard-Jones potential as

$$u(r) = u_{\text{ref}}(r) + u_1(r), \quad (8.155)$$

and add and subtract a factor of ϵ to write:

$$u_{\text{ref}}(r) = \begin{cases} u(r) + \epsilon & r < 2^{1/6}\sigma \\ 0 & r \geq 2^{1/6}\sigma \end{cases} \quad (8.156)$$

$$u_1(r) = \begin{cases} -\epsilon & r < 2^{1/6}\sigma \\ u(r) & r \geq 2^{1/6}\sigma \end{cases} \quad (8.157)$$

Note that we have added and subtracted a factor of ϵ to $u(r)$ for $r < 2^{1/6}\sigma$.

Problem 8.21. (a) Plot the dependence of $u_1(r)$ on r and confirm that $u_1(r)$ is a slowly varying function of r .

Because the reference system in the Chandler-Weeks-Andersen theory is not a hard sphere interaction, the properties of the reference system are not well known and further approximations are necessary. In the Chandler-Weeks-Andersen approach, the reference system is approximated by hard spheres with a temperature and density-dependent diameter d . As we have seen, the function $y(r) = e^{\beta u(r)} g(r)$ is a slowly varying function whose shape does not depend sensitively on the form of the interaction. In the Chandler-Weeks-Andersen theory $y(r)$ and the reference free energy are approximated by their hard sphere forms:

$$g_{\text{ref}}(r) \approx e^{-\beta u_{\text{ref}}(r)} y_{\text{hs}}(r, d), \quad (8.158)$$

and

$$F_{\text{ref}} = F_{\text{hs}}(d). \quad (8.159)$$

F_{hs} and y_{hs} are the free energy and the distribution functions for hard spheres of diameter d . The value of d at a given value of ρ and T is found by requiring that the compressibility of the reference system equal the compressibility of a hard sphere system of diameter d via the relation (see (8.130)):

$$kT \frac{\partial \rho}{\partial P} = 1 + \rho \int [g(r) - 1] d\mathbf{r}. \quad (8.160)$$

We write

$$\int [e^{-\beta u_{\text{ref}}} y_{\text{hs}}(r, d) - 1] d\mathbf{r} = \int e^{-\beta u_{\text{hs}}} [y_{\text{hs}}(r, d) - 1] d\mathbf{r}, \quad (8.161)$$

where u_{hs} is the hard sphere interaction. The numerical solution of (8.161) yields a unique value of d as a function of T and ρ .

8.10 *The Ornstein-Zernicke Equation

We have seen that we can derive a density expansion for the pressure and for the radial distribution function $g(r)$. However, we do not expect to obtain very accurate results by keeping only the first several terms. An alternative procedure is to express $g(r)$ in terms of the direct correlation function $c(r)$. The latter function is generally a more slowly varying of r . An approximation for $c(r)$ then yields a better approximation for $g(r)$ than would be found by approximating $g(r)$ directly.

Because $g(r) \rightarrow 1$ for $r \gg 1$, it is convenient to define the function $h(r)$ by the relation

$$h(r) = g(r) - 1 \quad (8.162)$$

so that $h(r) \rightarrow 0$ for sufficiently large r and $h(r) = 0$ for an ideal gas. The function $h(r)$ describes the correlations between two particles. It also is convenient to introduce a third correlation function, $c(r)$, known as the *direct correlation function*. We can think of the total correlation between particles 1 and 2 as due to the direct correlation between them and the indirect correlation due to the presence of increasingly larger numbers of intermediate particles. We define $c(r)$ by the relation (for a homogeneous and isotropic system):

$$h(r) = c(r) + \rho \int c(|\mathbf{r} - \mathbf{r}'|) h(\mathbf{r}') d\mathbf{r}'. \quad (\text{Ornstein-Zernicke equation}) \quad (8.163)$$

The relation (8.163) was first proposed in 1914 and is known as the *Ornstein-Zernicke equation*. It is plausible that the range of $c(r)$ is comparable to the range of the potential $u(r)$, and that $h(r)$ is longer ranged than $u(r)$ due to the effects of the indirect correlations. That is, in general, $c(r)$ has a much shorter range than $h(r)$. To lowest order in the density, $c(r) = f(r)$ and for large r , $c(r) = -\beta u(r)$ as expected.

We can find $c(r)$ from $h(r)$ by introducing the Fourier transforms

$$c(k) = \int c(r) e^{i\mathbf{k}\cdot\mathbf{r}} d\mathbf{r}, \quad (8.164)$$

and

$$h(k) = \int h(r) e^{i\mathbf{k}\cdot\mathbf{r}} d\mathbf{r}. \quad (8.165)$$

If we take the Fourier transform of both sides of (8.163), we find that

$$h(k) = c(k) + \rho c(k)h(k), \quad (8.166)$$

or

$$c(k) = \frac{h(k)}{1 + \rho h(k)}, \quad (8.167)$$

and

$$h(k) = \frac{c(k)}{1 - \rho c(k)}. \quad (8.168)$$

8.11 *Integral Equations for $g(r)$

The Ornstein-Zernicke equation can be used to motivate several approximate integral equations for $g(r)$ that are applicable to dense liquids. The most useful of these equations for systems with short-range repulsive interactions is known as the *Percus-Yevick equation*. Although this equation can be derived using graph theory and corresponds to ignoring an (infinite) subset of diagrams for $c(r)$, the derivation does not add much physical insight. Instead we will only summarize the nature of the equation.

Percus-Yevick equation. It is convenient to consider the function $y(r)$ defined by (8.132) instead of the function $g(r)$ because $y(r)$ is more slowly varying. One way to motivate the Percus-Yevick equation is to note that to lowest order in the density, $y(r) = \rho y_1(r)$, where y_1 is given by (8.134). Similarly, the lowest order density contributions to $c(r)$ are $c_0(r) = f(r)$ and $c_1(r) = f(r)y_1(r)$. We generalize this relation between $c(r)$ and $y(r)$ and assume that

$$c(r) = f(r)y(r) = [1 - e^{\beta u(r)}] g(r). \quad (8.169)$$

Equation (8.169) is correct to first order in the density. Note that the $c(r)$ as given by (8.169) is a short-range function, that is, the same range as $f(r)$ or $u(r)$. If we substitute the approximation (8.169) into the Ornstein-Zernicke equation, we find

$$y(r_{12}) = 1 + \rho \int f(r_{13})y(r_{13})h(r_{23}) d\mathbf{r}_3. \quad (\text{Percus-Yevick equation}) \quad (8.170)$$

Equation (8.170) is an example of a nonlinear integral equation. In general, the Percus-Yevick must be solved numerically, but it can be solved analytically for hard spheres (see Appendix 8C). The analytical solution of the Percus-Yevick equation for hard spheres can be expressed as

$$c(r) = \begin{cases} -(1-\eta)^{-4}[(1-2\eta)^2 - 6\eta(1+\frac{1}{2}\eta)^2(r/\sigma) + \frac{1}{2}\eta(1+2\eta)^2(r/s)^2] & r < \sigma \\ 0, & r > \sigma. \end{cases} \quad (8.171)$$

Given $c(r)$, we can find $g(r)$. Because the derivation is tedious, we will omit it and give only the result for $g(r)$ at contact:

$$g(\sigma) = \lim_{\epsilon \rightarrow 0^+} g(r = \sigma + \epsilon) = \frac{1 + \frac{1}{2}\eta}{(1-\eta)^2}. \quad (8.172)$$

Given the Percus-Yevick result for $g(\sigma)$ we can find the corresponding approximate equation of state for hard spheres from the virial equation of state (8.105). For a discontinuous potential we can simplify the form of (8.105). We write

$$\frac{du}{dr}g(r) = \frac{du}{dr}e^{-\beta u(r)}y(r) = -\frac{1}{\beta} \frac{d}{dr}e^{-\beta u(r)}y(r). \quad (8.173)$$

For hard spheres we know that $e^{-\beta u(r)} = 0$ for $r < \sigma$ and $e^{-\beta u(r)} = 1$ for $r > \sigma$. Hence, we can write $e^{-\beta u(r)} = \Theta(r - \sigma)$ and $de^{-\beta u(r)}/dr = \delta(r - \sigma)$. Using this result we have that the pressure of a hard sphere fluid is given by

$$P = \rho kT \left[1 + \frac{2\pi}{3} \rho \sigma^3 g(\sigma) \right]. \quad (8.174)$$

If we substitute (8.172) into (8.174), we find the virial equation of state for a hard sphere fluid

$$P = \rho kT \frac{1 + 2\eta + 3\eta^2}{(1-\eta)^2}, \quad (\text{virial equation of state}) \quad (8.175)$$

where $\eta = \pi\rho\sigma^3/6$.

An alternative way of calculating the pressure is to use the compressibility relation (8.130). We can write (8.130) in terms of $c(r)$ rather than $g(r) - 1$ by using the Ornstein-Zernicke equation:

$$g(r) - 1 = c(r) + \rho \int c(|\mathbf{r} - \mathbf{r}'|)[g(\mathbf{r}') - 1]d^3r'. \quad (8.176)$$

We multiply both sides of this equation by d^3r and integrate noting that $\int c(|\mathbf{r} - \mathbf{r}'|)d^3r = \int c(r)d^3r$ and rearranging the results to find

$$\int [g(r) - 1]d^3r = \frac{\int c(r)d^3r}{1 - \rho \int c(r)d^3r}. \quad (8.177)$$

Finally we combine (8.177) with (8.130) to find

$$(kT \frac{\partial \rho}{\partial P})^{-1} = 1 - \rho \int c(r)d^3r. \quad (8.178)$$

If we substitute the Percus-Yevick result (8.171) into (8.178) and integrate, we find

$$P = \rho kT \left[\frac{1 + \eta + \eta^2}{(1 - \eta)^3} \right]. \quad (\text{compressibility equation of state}) \quad (8.179)$$

If the Percus-Yevick equation were exact, the two ways of obtaining the equation of state would yield identical results.

The Percus-Yevick equation gives reasonable predictions for $g(r)$ and the equation of state for fluid densities. However, it predicts finite pressures for $\eta < 1$ even though the maximum density is $\rho_{\max} = \sqrt{2}/\sigma^3$ or $\eta_{\max} = \sqrt{2}\pi/6 \approx 0.74$.

Mean spherical approximation. Another simple closure approximation for the Ornstein-Zernicke equation can be motivated by the following considerations. Consider a fluid whose particles interact via a pair potential of the form

$$u(r) = \begin{cases} \infty & r < \sigma \\ v(r) & r > \sigma \end{cases} \quad (8.180)$$

where $v(r)$ is a continuous function of r . Because of the hard sphere cutoff, $g(r) = 0$ for $r < \sigma$. For large r the Percus-Yevick approximation for $c(r)$ reduces to

$$c(r) = -\beta v(r). \quad (8.181)$$

The *mean spherical approximation* is based on the assumption that (8.181) holds not just for large r , but for all r . Hence, the mean spherical approximation is

$$c(r) = -\beta v(r) \quad r > \sigma \quad (8.182a)$$

and

$$g(r) = 0 \quad r < \sigma \quad (8.182b)$$

together with the Ornstein-Zernicke equation.

The *hypernetted-netted chain approximation* is another useful integral equation for $g(r)$. It is equivalent to setting

$$c(r) = f(r)y(r) + y(r) - 1 - \ln y(r). \quad (\text{hyper-netted chain equation}) \quad (8.183)$$

If we analyze the Percus-Yevick and the hypernetted-chain approximations in terms of a virial expansion (see Problem 8.32), we find that the hypernetted-chain approximation appears to be more accurate than the Percus-Yevick approximation. However, it turns out that the Percus-Yevick approximation works better for hard spheres and other short-range potentials. In contrast, the hypernetted-chain approximation works better for the one-component plasma and other long-range potentials.

8.12 *Coulomb Interactions

The virial or density expansion of the free energy and other thermodynamic quantities is not applicable to a gas consisting of charged particles interacting via the Coulomb potential. For

example, we found in Problem 8.8 that the second virial coefficient does not exist if the interparticle potential $u(r)$ decreases less rapidly than $1/r^3$ at large distances. This divergence is symptomatic of the fact that a density expansion is meaningless for a system of particles interacting via long-range forces.

8.12.1 Debye-Hückel Theory

The simplest model of a system of particles interacting via the Coulomb potential is a gas of mobile electrons moving in a fixed, uniform, positive background. The charge density of the positive background is chosen to make the system overall neutral. Such a system is known as an electron gas or a *one-component plasma*.

Debye and Hückel developed a theory that includes the interactions between charged particles in an approximate, but very clever way. Consider an electron at $\mathbf{r} = 0$. The average electric potential $\phi(\mathbf{r})$ in the neighborhood of $\mathbf{r} = 0$ is given by Poisson's equation:

$$\begin{aligned}\nabla^2\phi(\mathbf{r}) = & -4\pi[(\text{negative point charge at origin}) \\ & + (\text{density of positive uniform background}) \\ & + (\text{density of negative electron gas charge})]\end{aligned}\quad (8.184)$$

or

$$\nabla^2\phi(\mathbf{r}) = -4\pi[-e\delta(\mathbf{r}) + e\rho - e\rho(\mathbf{r})], \quad (8.185)$$

where ρ is the mean number density of the electrons and the uniform positive background, and $\rho(\mathbf{r})$ is the number density of the electrons in the vicinity of $\mathbf{r} = 0$. We assume that to a good approximation $\rho(\mathbf{r})$ is given by the Boltzmann factor

$$\rho(\mathbf{r}) = \rho e^{e\phi(\mathbf{r})/kT}. \quad (8.186)$$

If we combine (8.185) and (8.186), we obtain the *Poisson-Boltzmann* equation for $\phi(\mathbf{r})$:

$$\nabla^2\phi(\mathbf{r}) = 4\pi e[\delta(\mathbf{r}) - \rho + \rho e^{\phi(\mathbf{r})/kT}]. \quad (8.187)$$

Equation (8.187) is a nonlinear differential equation for $\phi(\mathbf{r})$. For $\phi/kT \ll 1$, we can write $e^{\beta\phi(\mathbf{r})} \approx 1 + \beta\phi(\mathbf{r})$. In this way we obtain the linear Poisson-Boltzmann equation

$$(\nabla^2 - \kappa^2)\phi(r) = 4\pi e\delta(r), \quad (8.188)$$

where κ^2 is given by

$$\kappa^2 = \frac{4\pi\rho e^2}{kT}. \quad (8.189)$$

We look for solutions to (8.187) that are spherically symmetric. The solution of (8.189) can be shown to be

$$\phi(r) = -e\frac{e^{-\kappa r}}{r}. \quad (8.190)$$

The energy of the other electrons in the potential ϕ is $u = -e\phi$ so that the effective energy of interaction is given by

$$u_{\text{eff}}(r) = e^2\frac{e^{-\kappa r}}{r}. \quad (8.191)$$

The result (8.190) or (8.191) shows that the electrons collaborate in such a way as to screen the potential of a given electron over a distance $\lambda_D = 1/\kappa$. The quantity λ_D is called the *Debye length*. Note that to use statistical arguments, it is necessary that many particles have approximately the same potential energy, that is, many particles need to be within the range λ_D of ϕ . This requirement can be written as $\rho\lambda_D^3 \gg 1$ or

$$\rho\lambda_D^3 = \left(\frac{kT}{4\pi e^2 \rho^{1/3}}\right)^{3/2}. \quad (8.192)$$

The condition (8.192) holds in the limit of low density and high temperature.

Problem 8.22. Show that (8.192) is equivalent to the condition that the mean interaction energy is much smaller than the mean kinetic energy.

8.12.2 Linearized Debye-Hückel approximation

The Ornstein-Zernicke is exact, but $h(r)$ and $c(r)$ are not known in general and some type of closure approximation must be made. The simplest approximation is to assume that $c(r)$ is given by

$$c(r) = -\beta u(r) \quad (8.193)$$

for all r . For the one component plasma, $u(r) = e^2/r$, $u(k) = 4\pi e^2/k^2$, and (8.193) implies that

$$c(k) = -\beta \frac{4\pi e^2}{k^2}. \quad (8.194)$$

If we substitute (8.194) into (8.168), we find

$$h(k) = -\frac{4\pi\beta e^2}{k^2 + \kappa^2}, \quad (8.195)$$

where $\kappa^2 = 4\pi\beta\rho e^2$. Hence, we have

$$h(r) = -\frac{\beta e^2}{r} e^{-\kappa r}, \quad (8.196)$$

and

$$g(r) = 1 - \frac{\beta e^2}{r} e^{-\kappa r}. \quad (8.197)$$

Note that in this approximation $g(r)$ becomes negative at small r . This failure can be corrected by letting

$$g(r) = \exp\left(-\frac{\beta e^2}{r} e^{-\kappa r}\right). \quad (8.198)$$

Equation (8.198) is the Debye-Hückel form of $g(r)$.

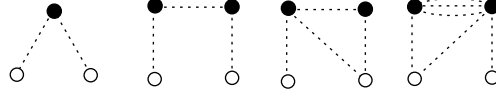


Figure 8.11: The first several diagrams for the high temperature expansion of $g(r)$. The bonds represent the Coulomb interaction $u(r) = e^2/r$.

8.12.3 Diagrammatic Expansion for Charged Particles

Recall that we derived the density expansion of the free energy by first doing a high temperature expansion. Although individual terms in this expansion diverge at short separations for systems with a strongly repulsive interaction, the divergence can be removed by rearranging the expansion so that all terms of a given density were grouped together and summed. However, an expansion in terms of the density and the interaction of small numbers of particles makes no sense if the interaction is long-range. We now discuss how to group the individual terms in the high temperature expansion so that the divergence at large separations for the Coulomb potential is removed.

Instead of considering the diagrammatic expansion for the free energy, we consider the diagrammatic expansion for $g(r)$, because the latter is easier to interpret physically. It is convenient to write $g(r)$ in the form

$$g(r) = e^{-\beta\psi(r)}, \quad (8.199)$$

where $\psi(r)$ is the *potential of mean force*. Instead of deriving the high temperature or low density expansion for $\psi(r)$, we will use our intuition to write down what we think are the relevant diagrams. Some typical diagrams for $\psi(r)$ are shown in Figure 8.11. It is easy to show that the contribution of the individual diagrams diverges for the Coulomb potential. Recall that we obtained the low density expansion by first summing up all possible u bonds between two particles. Because the Coulomb interaction is long-range, it is plausible that we should first sum up the infinite class of diagrams corresponding to the maximum number of particles for a given number of bonds. The first several ring diagrams are shown in Figure 8.12 and are called *ring diagrams*. Because we know that the Coulomb interaction is screened, we expect that we should add up the contributions of all the ring diagrams before we include the contributions of other diagrams.

The contribution of the ring diagrams to $\psi(r)$ is given by

$$\begin{aligned} -\beta\psi(r) = & -\beta u(r) + \rho \int [-\beta u(r_{13})][-\beta u(r_{32})] d^3 r_3 \\ & + \rho^2 \int [-\beta u(r_{13})][-\beta u(r_{34})][-\beta u(r_{42})] d^3 r_3 d^3 r_4 + \dots, \end{aligned} \quad (8.200)$$

where $r = r_{12}$. The structure of the integrals in (8.200) is the same as the convolution integral discussed in Appendix 8A. We follow the same procedure and take the spatial Fourier transform of both sides of (8.200). The result can be written as

$$-\beta\psi(k) = -\beta u(k) + \rho[-\beta u(k)]^2 + \rho^2[-\beta u(k)]^3 + \dots, \quad (8.201)$$

where $u(k)$ is the Fourier transform of $u(r) = e^2/r$. In Problem 8.34 it is shown that

$$u(k) = \frac{4\pi e^2}{k^2}. \quad (8.202)$$

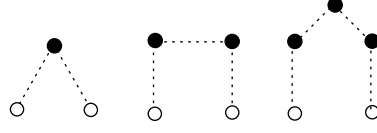


Figure 8.12: The first several ring diagrams for $g(r)$. The bonds represent the Coulomb interaction $u(r) = e^2/r$.

Because the terms in (8.201) form a geometrical series, we obtain

$$-\beta\psi(k) = \frac{-\beta u(k)}{1 + \rho\beta u(k)} \quad (8.203)$$

$$\begin{aligned} &= -\frac{\beta 4\pi e^2}{k^2 + \rho\beta 4\pi e^2} \\ &= -\beta \frac{4\pi e^2}{k^2 + \kappa^2}, \end{aligned} \quad (8.204)$$

where κ is given by (8.189). Hence

$$\psi(k) = \frac{4\pi e^2}{k^2 + \kappa^2} \quad (8.205)$$

and

$$\psi(r) = \frac{e^2}{kT} \frac{\epsilon^{-\kappa r}}{r}. \quad (8.206)$$

The form of (8.206) implies that

$$g(r) - 1 = -\frac{e^2}{kT} \frac{\epsilon^{-\kappa r}}{r}. \quad (8.207)$$

From (8.207) we see that the effective interaction is the Debye-Hückel screened potential. Note that the screening of the interaction between any two electrons is due to the collective effect of all the electrons.

Problem 8.23. The total energy per particle of the one-component plasma is given by

$$\frac{E}{N} = \frac{3}{2}NkT + \frac{\rho}{2} \int [g(r) - 1] u(r) d^3r. \quad (8.208)$$

The factor of -1 on the right-hand side of (8.208) is due to the uniform positive background. Substitute the approximation (8.207) for $g(r)$ and show that

$$\frac{E}{N} = \frac{3}{2}NkT - \frac{1}{2} \frac{e^2}{\lambda_D}. \quad (8.209)$$

8.13 Vocabulary

density expansion, virial coefficients

Mayer f function
 cumulant, high temperature expansion
 disconnected, reducible, and irreducible diagrams
 ladder diagrams, ring diagrams
 radial distribution function $g(r)$
 static structure function $S(k)$
 reference theory of liquids
 Debye-Hückel theory

Appendix 8A: The third virial coefficient for hard spheres

In Problem 8.4 we showed that $B_2 = 2\pi\sigma^3/3$ for hard spheres. The form of the third virial coefficient B_3 is (see (8.10b))

$$B_3 = -\frac{1}{3V} \int f(|\mathbf{r}_1 - \mathbf{r}_2|) f(|\mathbf{r}_1 - \mathbf{r}_3|) f(|\mathbf{r}_2 - \mathbf{r}_3|) d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3. \quad (8.210)$$

B_3 also can be calculated by geometrical considerations, but these considerations test one's geometrical intuition. An easier way to proceed is to take advantage of the fact that (8.210) is an example of a convolution integral which can be expressed more simply in terms of the Fourier transform of $f(r)$. We introduce the Fourier transform of $f(r)$ as

$$\begin{aligned} f(k) &= \int f(r) e^{-i\mathbf{k}\cdot\mathbf{r}} d^3r \\ &= 4\pi \int_0^\infty r^2 f(r) \frac{\sin kr}{kr} dr \end{aligned} \quad (8.211)$$

The form (8.211) follows from (8.211) by choosing \mathbf{k} to be along the z -axis of a spherical coordinate system. This choice allows us to write $\mathbf{k} \cdot \mathbf{r} = kr \cos \theta$ and $d^3r = r^2 dr \sin \theta d\theta d\phi$ and do the integration over θ and ϕ (see Problem 8.35). Because $f(r) = -1$ for $0 < r < 1$ and $f(r) = 0$ for $r > 1$, we can do the integral in (8.211) to find

$$f(k) = 4\pi\sigma^3 \left[\frac{\cos k\sigma}{(k\sigma)^2} - \frac{\sin k\sigma}{(k\sigma)^3} \right]. \quad (8.212)$$

The term in brackets in (8.212) can be related to a half-integer Bessel Function.

The main trick is to express B_3 in (8.210) in terms of $f(k)$. To do so, we introduce the inverse transform

$$f(r) = \int \frac{d^3k}{(2\pi)^3} f(k) e^{i\mathbf{k}\cdot\mathbf{r}} \quad (8.213)$$

for any function $f(r)$. If we substitute (8.213) into (8.210), we find

$$B_3 = -\frac{1}{3V} \int \frac{d\mathbf{k}_1}{(2\pi)^3} \frac{d\mathbf{k}_2}{(2\pi)^3} \frac{d\mathbf{k}_3}{(2\pi)^3} e^{i\mathbf{k}_1 \cdot (\mathbf{r}_2 - \mathbf{r}_1)} e^{i\mathbf{k}_2 \cdot (\mathbf{r}_3 - \mathbf{r}_1)} e^{i\mathbf{k}_3 \cdot (\mathbf{r}_3 - \mathbf{r}_2)} f(\mathbf{k}_1) f(\mathbf{k}_2) f(\mathbf{k}_3) d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3. \quad (8.214)$$

We first group the exponentials in (8.214) so that we can do the integrals over \mathbf{r}_1 and \mathbf{r}_2 by using the property that

$$\int d^3r e^{i\mathbf{k} \cdot \mathbf{r}} = (2\pi)^3 \delta(\mathbf{k}). \quad (8.215)$$

The result is that $\mathbf{k}_1 = \mathbf{k}_3 = -\mathbf{k}_2$. The integral over \mathbf{r}_3 gives a factor of V . Because f depends only on $|\mathbf{k}|$, we can write (8.214) as

$$B_3 = -\frac{1}{3} \int \frac{d^3k}{(2\pi)^3} f(k)^3, \quad (8.216)$$

where $f(k)$ is given by (8.212). It is straightforward to evaluate the resultant integral by numerical methods. The resultant integral can also be evaluated analytically (see Problem 8.35). The result is

$$B_3 = \frac{5\pi^2}{18} \sigma^6. \quad (8.217)$$

B_4 can also be evaluated analytically, but higher order virial coefficients have to be evaluated by Monte Carlo methods (see Problem 8.38).

Appendix 8B: Relation of Scattered Intensity of X-Rays to $g(\mathbf{r})$

Consider a plane wave of the form $a_0 e^{i\mathbf{q} \cdot \mathbf{r}}$ incident on a fluid sample that contains N atoms of atomic number Z . We want to know the intensity of the scattered radiation at an angle θ relative to the incident beam (see Figure 8.13). The scattering is the result of the interaction of the incident beam with the atomic electrons. We let \mathbf{r}_i be the position of the i th atom and $\mathbf{r}_i^{(n)}$ the position of the n th electron of the i th atom. The amplitude at a distance r of the wave scattered by an electron at the origin is

$$A(\theta) = f(\theta) \frac{e^{iq'r}}{r}, \quad (8.218)$$

where q' is the magnitude of the wave vector of the scattered wave. Note that (8.218) has the form of a spherical wave. The atomic scattering form factor depends on the polarization of the incident beam according to Thomson's formula:

$$f(\theta) = a_0 \frac{e^2}{mc^2} \cos \theta \quad (\text{polarization vector in the scattering plane}) \quad (8.219a)$$

$$= a_0 \frac{e^2}{mc^2} \quad (\text{polarization is orthogonal}) \quad (8.219b)$$

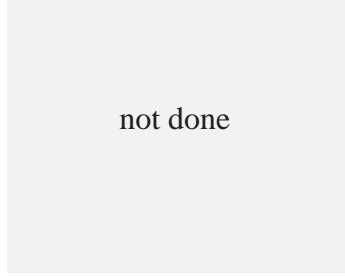


Figure 8.13: The geometry of elastic scattering.

An electron at $\mathbf{r}_i^{(n)}$ scatters in the direction θ (wave vector \mathbf{q}') with a phase difference such that

$$\mathbf{q}' \cdot \mathbf{r}_i^{(n)} - \mathbf{q} \cdot \mathbf{r}_i^{(n)} = \mathbf{k} \cdot \mathbf{r}_i^{(n)}, \quad (8.220)$$

where

$$\mathbf{k} = \mathbf{q}' - \mathbf{q} \quad (8.221)$$

is the scattering vector. The amplitude of the wave scattered by the electron $\mathbf{r}_i^{(n)}$ is given by

$$A_i^{(n)}(\theta) = f(\theta) \frac{e^{iq'r}}{r} e^{i\mathbf{k} \cdot \mathbf{r}_i^{(n)}}. \quad (8.222)$$

Because the scattering is elastic, $|\mathbf{q}| = |\mathbf{q}'|$, and the magnitude of \mathbf{k} is

$$k = |\mathbf{k}| = 2|\mathbf{q}| \sin \frac{\theta}{2}. \quad (8.223)$$

The amplitude of the wave scattering by the i th atom is the sum of the amplitudes scattered by each of the Z electrons:

$$A_i(\theta) = f(\theta) \frac{e^{iq'r}}{r} \sum_{n=1}^Z e^{i\mathbf{k} \cdot \mathbf{r}_i^{(n)}} \quad (8.224a)$$

$$= f(\theta) \frac{e^{iq'r}}{r} e^{i\mathbf{k} \cdot \mathbf{r}_i} \sum_{n=1}^Z e^{i\mathbf{k} \cdot (\mathbf{r}_i^{(n)} - \mathbf{r}_i)}. \quad (8.224b)$$

Note that $\mathbf{r}_i^{(n)} - \mathbf{r}_i$ is the position of the n th electron of the i th atom relative to its own nucleus. The amplitude of the wave scattered by the fluid is given by

$$A(\theta) = \sum_{i=1}^N A_i(\theta). \quad (8.225)$$

The intensity of the radiation that is scattered in the direction θ is given by $\langle |A(\theta)|^2 \rangle$, where the average represents the quantum average over the electronic states of each atom and an ensemble average over the positions of the atoms in the fluid. We have

$$I(\theta) = \langle |A(\theta)|^2 \rangle = \frac{\langle a(\theta)^2 \rangle}{r^2} NF(k)S(k), \quad (8.226)$$

where $\langle a(\theta)^2 \rangle$ is an average over the two polarization states:

$$\langle a(\theta)^2 \rangle = a_0^2 \frac{e^4}{m^2 c^4} \frac{1 + \cos^2 \theta}{2}. \quad (8.227)$$

The form factor $F(k)$ is the same for each atom and is given by

$$F(k) = \langle \left| \sum_{n=1}^Z e^{i\mathbf{k} \cdot (\mathbf{r}_i^{(n)} - \mathbf{r}_i)} \right|^2 \rangle, \quad (8.228)$$

where the average in (8.228) denotes a quantum average. The structure function $S(k)$ is defined by the statistical average:

$$S(k) = \frac{1}{N} \langle \left| \sum_{i=1}^N e^{i\mathbf{k} \cdot \mathbf{r}_i} \right|^2 \rangle. \quad (8.229)$$

We see that the scattered intensity is proportional to $S(k)$, the quantity of interest.

Appendix 8C: Solution of the Percus-Yevick Equation

[xx not finished xx]

8.14 Additional Problems

Problem 8.24. Why is the method that we have used to obtain the virial expansion for a classical fluid not applicable to a quantum system?

Problem 8.25. Show that the virial coefficient B_2 given in (8.33) can be written in the form

$$B_2 = -\frac{1}{6kT} \int_0^\infty r \frac{du(r)}{dr} e^{-\beta u(r)} 4\pi r^2 dr. \quad (8.230)$$

What is the condition on $u(r)$ for this form to be meaningful?

Problem 8.26. Calculate Z_N/Z_{ideal} for a system of $N = 3$ particles using (8.24). Express B_3 in terms of Z_3/Z_{ideal} and Z_2/Z_{ideal} .

Problem 8.27. Assume that $g(r)$ can be written in the form

$$g(r) = g_0 + \rho g_1(r) + \rho^2 g_2(r) + \dots \quad (8.231)$$

Use the virial equation of state (8.105) to obtain

$$\frac{PV}{NkT} = 1 - \frac{\rho}{6kT} \sum_{n=0}^{\infty} \rho^n \int_0^\infty r \frac{du}{dr} g_n(r) 4\pi r^2 dr. \quad (8.232)$$

Compare the density expansion (8.9) of PV/NkT with (8.231) and show that

$$B_{n+2} = -\frac{1}{6kT} \int_0^\infty r \frac{du}{dr} g_n(r) 4\pi r^2 dr. \quad (8.233)$$

From the result of Problem 8.25 show that

$$g_0(r) = e^{-\beta u(r)}. \quad (8.234)$$

Problem 8.28. Show that a system of hard disks attains its maximum packing density in a regular triangular lattice with each disk touching six neighbors. In this arrangement $\rho_0 \sigma^2 = 2/3^{1/2} \approx 1.1547$.²

***Problem 8.29.** Use the applet at xx to find the pressure of the hard disk crystal as a function of the density ρ . It is generally accepted that the pressure exhibits a simple-pole divergence at close packing:

$$\beta P \sigma^2 = \frac{4/3^{1/2}}{1 - \rho/\rho_0}. \quad (8.235)$$

Problem 8.30. Use the relation (8.105) to find the form of B_2 implied by (8.85).

Problem 8.31. Use the fact that the Fourier transform of the density $\rho(\mathbf{r})$ is

$$\rho_{\mathbf{k}} = \int e^{-i\mathbf{k}\cdot\mathbf{r}} \rho(\mathbf{r}) d\mathbf{r} = \sum_{i=1}^N e^{-i\mathbf{k}\cdot\mathbf{r}_i} \quad (8.236)$$

to show that $S(\mathbf{k})$ can be expressed as

$$S(\mathbf{k}) = \frac{1}{N} \langle \rho_{\mathbf{k}} \rho_{-\mathbf{k}} \rangle. \quad (8.237)$$

From (8.237) is straightforward to show that $S(\mathbf{k})$ can be written as

$$S(\mathbf{k}) = \frac{1}{N} \left\langle \sum_{i=1}^N \sum_{j=1}^N e^{-i\mathbf{k}\cdot\mathbf{r}_i} e^{i\mathbf{k}\cdot\mathbf{r}_j} \right\rangle \quad (8.238)$$

$$= \frac{1}{N} \left\langle \left| \sum_{i=1}^N e^{-i\mathbf{k}\cdot\mathbf{r}_i} \right|^2 \right\rangle. \quad (8.239)$$

Problem 8.32. Write $y(r)$ in the form of a density expansion

$$y(r) = e^{\beta u} g(r) = 1 + \rho y_1(r) + \rho^2 y_2(r) + \cdots \quad (8.240)$$

What is the form of y_1 and y_2 implied by the Percus-Yevick and hyper-netted chain approximations?

Problem 8.33. *Padé approximation for the equation of state.* [xx not finished xx]

Problem 8.34. Derive the form of the Fourier transform of the Coulomb potential $u(r) = e^2/r$.

²See for example, C. A. Rogers, *Packing and Covering*, Cambridge University Press (1964), Chapter 1.

Problem 8.35. Do the integral (8.211) in Appendix 8A.

Problem 8.36. Use the approximate results (8.175) and (8.179) for the Percus-Yevick equation of state of hard spheres to compare the exact virial coefficients summarized in Table 8.1 with those predicted by (8.175) and (8.179). Which equation of state gives better results?

Problem 8.37. Show that the mean spherical approximation (8.182) is equivalent to the Percus-Yevick equation (8.170) for hard spheres.

Problem 8.38. (a) Use a Monte Carlo method to evaluate the integrals associated with B_3 for a hard core interaction. Your estimate should be consistent with the result $B_3 = 5\pi\sigma^6/18$ (see (8.73)). Choose units such that $\sigma = 1$. One simple procedure is to generate points [xx not finished xx] Higher order virial coefficients are given by Rhee.

Suggestions for Further Reading

Earlier work on hard disks was done by B. J. Alder and T. E. Wainwright, *Phys. Rev.* **127**, 349 (1962). See also A. C. Mitus, H. Weber, and D. Marx, *Phys. Rev. E* **55**, 6855 (1997).

John A. Barker and Douglas Henderson, “What is “liquid”? Understanding the states of matter,” *Rev. Mod. Phys.* **48**, 587 (1976).

R. Brout and P. Carruthers, *Lectures on the Many-Electron Problem*, Interscience Publishers (1963). Chapter 1 has an excellent introduction to the cumulant expansion.

David Chandler, *Introduction to Modern Statistical Mechanics*, Oxford University Press (1987).

Herbert Goldstein, *Classical Mechanics*, second edition, Addison-Wesley (1980).

Jean-Pierre Hansen and Ian R. McDonald, *Theory of Simple Liquids*, second edition, Academic Press (1986).

Joseph Kestin and J. R. Dorfman, *A Course in Statistical Thermodynamics*, Academic Press (1971). Chapter 7 in this senior/graduate text has a good discussion of the properties of real gases.

Chapter 9

Critical Phenomena and the Renormalization Group

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One of the greatest recent achievements of theoretical physics has been the development of the *renormalization group*. This development has had a major impact on our understanding of phase transitions, quantum field theory, turbulence, and the emerging science of dynamical systems. We first introduce the renormalization group in the context of a simple geometrical model that exhibits a continuous transition. We then discuss some of the ideas associated with critical phenomena by discussing the van der Waals equation of state and introducing more sophisticated versions of mean-field theory. Finally, we discuss two renormalization group methods for the Ising model.

9.1 A Geometrical Phase Transition

We first consider a simple geometrical model that exhibits a continuous phase transition. The model, known as *percolation*, does not involve the temperature or the evaluation of a partition function. Although this transition is easy to imagine, especially by implementing the model on a computer, the questions that are raised by the model are as profound as they are for more complex systems such as the Ising model.

The applications of percolation are more difficult to understand than percolation in the context of a well-defined mathematical problem. The flow of oil through porous rock, the behavior of a random resistor network, and the spread of a forest fire are just a few of the many applications.

The problem of percolation is easiest to formulate on a lattice. Consider a large lattice and assume that every site in the lattice can be in one of two states, “occupied” or “empty.” Each site is occupied independently of its neighbors with probability p . This model of percolation is called *site* percolation. The nature of percolation is related to the connectivity properties of the lattice. We define a *cluster* as a group of occupied sites that are connected by nearest-neighbor distances

(see Figure 9.1). Two occupied sites belong to the same cluster if they are linked by a path of nearest-neighbor connections joining occupied sites.

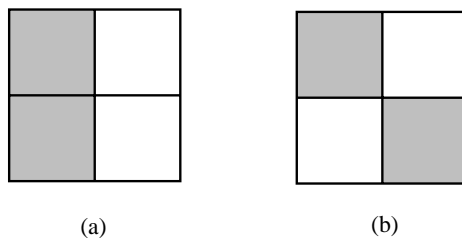


Figure 9.1: The definition of a cluster on a square lattice. In (a) the two sites are in the same cluster, and in (b) they are not.

We can use the random number generator on a calculator to study the qualitative properties of percolation. The idea is to generate a random number for each lattice site and occupy a site if its random number is less than p . Because each site is independent, the order that the sites are visited is irrelevant. If p is small, there are many small disconnected clusters (see Figure 9.2a). As p is increased, the size of the clusters increases. If $p \sim 1$, most of the occupied sites form one large cluster that extends from one end of the lattice to the other (see Figure 9.2c). Such a cluster is said to “span” the lattice and to be a *spanning* cluster. What happens for intermediate values of p , for example between $p = 0.5$ and $p = 0.7$ (see Figure 9.2b)? We shall find that in the limit of an infinite lattice, there exists a well defined threshold probability p_c such that

For $p \geq p_c$, one spanning cluster or path exists.

For $p \leq p_c$, no spanning cluster exists and all clusters are finite.

The essential characteristic of percolation is *connectedness*. Because the connectedness exhibits a qualitative change at a well defined value of p , the transition from a state with no spanning cluster to a state with one spanning cluster is an example of a *phase transition*. From our introductory

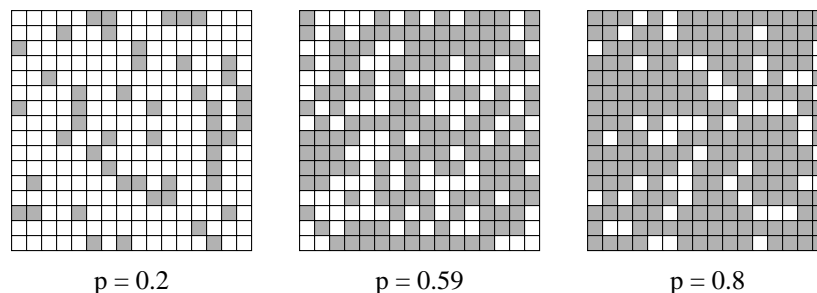


Figure 9.2: Examples of site percolation configurations for different values of p .

discussion of critical phenomena in Chapter 5, we know that it is convenient to define an order parameter, a quantity that vanishes for $p < p_c$ and is nonzero for $p \geq p_c$. The order parameter for percolation is P_∞ , the probability that an occupied site is part of the spanning cluster. We can estimate P_∞ for a given configuration from its definition:

$$P_\infty = \frac{\text{number of sites in the spanning cluster}}{\text{total number of occupied sites}}. \quad (9.1)$$

To calculate P_∞ exactly we need to average over all configurations. For $p < p_c$, $P_\infty = 0$ because there is no spanning cluster. At $p = 1$, P_∞ has its maximum value of unity because only the spanning cluster exists. These properties suggest that P_∞ is a reasonable choice for the order parameter.

Because p can be varied continuously, we expect that the phase transition at p_c is continuous. In the critical region near and above p_c , we assume that P_∞ vanishes as

$$P_\infty \sim (p - p_c)^\beta, \quad (9.2)$$

where β is an example of a critical exponent.

More information can be obtained from the cluster size distribution $n_s(p)$ defined as

$$n_s(p) = \frac{\text{mean number of clusters of size } s}{\text{total number of lattice sites}}. \quad (9.3)$$

For $p \geq p_c$, the spanning cluster is excluded from n_s . To get an idea of how we can calculate n_s , we consider $n_s(p)$ for small s on the square lattice. The probability of finding a single isolated occupied site ($s = 1$) is

$$n_1(p) = p(1 - p)^4, \quad (9.4)$$

because the probability that one site is occupied is p and the probability that all of its four neighboring sites are empty is $(1 - p)^4$. Similarly, $n_2(p)$ is given by

$$n_2(p) = 4p^2(1 - p)^6. \quad (9.5)$$

The factor of 4 in (9.5) is due to the four possible orientations of a cluster of two particles. Because $N \sum_s s n_s$ is the total number of occupied sites not in the spanning cluster (N is the total number of lattice sites), we have the relation

$$\sum_s s n_s(p) + P(p) = p, \quad (9.6)$$

where the sum is over all non-spanning clusters.

Similarly, because $N s n_s$ is the number of occupied sites in clusters of size s , the quantity

$$w_s = \frac{s n_s}{\sum_s s n_s}, \quad (9.7)$$

is the probability that an occupied site chosen at random is part of an s -site cluster.

At $p = p_c$, n_s scales as

$$n_s \sim s^{-\tau}. \quad (9.8)$$

The meaning of the power law relation (9.8) is that at $p = p_c$ on an infinite lattice, clusters of all sizes exist.

Many of the properties of interest are related to moments of n_s . For example, the mean size (number of particles) of the clusters is defined as

$$S(p) = \sum_s s w_s = \frac{\sum_s s^2 n_s}{\sum_s s n_s}. \quad (9.9)$$

The sum in (9.9) is over the finite clusters. The quantity $S(p)$ behaves near p_c as

$$S(p) \sim (p - p_c)^{-\gamma}. \quad (9.10)$$

It is convenient to associate a characteristic length ξ with the clusters. One way to do so is to introduce the radius of gyration R_s of a single cluster of s particles:

$$R_s^2 = \frac{1}{s} \sum_{i=1}^s (\mathbf{r}_i - \bar{\mathbf{r}})^2, \quad (9.11)$$

where

$$\bar{\mathbf{r}} = \frac{1}{s} \sum_{i=1}^s \mathbf{r}_i, \quad (9.12)$$

and \mathbf{r}_i is the position of the i th site in the cluster. The correlation length ξ is defined as a weighted average over the radius of gyration of all the finite clusters.¹ The statistical weight of the clusters of size s is the probability w_s that a given site is a member of such a cluster times the number of sites s in the cluster, that is, $s^2 n_s(p)$. Hence, the average radius of gyration of all the non-spanning clusters is given by ξ as

$$\xi^2 = \frac{\sum_s s^2 n_s R_s^2}{\sum_s s^2 n_s}. \quad (9.13)$$

Near p_c we assume that the correlation length ξ diverges as

$$\xi \sim |p_c - p|^{-\nu}. \quad (9.14)$$

Why do systems exhibit power law behavior as the critical point is approached? For example, the order parameter goes to zero as a power of $(p_c - p)/p_c$ for percolation and as a power of $\epsilon = (T_c - T)/T_c$ for thermal systems. In the limit that $(p_c - p)/p_c$ or ϵ becomes small, there is no other quantity to set the scale for ϵ or $(p_c - p)/p_c$. For example, we cannot have functions such as $\sin \epsilon$, because as ϵ goes to zero, $\sin \epsilon$ reduces to ϵ . The simplest functions without a characteristic scale are powers. Hence, we should not be surprised that various quantities show power law behavior near the critical points.

How can we determine the values of p_c and the critical exponents

Problem 9.1. Run the applet at xxx to simulate percolation of the square and triangular lattices. Define a spanning cluster as one that connects the top and bottom of the lattice and the left and right. Visually estimate the value of p_c at which a spanning cluster first occurs. Choose progressively larger lattices and try to extrapolate your estimated values of p_c for various lattice dimensions L to $L \rightarrow \infty$.

¹More precisely, ξ should be called the connectedness length.

lattice	d	q	p_c (site)	p_c (bond)
linear chain	1	2	1	1
square	2	4	0.59275	$\frac{1}{2}$
triangular	2	6	$\frac{1}{2}$	0.3473
honeycomb	2	3	0.698(3)	0.6527
diamond	3	4	0.4299(8)	0.3886(5)
simple cubic	3	6	0.3117(3)	0.2492(2)
bcc	3	8	0.24674(7)	0.1795(3)
fcc	3	12	0.1998	0.1198(3)

Table 9.1: Summary of known results for the percolation threshold. The figure in parentheses is the probable error in the last figure.

quantity	functional form	exponent	$d = 2$	$d = 3$
order parameter	$P_\infty \sim (p - p_c)^\beta$	β	5/36	0.403(8)
mean size of finite clusters	$S(p) \sim p - p_c ^{-\gamma}$	γ	43/18	1.73(3)
connectedness length	$\xi(p) = p - p_c ^{-\nu}$	ν	4/3	0.89(1)
cluster distribution	$n_s \sim s^{-\tau} \quad (p = p_c)$	τ	187/91	2.2

Table 9.2: Summary of known results for the static critical exponents associated with the percolation transition. The number in parentheses is the probable error in the last figure.

The values of the percolation threshold depend on the symmetry of the lattice and are summarized in Table 9.1. A summary of the known values of the various critical exponents for percolation is given in Table 9.2. For two dimensions, the static exponents are known exactly. For three dimensions no exact results are known, and the exponents have been estimated using various approximate methods. The accuracy of the numerical values for the critical exponents is consistent with the assumption that the exponents are independent of the symmetry of the lattice and depend only on d .

The critical exponents for percolation satisfy a set of relations that are identical to the scaling relations for thermal systems (see Table 9.3). For example, we will find that

$$2\beta + \gamma = d\nu, \quad (9.15)$$

where d is the spatial dimension.

We would like to be able to understand these results on a deeper level than the qualitative description we have given. To do this end we next introduce a renormalization group method for percolation.

9.2 Renormalization Group for Percolation

The important idea that is incorporated into the renormalization group is that all length scales are important at the critical point. For percolation this idea implies that clusters of all sizes exist

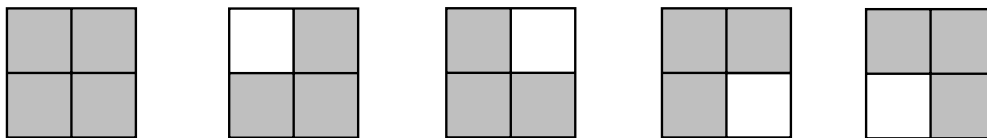


Figure 9.3: The five vertically and horizontally spanning configurations for a 2×2 cell on a square lattice.

on an infinite lattice at $p = p_c$. If all length scales are present at $p = p_c$, then the system looks the same on any length scale. This property is called *self-similarity*. In contrast, this behavior is not seen for p far from p_c .

The renormalization group is a general approach for extracting quantitative information from self-similarity. The approach is to average over smaller length scales and to find how the system is changed by such an average. The rate at which the system changes gives us information on the critical exponents. What kind of averaging is appropriate for site percolation? The averaging should be such that it preserves the important physics. For percolation the important physics is associated with connectivity. Suppose that the lattice is divided into $b \times b$ cells each with b^2 sites. We adopt the rule that a cell is replaced by a single *renormalized* occupied site if the cell spans, and replaced by an unoccupied site if it does not. It is not clear which spanning rule to adopt, for example, vertical spanning, horizontal spanning, vertical and horizontal spanning, and vertical or horizontal spanning. In the following, we will adopt horizontal *and* vertical spanning. In the limit of very large cells, these different rules should yield results for p_c and ν that converge to the same value.

Suppose that we make the approximation that each cell is independent of all the other cells and is characterized only by the probability p' that the cell is occupied. If the sites are occupied with probability p , then the cells are occupied with probability p' , where p' is given by a renormalization transformation of the form

$$p' = R(p). \quad (9.16)$$

$R(p)$ is the total probability that the sites form a spanning path.

An example will make the meaning of the formal relation (9.16) more clear. In Figure 9.3 we show the five vertically and horizontally spanning site configurations for a $b = 2$ cell. The probability p' that the renormalized site is occupied is given by the sum of all the possibilities:

$$p' = R(p) = p^4 + 4p^3(1 - p). \quad (9.17)$$

In general, the probability p' that the renormalized site is occupied is different than the occupation probability p of the original sites. For example, suppose that we begin with $p = p_0 = 0.5$. After a single renormalization transformation, the value of p obtained from (9.17) is $p_1 = R(p_0 = 0.5) = 0.3125$. A second renormalization transformation yields $p_2 = R(p_1) = 0.0934$. It is easy to see that further transformations drives the system to the *trivial fixed point* $p^* = 0$. Similarly, if we begin with $p = p_0 = 0.8$, we find that successive transformations drive the system to the trivial fixed point $p^* = 1$.

To find the nontrivial fixed point associated with the critical threshold p_c , we need to find the special value of $0 < p < 1$ such that

$$p^* = R(p^*). \quad (9.18)$$

For the recursion relation (9.17) we find that the solution of the fourth degree polynomial equation for p^* yields the two trivial fixed points $p^* = 0$ and $p^* = 1$, and the nontrivial fixed point $p^* = 0.7676$ that we associate with p_c . This calculated value of p^* for a 2×2 cell should be compared with the best known estimate $p_c = 0.5927$ for the square lattice. Note that p^* is an example of an *unstable* fixed point because the iteration of (9.17) for p arbitrarily close to p^* will drive p to one of the stable fixed points.

To calculate the critical exponent ν from the renormalization transformation, we note that on the renormalized lattice all lengths are reduced by a factor of b in comparison to all lengths in the original system. Hence ξ' , the connectedness length in the renormalized lattice, is related to ξ , the connectedness length in the original lattice, by

$$\xi' = \frac{\xi}{b}. \quad (9.19)$$

Because $\xi(p) = \text{const}|p - p_c|^{-\nu}$ for $p \sim p_c$ and p_c corresponds to p^* , we have

$$|p' - p^*|^{-\nu} = \frac{1}{b}|p - p^*|^{-\nu}. \quad (9.20)$$

To find the relation between p' and p near p_c , we expand the renormalization transformation (9.16) about $p = p^*$ and obtain to first order

$$p' - p^* = R(p) - R(p^*) \approx \lambda(p - p^*), \quad (9.21)$$

where

$$\lambda = \left. \frac{dR}{dp} \right|_{p=p^*}. \quad (9.22)$$

We need to do a little algebra to obtain an explicit expression for ν . We first raise the left and right sides of (9.21) to the $-\nu$ power and write

$$|p' - p^*|^{-\nu} = \lambda^{-\nu}|p - p^*|^{-\nu}. \quad (9.23)$$

We compare (9.20) and (9.23) and obtain

$$\lambda^{-\nu} = b^{-1}. \quad (9.24)$$

Finally, we take the logarithm of both sides of (9.24) and obtain the desired relation for the critical exponent ν :

$$\nu = \frac{\ln b}{\ln \lambda}. \quad (9.25)$$

As an example, we calculate ν for $b = 2$ using (9.17). We write $R(p) = p^4 + 4p^3(1 - p) = -3p^4 + 4p^3$ and find $\lambda = dR/dp|_{p=p^*} = 12p^2(1 - p)|_{p=0.7676} = 1.6432$. We then use the relation (9.25) to obtain

$$\nu = \frac{\ln 2}{\ln 1.6432} = 1.40. \quad (9.26)$$



Figure 9.4: Example of an error after one renormalization.

The agreement of the numerical result (9.26) with the exact result $\nu = 4/3$ in $d = 2$ is remarkable given the simplicity of our calculation. In comparison, what would we be able to conclude if we were to measure $\xi(p)$ directly on a 2×2 lattice? However, this agreement is fortuitous because the accuracy of our calculation of ν is not known *a priori*.

What is the nature of the approximations that we have made in calculating ν and p_c ? Our basic assumption has been that the occupancy of each cell is independent of all other cells. This assumption is correct for the original sites but after one renormalization, we lose some of the original connecting paths and gain connecting paths that were not present in the original lattice. An example of this “interface” problem is shown in Figure 9.4. Because this surface effect becomes less important with increasing cell size, one way to improve our renormalization group calculation is to consider larger cells.

Problem 9.2. Choose a simple cell for one-dimensional percolation and show that $p_c = 1$ and $\nu = 1$ exactly.

Problem 9.3. What are the four spanning configurations for the smallest possible cell ($b = \sqrt{3}$) on a triangular lattice? Show that the corresponding recursion relation can be expressed as $R(p) = 3p^2 - 2p^3$. Find p^* and ν . The result $p^* = 1/2$ is exact.

Problem 9.4. Enumerate all the possible spanning configurations for a $b = 3$ cell. Assume that a cell is occupied if a cluster spans the cell vertically and horizontally. Determine the probability of each configuration and find the renormalization transformation $R(p)$. Then solve for the nontrivial fixed point p^* and ν . The simplest way to find the fixed point is by trial and error using a hand calculator or computer. Another way is to plot the difference $R(p) - p$ versus p and find the value of p at which $R(p) - p$ crosses the horizontal axis. Are your results for p_c and ν closer to their known values than for $b = 2$?

Problem 9.5. Instead of renormalizing the set of all spanning 3×3 cells to a single occupied site, an alternative is go from cells of linear dimension $b_1 = 3$ to cells of linear dimension $b_2 = 2$. Use the fact that the connectedness lengths of the two lattices are related by $\xi(p_2)/\xi(p_1) = (b_1/b_2)^{-1}$ to derive the relation

$$\nu = \frac{\ln b_1/b_2}{\ln \lambda_1/\lambda_2}, \quad (9.27)$$

where $\lambda_i = dR(p^*, b_i)/dp$ is evaluated at the solution p^* of the fixed point equation, $R_2(b_2, p^*) = R_3(b_1, p^*)$. The “cell-to-cell” transformation yields better results in the limit in which the change in length scale is infinitesimal and is the preferred method.

9.3 The Liquid-Gas Transition

Experimentally we know that a simple system of say, Argon atoms, is a gas at high temperatures and a liquid at low temperatures. The van der Waals equation of state is the simplest equation of state that exhibits a gas-liquid transition. We derived its form in Section 8.9.1 and obtained:

$$P = \frac{NkT}{V - Nb} - \rho^2 a^2. \quad (9.28)$$

The parameter a is a measure of the attractive interactions among the particles and the parameter b is a measure of the repulsive interactions. The latter become important when two particles come too close to each other. In the following we rederive the van der Waals equation to emphasize its mean-field nature.

Let us assume that the intermolecular interaction consists of a hard-core repulsion and a weak long-range interaction:

$$u(r) = u_{\text{hc}} + u_{\text{attr}}. \quad (9.29)$$

The partition function can be expressed as

$$\frac{Z}{Z_{\text{ideal}}} = \int d\mathbf{r}_1 \dots d\mathbf{r}_N e^{-\beta \sum_{i < j} u(|\mathbf{r}_i - \mathbf{r}_j|)}. \quad (9.30)$$

We assume that u_{attr} has the special form, $u_{\text{attr}} \propto \lambda^d \phi(\lambda r)$ such that $\int u_{\text{attr}} d^d r$ is a constant as $\lambda \rightarrow 0$ and d is the spatial dimension. This form implies that as the range of u_{attr} increases, its strength decreases. An example of such an interaction is

$$u_{\text{attr}} = -ca\lambda^d e^{-\lambda r}, \quad (9.31)$$

where a will be associated with the van der Waals parameter. The constant c is chosen so that

$$-\int u_{\text{attr}}(r) d\mathbf{r} = a. \quad (9.32)$$

The basic assumption of mean-field theory is that the fluctuating field experienced by an individual particle can be replaced by its average. This assumption is reasonable if a large number of particles contribute to the fluctuating field and can be shown to be rigorously correct for a potential of the form $\lambda^d \phi(\lambda r)$ in the limit $\lambda \rightarrow 0$.

This assumption allows us to replace the potential $\sum_j \int u_{\text{attr}}(|\mathbf{r}_i - \mathbf{r}_j|)$ seen by particle i by its average

$$\frac{N}{V} \int u_{\text{attr}}(r) d\mathbf{r} = -\frac{N}{V} a. \quad (9.33)$$

Note that the average in (9.33) is independent of \mathbf{r}_i . We now sum over all $i < j$ and obtain

$$\left\langle \sum_{i < j} u_{\text{attr}}(|\mathbf{r}_i - \mathbf{r}_j|) \right\rangle = -\frac{1}{2} a \frac{N^2}{V}. \quad (9.34)$$

The factor one-half enters because of the condition $i < j$. Hence, we can rewrite (9.30) as

$$Z = Z_{\text{hc}} e^{\beta a N^2 / 2V}, \quad (9.35)$$

where Z_{hc} represents the partition function for a system of hard core particles. The free energy is given by

$$F = -kT \ln Z(T, V, N) = F_{\text{hc}} - \frac{1}{2}a \frac{N^2}{V}, \quad (9.36)$$

and the pressure is given by

$$P = -\left(\frac{\partial F}{\partial V}\right)_T = P_{\text{hc}} - \rho^2 a. \quad (9.37)$$

As we discussed in Section 8.9.1, van der Waals assumed that Z_{hc} is given by

$$Z_{\text{hc}} = \frac{1}{N!} \frac{1}{\lambda^{3N}} (V - Nb)^N. \quad (9.38)$$

It is straightforward to use (9.38) to obtain (9.28).

We now consider the isotherms predicted by (9.28). For fixed T , P approaches infinity as $V/N \rightarrow b$. In contrast, for an ideal gas, P becomes infinite only in the limit $V/N \rightarrow 0$. For $V/N \gg b$, the van der Waals equation of state reduces to the ideal gas equation. Between these two limits, the van der Waals equation exhibits behavior very different from the ideal gas. For example, both the first and second derivatives of P may vanish (see Problem 9.6).

Problem 9.6. Sketch several isotherms (P versus V at constant T and N) of the van der Waals equation of state (9.28). The isotherms above $T = T_c$ are monotonic, but those below T_c develop a region of positive slope, $(\partial P / \partial V)_T > 0$. Explain why the latter behavior is nonphysical. Find the value of T_c by solving the equations

$$\left(\frac{\partial P}{\partial V}\right)_T = 0, \quad (9.39)$$

and

$$\left(\frac{\partial^2 P}{\partial V^2}\right)_T = 0. \quad (9.40)$$

These two conditions together with (9.28) give three conditions for the three unknowns T_c , P_c , and V_c in terms of the parameters a and b . To obtain the solution, rewrite (9.28) as a cubic equation in V . Confirm that

$$V^3 - \left(Nb + \frac{NkT}{P}\right)V^2 + \frac{aN^2}{P}V - \frac{a^2bN^3}{P} = 0. \quad (9.41)$$

On any isotherm, there should be three solutions for any value of P . At the critical point, these three solutions merge so that

$$(V - V_c)^3 = V^3 - 3V_c V^2 + 3V_c^2 V - V_c^3 = 0. \quad (9.42)$$

Compare the coefficients of each power of V in (9.41) and (9.42) and confirm that

$$V_c = 3Nb, \quad P_c = \frac{a^2}{27b^2}, \quad kT_c = \frac{8a}{27b}. \quad (9.43)$$

Problem 9.7 shows that the van der Waals equation can be written in the same form for all substances.

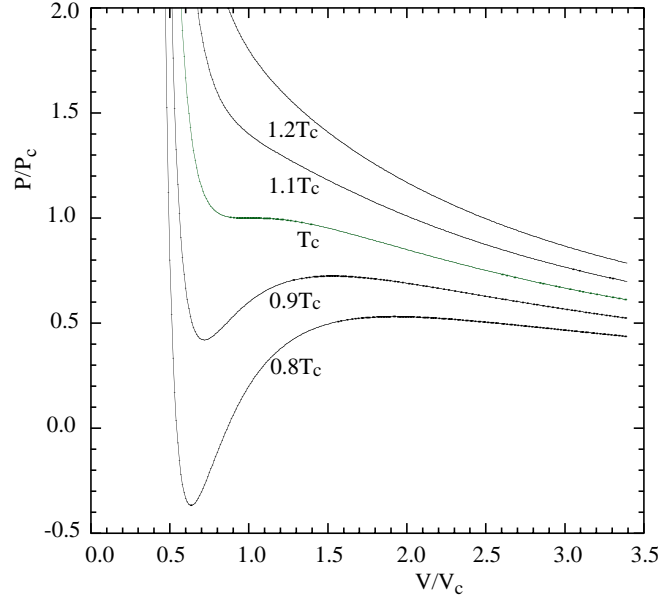


Figure 9.5: The van der Waals isotherms near the critical temperature. Note that for $T > T_c$, the isotherms have no minima or maxima.

Problem 9.7. Define the dimensionless quantities

$$\tilde{T} = \frac{T}{T_c}, \quad \tilde{P} = \frac{P}{P_c}, \quad \tilde{V} = \frac{V}{V_c}, \quad (9.44)$$

and confirm that all van der Waals fluids have the same form of the equation of state

$$\left(\tilde{P} + \frac{3}{\tilde{V}^2}\right)(3\tilde{V} - 1) = 8\tilde{T}. \quad (9.45)$$

Equation (9.45) implies that the equation of state is the same form for all gases, which is called the law of corresponding states. In reality, such a statement is only approximately true.

Now let us examine the conditions for which a van der Waals isotherm has minima and maxima. For $\partial\tilde{P}/\partial\tilde{V}$ to vanish, we must have

$$f(\tilde{V}) = \frac{(3\tilde{V} - 1)^2}{4\tilde{V}^3} = \tilde{T}. \quad (9.46)$$

The function $f(\tilde{V})$ vanishes at $\tilde{V} = 1/3$ and in the limit $\tilde{V} \rightarrow \infty$. The derivative of f vanishes for $\tilde{V} = 1$ and hence the maximum value of $f(\tilde{V})$ is $f(1) = 1$. This behavior implies that (9.46) cannot be satisfied for $\tilde{T} > 1$ or equivalently $T > T_c$. For $T > T_c$, the van der Waals isotherms have no minima or maxima.

Now let us consider the van der Waals isobars. From (9.45), we obtain

$$\tilde{T} = \left(\frac{3\tilde{V} - 1}{8} \right) \left(\tilde{P} + \frac{3}{\tilde{V}^2} \right). \quad (9.47)$$

For \tilde{T} to have a maximum or minimum requires that

$$\frac{3}{\tilde{V}^2} - \frac{2}{\tilde{V}^3} = \tilde{P} \quad (9.48)$$

Because the values of the left-hand side of (9.48) are less than or equal to one, we conclude that \tilde{T} has no extrema if $\tilde{P} > 1$ ($P > P_c$).

For $T < T_c$ the isotherms have one maximum and one minimum between which the slope is positive. What is the significance of a positive slope?

9.4 Bethe Approximation

In Section 5.6 we introduced a simple mean-field approach in the context of the Ising model. The basic approximation was to ignore all correlations between the spins, including nearest neighbors, and approximate $\langle s_i s_j \rangle$ as $\langle s_i s_j \rangle \approx \langle s_i \rangle \langle s_j \rangle = m^2$. In the following, we discuss how to improve this approximation. This approximation method is due to Bethe.²

The idea is that instead of considering the effective field felt by a single spin, we consider the effective field felt by a group of spins. In particular, consider a central spin and its nearest neighbors (see Figure 9.6). The interactions of the nearest neighbors with the central spin is calculated exactly, and the rest of the spins in the system are assumed to act on the nearest neighbors through an effective field that we calculate self-consistently. The energy of the central cluster is

$$H_c = -J s_0 \sum_{j=1}^q s_j - B s_0 - B_{\text{eff}} \sum_{j=1}^q s_j \quad (9.49a)$$

$$= -(J s_0 + B_{\text{eff}}) \sum_j s_j - B s_0, \quad (9.49b)$$

where q is the coordination number of the lattice. (For a square lattice $q = 4$.) Note that the fluctuating field acting on the nearest neighbor spins s_1, \dots, s_q has been replaced by the effective field B_{eff} .

The cluster partition function Z_c is given by

$$Z_c = \sum_{s_0=\pm 1, s_j=\pm 1} e^{-\beta H}. \quad (9.50)$$

We first do the sum over $s_0 = \pm 1$ and write

$$Z_c = e^{\beta B} \sum_{s_j=\pm 1} e^{\beta(J+B_{\text{eff}}) \sum_j s_j} + e^{-\beta B} \sum_{s_j=\pm 1} e^{\beta(-J+B_{\text{eff}}) \sum_j s_j}. \quad (9.51)$$

²Bethe is probably better known for his work in nuclear physics and other areas. The reference is H. Bethe, *Proc. Royal Society A* **150**, 552 (1935).

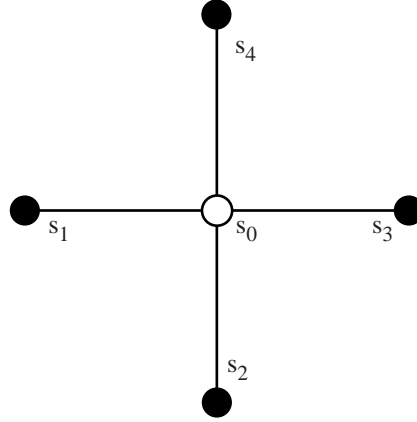


Figure 9.6: The simplest cluster on the square lattice used in the Bethe approximation.

For simplicity, we first evaluate the partition function of the cluster for the one-dimensional lattice for which $q = 2$. Because the two neighboring cluster spins can take the values $\uparrow\uparrow$, $\uparrow\downarrow$, $\downarrow\uparrow$, and $\downarrow\downarrow$, the sums in (9.51) becomes

$$Z_c = e^{\beta B} [e^{2\beta(J+B_{\text{eff}})} + 2 + e^{-2\beta(J+B_{\text{eff}})}] \quad (9.52a)$$

$$+ e^{-\beta B} [e^{2\beta(-J+B_{\text{eff}})} + 2 + e^{-2\beta(-J+B_{\text{eff}})}] \\ = 4[e^{\beta B} \cosh^2 \beta(J+B_{\text{eff}}) + e^{-\beta B} \cosh^2 \beta(J-B_{\text{eff}})]. \quad (9.52b)$$

For general q , it can be shown that Z_c is given by

$$Z_c = 2^q [e^{\beta B} \cosh^q \beta(J+B_{\text{eff}}) + e^{-\beta B} \cosh^q \beta(J-B_{\text{eff}})]. \quad (9.53)$$

The expectation value of the central spin is given by

$$\langle s_0 \rangle = \frac{1}{\beta} \frac{\partial}{\partial B} \ln Z_c = \frac{2^q}{Z_c} [e^{\beta B} \cosh^q \beta(J+B_{\text{eff}}) - e^{-\beta B} \cosh^q \beta(J-B_{\text{eff}})]. \quad (9.54)$$

We also want to calculate the expectation value of the spin of the nearest neighbors $\langle s_j \rangle$ for $j = 1, \dots, q$. Because the system is translationally invariant, we require that $\langle s_0 \rangle = \langle s_j \rangle$ and find the effective field B_{eff} by requiring that it satisfy this condition. From (9.51) we see that

$$\langle s_j \rangle = \frac{1}{q} \frac{\partial}{\partial (\beta B_{\text{eff}})} \ln Z_c. \quad (9.55)$$

If we substitute (9.53) for Z_c in (9.55), we find

$$\langle s_j \rangle = \frac{2^q}{Z_c} \left[e^{\beta B} \sinh \beta(J+B_{\text{eff}}) \cosh^{q-1} \beta(J+B_{\text{eff}}) \right. \\ \left. - e^{-\beta B} \sinh \beta(J-B_{\text{eff}}) \cosh^{q-1} \beta(J-B_{\text{eff}}) \right]. \quad (9.56)$$

To find the critical temperature, we set $B = 0$. The requirement $\langle s_0 \rangle = \langle s_j \rangle$ yields the equation

$$\cosh^q \beta(J + B_{\text{eff}}) - \cosh^q \beta(J - B_{\text{eff}}) = \sinh \beta(J + B_{\text{eff}}) \cosh^{q-1} \beta(J + B_{\text{eff}}) - \sinh \beta(J - B_{\text{eff}}) \cosh^{q-1} \beta(J - B_{\text{eff}}). \quad (9.57)$$

Equation (9.57) can be simplified by writing $\sinh x = \cosh x - e^{-x}$ with $x = \beta(J \pm B_{\text{eff}})$:

$$\frac{\cosh^{q-1} \beta(J + B_{\text{eff}})}{\cosh^{q-1} \beta(J - B_{\text{eff}})} = e^{2\beta B_{\text{eff}}}. \quad (9.58)$$

Equation (9.58) always has the solution $B_{\text{eff}} = 0$ corresponding to the disordered high temperature phase. As $B_{\text{eff}} \rightarrow \infty$, the left-hand side of (9.58) approaches $e^{2\beta J(q-1)}$, a constant independent of B_{eff} , and the right-hand side diverges. Therefore, if the slope of the function on the left at $B_{\text{eff}} = 0$ is greater than 2β , the two functions must intersect again at finite B_{eff} . If we take the derivative of the left-hand side of (9.58) with respect to B_{eff} and set it equal to 2β , we find that the condition for a solution to exist is

$$\coth \beta_c J = q - 1, \quad (9.59)$$

where $\coth x = \cosh x / \sinh x$. Because (9.58) is invariant under $B_{\text{eff}} \rightarrow -B_{\text{eff}}$, there will be two solutions for $T \leq T_c$.

On the square lattice, (9.59) yields $kT_c/J = 2.888\dots$ in comparison to the exact result $kT_c/J = 2.269\dots$ (see (5.76)) and the result of simple mean-field theory, $kT_c/J = 4$. Note that for the one-dimensional Ising model, $q = 2$ and the Bethe approximation predicts $T_c = 0$ in agreement with the exact result.

Better results can be found by considering larger clusters. However, although such an approach yields more accurate phase diagrams, it always yields the same mean-field exponents because it depends on the truncation of correlations beyond a certain distance. This approximation must break down in the vicinity of a critical point where the correlations become infinite.

Problem 9.8. Work out the details of the Bethe approximation, an improved mean-field method discussed in Section 9.4, for the Ising chain. Show that the effective three spin Hamiltonian can be written as

$$H_3 = -J(s_1 + s_2 + s_3) - mJ(s_1 + s_3), \quad (9.60)$$

where $m = \langle s \rangle$. (Explain why the effective field B_{eff} is given by $B_{\text{eff}} = Jm$.) Evaluate the partition function for the cluster Z_3 by summing over the possible values of s_1, s_2 and s_3 . The magnetization per spin, m , can be found by evaluating $\langle s_2 \rangle$. Expand your result for m near $m = 0$ and show that $T_c = 0$.

9.5 Landau Theory of Phase Transitions

As we have discussed, the key idea of mean-field theory is the neglect of correlations between the spins or other relevant coordinates. For the Ising model we can write the spin at lattice point \mathbf{r} as

$m(\mathbf{r}) = m + \phi(\mathbf{r})$ and express the interaction term in the energy as

$$\begin{aligned} m(\mathbf{r})m(\mathbf{r}') &= [m + \phi(\mathbf{r})][m + \phi(\mathbf{r}')] \\ &= m^2 + m[\phi(\mathbf{r}) + \phi(\mathbf{r}')] + \phi(\mathbf{r})\phi(\mathbf{r}'). \end{aligned} \quad (9.61)$$

If we assume that $\phi(\mathbf{r}) \ll m$, we may neglect the last term in (9.61) and obtain

$$m(\mathbf{r})m(\mathbf{r}') \approx m^2 + m[\phi(\mathbf{r}) + \phi(\mathbf{r}')] = m^2 + m[m(\mathbf{r}) + m(\mathbf{r}') - 2m], \quad (9.62a)$$

$$= m[\phi(\mathbf{r}) + \phi(\mathbf{r}')] - m^2. \quad (9.62b)$$

Using this approximation, we write the total energy as

$$-J \sum_{\mathbf{r}, \mathbf{r}'} m(\mathbf{r})m(\mathbf{r}') - B \sum_{\mathbf{r}} m(\mathbf{r}) \approx -J \sum_{\mathbf{r}, \mathbf{r}'} [m[m(\mathbf{r}) + m(\mathbf{r}')] - m^2] - B \sum_{\mathbf{r}} m(\mathbf{r}) \quad (9.63a)$$

$$= \frac{1}{2}NJm^2 - (Jm + B) \sum_{\mathbf{r}} m(\mathbf{r}). \quad (9.63b)$$

Note that the spin $m(\mathbf{r})$ enters only linearly in (9.63b). We evaluate the partition function as in Chapter 5 and find

$$Z \approx Z_{\text{mf}} = e^{-\frac{1}{2}NJm^2} [2 \cosh \beta(Jm + B)]^N. \quad (9.64)$$

The free energy for a given value of m in this simple mean-field approximation is proportional to $-kT \ln Z_{\text{mf}}$ and can be expressed as

$$F_{\text{mf}} = \frac{1}{2}NJm^2 - N\beta \ln \cosh \beta(Jm + B), \quad (9.65)$$

apart from an irrelevant constant. Because the equilibrium free energy must be a minimum for a given value of T and B , we can determine m by requiring that it minimize F_{mf} . The result is

$$m = \tanh \beta(Jm + B), \quad (9.66)$$

as we found in (5.94).

Problem 9.9. (a) Derive (9.66) from the requirement that F in (9.65) is a minimum in equilibrium. (b) Expand F_{mf} in a power series in m and show that F_{mf} can be written in the Landau form (9.67).

Landau realized that the qualitative features of mean-field theory can be summarized by a simple expression for the free energy. Because m is small near the critical point, it is reasonable to assume that the free energy density (free energy per unit volume) can be written in the form

$$f(m, T) = a + \frac{b}{2}m^2 + \frac{c}{4}m^4 - Bm, \quad (9.67)$$

where the parameters a , b , and c depend on T . The assumption underlying the form (9.67) is that f can be expanded in a power series in m about $m = 0$ near the critical point. Although this assumption is not correct, Landau theory, like mean-field theory in general, is still a useful tool. For the Ising model, Landau also assumed that $f(m)$ is symmetrical about $m = 0$ so that the m^3

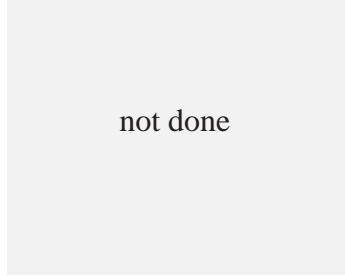


Figure 9.7: The dependence of the Landau form of the free energy on the order parameter m .

term can be omitted. The quantity m is called the *order parameter* because it is zero for $T > T_c$, is nonzero for $T \leq T_c$, and characterizes the nature of the transition.

The equilibrium value of m is the value that minimizes the free energy. In Figure 9.7 we show the dependence of f on m for $B = 0$. We see that if $b > 0$ and $c > 0$, then the minimum of f is at $m = 0$. However if $b < 0$ and $c > 0$, then the minimum of f is at $m \neq 0$. We have for $B = 0$ that

$$\frac{\partial f}{\partial m} = bm + cm^3 = 0. \quad (9.68)$$

If we assume that $b = b_0(T - T_c)$ and $c > 0$, we find

$$m = \pm \left(\frac{b_0}{c}\right)^{1/2} (T_c - T)^{1/2}. \quad (9.69)$$

The behavior of the specific heat can be found from the relation $C = T\partial s/\partial T$. The entropy density is given by

$$s = -\frac{\partial f}{\partial T} = -a' - \frac{b'}{2}m^2 - \frac{b}{2}(m^2)' - \frac{c}{4}(m^4)', \quad (9.70)$$

where the primes in (9.70) denote the derivative with respect to T . From (9.70) we have

$$C = T \frac{ds}{dT} = -Ta'' - Tb'(m^2)' - \frac{cT}{4}(m^4)'', \quad (9.71)$$

where we have used the fact that $b'' = 0$, and have assumed that c is independent of T . Because $m = 0$ for $T \geq T_c$, we have $C \rightarrow -Ta''$ as $T \rightarrow T_c$ from above. For $T \rightarrow T_c$ from below, we have $(m^2)' = b_0/c$, $b' = b_0$, and $(m^4)'' \rightarrow 2(b_0/c)^2$. Hence, we obtain

$$C \rightarrow \begin{cases} -Ta'' & T \rightarrow T_c^+ \\ -Ta'' + Tb_0^2/2c & T \rightarrow T_c^- \end{cases} \quad (9.72)$$

We see that the order parameter m and the specific heat C have the same behavior near T_c as we previously obtained in our simple mean-field treatment of the Ising model.

Problem 9.10. The susceptibility per spin can be found from the relation

$$\chi = \frac{\partial m}{\partial B}.$$

(a) Show that if $B \neq 0$, $bm + cm^3 - B = 0$ in the Landau theory, and hence $\chi^{-1} = (b + 3cm^2)$. For $T > T_c$, $m = 0$ and $\chi^{-1} = b = b_0(T - T_c)$. For $T < T_c$, $m^2 = -b/c$, and hence $\chi^{-1} = 2b_0(T_c - T)$. Hence Landau theory predicts that $\gamma = \gamma' = 1$. (b) Show that at the critical point $cm^3 = B$, and hence $\delta = 3$.

We can generalize Landau theory to incorporate spatial fluctuations by writing

$$f(\mathbf{r}) = a + \frac{b}{2}m^2(\mathbf{r}) + \frac{c}{4}m^4(\mathbf{r}) + \frac{g}{2}[\nabla m(\mathbf{r})]^2 - Bm(\mathbf{r}), \quad (9.73)$$

where the parameter $g > 0$. This form of the free energy density is commonly known as the *Landau-Ginzburg* form. The gradient term in (9.73) expresses the fact that the free energy is raised by spatial fluctuations in the order parameter. The total free energy is given by

$$F = \int f(\mathbf{r}) d^3r, \quad (9.74)$$

and the total magnetization is

$$M = \int m(\mathbf{r}) d^3r. \quad (9.75)$$

We follow the same procedure as before and minimize the total free energy:

$$\delta F = \int \{ \delta m(\mathbf{r}) [bm(\mathbf{r}) + cm^3(\mathbf{r}) - B] + g \nabla \delta m(\mathbf{r}) \cdot \nabla m(\mathbf{r}) \} d^3r = 0. \quad (9.76)$$

The last term in the integrand of (9.76) can be simplified by integrating by parts and requiring that $\delta m(\mathbf{r}) = 0$ at the surface. In this way we obtain

$$B(\mathbf{r}) = bm(\mathbf{r}) + cm(\mathbf{r})^3 - g \nabla^2 m(\mathbf{r}). \quad (9.77)$$

It is clear that (9.77) reduces to the usual Landau theory by letting $B(\mathbf{r}) = B$ and $\nabla m(\mathbf{r}) = 0$.

If we imagine that a localized perturbation $B(\mathbf{r}) = B_0 \delta(\mathbf{r})$ is applied to the system, we can use (9.77) to calculate its effect. We write

$$m(\mathbf{r}) = m_0 + \phi(\mathbf{r}), \quad (9.78)$$

and assume that the spatially varying term $\phi(\mathbf{r})$ is small so that $m(\mathbf{r})^3 \approx m_0^3 + 3m_0^2\phi(\mathbf{r})$. We substitute (9.78) into (9.77) and obtain

$$\nabla^2 \phi - \frac{b}{g} \phi - 3 \frac{c}{g} m_0^2 \phi - \frac{b}{g} m_0 - \frac{c}{g} m_0^3 = -\frac{B_0}{g} \delta(\mathbf{r}). \quad (9.79)$$

If we substitute $m_0 = 0$ for $T > T_c$ and $m_0^2 = -b/c$ for $T < T_c$ into (9.79), we obtain

$$\nabla^2 \phi - \frac{b}{g} \phi = -\frac{B_0}{g} \delta(\mathbf{r}) \quad (T > T_c) \quad (9.80a)$$

$$\nabla^2 \phi + 2 \frac{b}{g} \phi = -\frac{B_0}{g} \delta(\mathbf{r}). \quad (T < T_c) \quad (9.80b)$$

Note that ϕ in (9.80) satisfies an equation of the same form as the one we found in the Debye-Hückel theory (see Section 8.12). The solution of (9.80) can be written in spherical coordinates as

$$\phi(r) = \frac{B_0}{4\pi g} \frac{1}{r} e^{-r/\xi}, \quad (9.81)$$

with

$$\xi(T) = \left[\frac{g}{b(T)} \right]^{1/2} \quad (T > T_c) \quad (9.82a)$$

and

$$\xi(T) = \left[\frac{-g}{2b(T)} \right]^{1/2}. \quad (T < T_c) \quad (9.82b)$$

We will see that the quantity $\xi(T)$ can be interpreted as the *correlation length*. Because $b(T) = b_0(T - T_c)$, we see that ξ diverges from both above and below T_c as

$$\xi(T) \sim |T - T_c|^{-\nu}. \quad (9.83)$$

In general, $\xi \sim |T - T_c|^{-\nu}$; mean-field theory predicts that $\nu = 1/2$.

The correlation function of the order parameter is given by

$$G(r) = \langle m(r)m(0) \rangle - \langle m \rangle^2. \quad (9.84)$$

We can relate $\phi(\mathbf{r})$ to $G(r)$ by the following considerations. Because we can write the total energy in the form

$$H = H_0 - \int m(\mathbf{r})B(\mathbf{r}) d^3r, \quad (9.85)$$

we have

$$\langle m(\mathbf{r}) \rangle = \frac{\sum_s m_s(\mathbf{r}) e^{-\beta[H_{0,s} - \int B(\mathbf{r}')m_s(\mathbf{r}')d^3r']}}{\sum_s e^{-\beta[H_{0,s} - \int B(\mathbf{r}')m_s(\mathbf{r}')d^3r']}}, \quad (9.86)$$

where H_0 is the part of H that is independent of $B(\mathbf{r})$, and $H_{0,s}$ and $m_s(\mathbf{r})$ denote the values of H_0 and $m(\mathbf{r})$ in state s . We see that

$$\frac{\delta \langle m(\mathbf{r}) \rangle}{\delta B(0)} = \beta [\langle m(\mathbf{r})m(0) \rangle - \langle m(\mathbf{r}) \rangle \langle m(0) \rangle] = \beta G(\mathbf{r}). \quad (9.87)$$

Because $m(\mathbf{r}) = m_0 + \phi(\mathbf{r})$, we also have $\delta \langle m(\mathbf{r}) \rangle / \delta B(0) = \phi(\mathbf{r})/B_0$. Hence, $G(r) = kT\phi(\mathbf{r})/B_0$ and we find using (9.81) that

$$G(r) = \frac{kT}{4\pi g} \frac{1}{r} e^{-r/\xi}. \quad (9.88)$$

From the form of (9.88) we recognize ξ as the correlation length in the neighborhood of T_c . At $T = T_c$, $b = 0$, and we find from (9.88) that $G(r) \sim 1/r$. For arbitrary spatial dimension d we can write this spatial dependence as

$$G(r) \sim \frac{1}{r^{d-2+\eta}}, \quad (T = T_c) \quad (9.89)$$

where we have introduced another critical exponent η . We see that Landau theory yields $\eta = 0$.

Problem 9.11. Derive the relation (9.87) between the linear response $\delta\langle m(\mathbf{r}) \rangle / \delta B(0)$ and the spin correlation function $G(r)$.

The existence of long-range correlations in the correlation function of the order parameter $G(r)$ is associated with the divergence of χ , the susceptibility per spin. As we showed in Chapter 5, χ is related to the fluctuations in M (see (5.18)):

$$\chi = \frac{1}{NkT} [\langle M^2 \rangle - \langle M \rangle^2] \quad (9.90a)$$

$$= \frac{1}{NkT} \langle [M - \langle M \rangle]^2 \rangle. \quad (9.90b)$$

(We have defined χ as the isothermal susceptibility per spin.) We write

$$M - \langle M \rangle = \sum_{i=1}^N [s_i - \langle s_i \rangle], \quad (9.91)$$

and

$$\chi = \frac{1}{NkT} \sum_{i,j=1}^N [\langle s_i s_j \rangle - \langle s_i \rangle \langle s_j \rangle] \quad (9.92a)$$

$$= \frac{1}{kT} \sum_{j=1}^N G_{1j}, \quad (9.92b)$$

where $G_{ij} = \langle s_i s_j \rangle - \langle s_i \rangle \langle s_j \rangle$. We have used the definition of G_{ij} and the fact that all lattice sites are equivalent. The generalization of (9.92b) to a continuous system is

$$\chi = \frac{1}{kT} \int G(r) d^3r. \quad (9.93)$$

From (9.93) we see that the divergence of the susceptibility is associated with the existence of long-range correlations.

Problem 9.12. Show that the relation (9.93) and the form (9.88) implies that $\chi \sim |T - T_c|^{-1}$.

Range of Validity of Mean-Field Theory. It is interesting that mean-field theory carries with it the seeds of its own destruction and must break down when the system is sufficiently close to its critical point. That is, mean-field theory should be applicable if the fluctuations in the order parameter are much smaller than its mean value so that the fluctuations can be ignored. Conversely, if fluctuations are larger than the mean value, mean-field theory should break down.

$$\frac{\int [\langle m(\mathbf{r})m(0) \rangle - \langle m(\mathbf{r}) \rangle \langle m(0) \rangle] d^3r}{\int m^2 d^3r} \ll 1. \quad (9.94)$$

The condition (9.94) is known as the *Ginzburg criterion* and gives a criterion for the self-consistency of mean-field theories. If we substitute $G(r)$ from (9.88) into (9.94) and integrate over a sphere of radius ξ , we find

$$\frac{kT}{4\pi g} \int_0^\xi e^{-r/\xi} 4\pi r dr = \frac{kT\xi^2}{g} \left(1 - \frac{2}{e}\right) = \frac{0.264kT\xi^2}{g}. \quad (9.95)$$

The Ginzburg criterion for the validity of mean-field theory becomes

$$\frac{0.264kT\xi^2}{g} \ll \frac{4\pi}{3}\xi^3 m^2 \quad (9.96)$$

or

$$\frac{0.063}{g} \ll \xi m^2. \quad (\text{Ginzburg criterion}) \quad (9.97)$$

Because $\xi \sim |T - T_c|^{-1/2}$ and $m^2 \sim (T - T_c)$, we see that the magnitude of the product ξm_0^2 approaches zero as $T \rightarrow T_c$ and the Ginzburg criterion will not be satisfied for T sufficiently close to T_c . Hence, mean-field theory contains the seeds of its own destruction and must break down when the system is sufficiently close to its critical point. However, there exist some systems, for example, superconductivity as described by BCS theory, for which ξ is very large and (9.97) is satisfied in practice down to temperature differences as small as $|T - T_c| \sim 10^{-14}$.

Problem 9.13. We can generalize the results of mean-field theory to arbitrary spatial dimension d . Equation (9.80) can be generalized to arbitrary d by replacing the operator ∇^2 by the analogous d -dimensional operator. The general solution is not as simple as (9.5), but has the asymptotic form

$$G(r) \sim \frac{e^{-r/\xi}}{r^{d-2}}. \quad (9.98)$$

Generalize the Ginzburg criterion (9.94) to arbitrary d and show the inequality is satisfied if $d\nu - 2\beta - 2\nu$, or

$$d > 2 + 2\beta/\nu. \quad (9.99)$$

Ignore all numerical factors. Because mean-field theory yields $\beta = \frac{1}{2}$ and $\nu = \frac{1}{2}$, we find that mean-field theory is valid for all T near T_c if $d > d_c = 4$. At $d = d_c$, the *upper critical dimension*, there are small logarithmic corrections to the mean-field critical exponents. That is, near the critical point, mean-field theory is only reliable for dimensions greater than four.

9.6 Other Models of Magnetism

The Ising model is an excellent model for testing methods of statistical mechanics, and there are still aspects of the model that are of much current interest.³ Many variations of the Ising model and the Heisenberg model provide the basis for models of magnetic phenomena. One interesting limit is $S \rightarrow \infty$, corresponding to classical spins. In this limit the direction of \mathbf{S} is not quantized. It is convenient to replace the spin \mathbf{S} by a unit vector $\mathbf{s} = \mathbf{S}/S$ and redefine the coupling constant such that the old J is replaced by J/S^2 . The factor of S^2 cancels, and we are left with the Hamiltonian

$$H = -J \sum s_i \cdot s_j. \quad (\text{classical Heisenberg model}) \quad (9.100)$$

If the spins can point in any direction in three-dimensional space, this model is referred to as the classical Heisenberg model or sometimes the $O(2)$ model from group theory. If the spins are restricted to stay in a plane, then the model is called the planar or x - y model. The properties

³The existence of many papers on the Ising model has led some workers in statistical mechanics to dub the Ising model as the “fruit-fly” of statistical mechanics.

of these models depends on the dimension of the lattice. For example, in three dimensions the classical Heisenberg model has a phase transition between a low temperature ferromagnetic state and a high temperature paramagnetic state. However, on a two-dimensional lattice the classical Heisenberg model has no phase transition and is always in the disordered paramagnetic state except at $T = 0$. This result is related to the issue of confinement of quarks in the theory of quantum chromodynamics.

The planar model has some very interesting properties on a two-dimensional lattice. Although there is no spontaneous magnetization, there nevertheless is a phase transition between a low temperature quasi-ordered phase and a high temperature disordered phase. The phase transition is caused by the unbinding of spin vortex pairs.

We also can include the effects of anisotropy by replacing $J\mathbf{S}_i \cdot \mathbf{S}_j$ by $J_x\mathbf{S}_{x,i}\mathbf{S}_{x,j} + J_y\mathbf{S}_{y,i}\mathbf{S}_{y,j} + J_z\mathbf{S}_{z,i}\mathbf{S}_{z,j}$, and giving J_x , J_y , and J_z different values. An important special case is $J_x = J_y \neq J_z$. Interesting models can be created by extending the interactions between the spins beyond nearest neighbors, and adjusting the interaction to be different for different neighbors and for different distances. An example is the ANNNI model or antiferromagnetic next-nearest neighbor model. In this model the nearest neighbors have ferromagnetic couplings, but next-nearest neighbors have antiferromagnetic couplings. We also can give the coupling $J_{i,j}$ for each pair of spins, i and j , a random value. Such a model is called a *spin glass* and is currently an area of active research. Other extensions include adding a random magnetic field at each site to favor a particular direction of the spin (the random field Ising model).

In addition to magnetic systems, the above models are useful for studying other systems. For example, “up” and “down” in the Ising model can represent A and B atoms in an AB alloy. In this case the model is referred to as a lattice gas. The principal difference is that the net spin or magnetization (or total number of A atoms or total number of gas particles) is fixed. This distinction means that a different ensemble is appropriate.

Superfluids can be modeled by the planar model near the superfluid phase transition. The reason is that the spin-spin interaction in the planar model can be expressed as $\cos(\theta_i - \theta_j)$, where θ_i is an angle that goes from 0 to 2π . In superfluids the order parameter is described by a quantum mechanical phase that also is an angle.

Another extension to the Heisenberg model is the q -state *Potts model* for which there are q discrete states at each site; the energy is $-J$ if two neighboring sites are in the same state and zero otherwise. A related extension is the q -state *clock model*, where the spin is restricted to point in a two-dimensional plane at q equally spaced angles. These models are useful for modeling the behavior of atoms absorbed on surfaces, when there are q possible types of sites on the surface at which the atom can stick.

Similar spin models are being extended to understand the field theories used in high energy physics. The principal difference is that the interactions are typically four spin interactions between spins located at the corners of the square plaquettes of the lattice. The planar model turns out to represent electromagnetism. We can obtain the other fundamental interactions by invoking more complicated spins that become matrices instead of simple vectors.

9.7 Universality and Scaling Relations

For convenience, we summarize the standard static critical exponents in Table 9.3. The quantity $\epsilon = (T_c - T)/T_c$. The notation $C \sim |\epsilon|^{-\alpha}$ means that C has a singular contribution proportional to $|\epsilon|^{-\alpha}$.

heat capacity	$C \sim \epsilon ^{-\alpha}$
order parameter	$m \sim \epsilon^\beta$
susceptibility	$\chi \sim \epsilon ^{-\gamma}$
equation of state ($\epsilon = 0$)	$m \sim B^{-1/\delta}$
correlation length	$\xi \sim \epsilon ^{-\nu}$
power law decay at $\epsilon = 0$	$G(r) \sim 1/r^{d-2+\eta}$

Table 9.3: Summary of the definition of the standard critical exponents expressed in the language of magnetic systems.

The above definitions of the critical exponents implicitly assume that the singularities are the same whether the critical point is approached from above or below. (The exception is m which is zero for $T > T_c$.) In the following, we will not bother to write $|\epsilon|$ instead of ϵ .

The importance of the critical exponents is that they are *universal*, that is, they depend only on the spatial dimension of the lattice d and the number of components of the order parameter, and do not depend on the details of the interactions. For example, the critical exponents for the Ising model are the same as those for the liquid-gas critical point. The standard universality classes correspond to the scalar, planar, and three-dimensional vector order parameter for which $n = 1$, $n = 2$, and $n = 3$, respectively. Examples of $n = 1$ are the Ising model, the lattice gas model, and the liquid-gas transition. Examples of $n = 2$ are planar ferromagnets, the superfluid, and ordinary superconductivity. The latter two cases correspond to $n = 2$ because the order parameter is complex. The case $n = 3$ corresponds to the Heisenberg model.

We will find in the following that only two of the above six critical exponents are independent. The exponents are related by the scaling relations which are summarized in Table 9.4.

Fisher	$\gamma = \nu(2 - \eta)$
Rushbrooke	$\alpha + 2\beta + \gamma = 2$
Widom	$\gamma = \beta(d - 1)$
Josephson	$\nu d = 2 - \alpha$

Table 9.4: Examples of simple scaling relations between the critical exponents.

The essential physics of the critical point is that the correlation length ξ is the only characteristic length of the system. This assumption is known as the “scaling hypothesis,” although now it is more than a hypothesis. A simple way to obtain the above scaling relations is to use dimensional analysis and assume that a quantity that has dimension L^{-d} is proportional to ξ^{-d} near the critical point.

Because the quantity βF is dimensionless and proportional to N , we have that $\beta F/V$ has dimensions

$$[\beta f] = L^{-d}. \quad (9.101)$$

Similarly the correlation function $G(r)$ depends on L according to

$$[G(r)] = L^{2-d-\eta}. \quad (9.102)$$

By definition $G(r)$ has the same dimension as m^2 so

$$[m] = L^{(2-d-\eta)/2}. \quad (9.103)$$

If we use the relation (9.90b), we have

$$[kT\chi] = L^{2-\eta}. \quad (9.104)$$

Finally, because $M = -\partial F/\partial B$ (see (5.16)), we have

$$[B/kT] = L^{(2+d-\eta)/2}. \quad (9.105)$$

We now replace the L in the above formulae by ξ and let $\xi \sim \epsilon^{-\nu}$. Because the dimensions of the heat capacity are the same as βf in (9.101), we obtain $2 - \alpha = \nu d$. We leave it as an exercise for the reader to obtain the other scaling relations (see Problem 9.14).

Problem 9.14. Use the above dimensional analysis arguments to obtain the relations $-\nu(2 - d - \eta)/2 = \beta$, $-\nu(2 - \eta) = -\gamma$, and $\nu(2 + d - \eta)/2 = \beta\delta$. Then do some simple algebra to derive the Rushbrooke and Widom scaling laws.

9.8 The Renormalization Group and the 1D Ising Model

Although the one-dimensional Ising model does not have a critical point, the application of the renormalization group method has much pedagogical value and is the only case in which a simple grouping of spins can be carried out analytically. The Hamiltonian for the Ising chain with periodic boundary conditions is (see (5.57))

$$H = -J \sum_{i=1}^N s_i s_{i+1} - \frac{1}{2} \tilde{B} \sum_{i=1}^N (s_i + s_{i+1}). \quad (9.106)$$

It is convenient to define the dimensionless parameters $K = \beta J$ and $B = \beta \tilde{B}$. For periodic boundary conditions the partition function can be written as

$$Z = \sum_{\{s\}} \exp \left[\sum_{i=1}^N (K s_i s_{i+1} + \frac{1}{2} B (s_i + s_{i+1})) \right]. \quad (9.107)$$

The sum in (9.107) is over all possible spin configurations. For simplicity, we first consider $B = 0$.

One way to obtain a renormalized lattice is to group sites into cells. Another way to reduce the number of degrees of freedom is to average or sum over them. For example, for the $d = 1$ Ising model we can write Z as

$$Z(K, N) = \sum_{\{s\}} e^{K(s_1 s_2 + s_2 s_3)} e^{K(s_3 s_4 + s_4 s_5) \dots} \quad (9.108)$$

The form (9.108) suggests that we sum over even spins:

$$Z(K, N) = \sum_{\text{odd spins}} [e^{K(s_1 + s_3)} + e^{-K(s_1 + s_3)}] \times [e^{K(s_3 + s_5)} + e^{-K(s_3 + s_5)}] \times \dots \quad (9.109)$$

This method of reducing the degrees of freedom is called *decimation*.

We next try to write the partially averaged partition function (9.109) in its original form with $N/2$ spins and, in general, a different interaction K' . If such a rescaling were possible, we could obtain a recursion relation for K' in terms of K . We require that

$$e^{K(s_1 + s_3)} + e^{-K(s_1 + s_3)} = A(K) e^{K' s_1 s_3}, \quad (9.110)$$

where the function A does not depend on s_1 or s_3 . If the relation (9.110) exists, we can write

$$Z(K, N) = \sum_{s_1, s_3, s_5, \dots} A(K) e^{K' s_1 s_3} A(K) e^{K' s_3 s_5} \dots, \quad (9.111a)$$

$$= [A(K)]^{N/2} Z(K', N/2). \quad (9.111b)$$

In the limit $N \rightarrow \infty$, we know that $\ln Z$ is proportional to N , that is,

$$\ln Z = N f(K), \quad (9.112)$$

where $f(K)$ depends on K and is independent of N . From (9.111b) and (9.112) we obtain

$$\ln Z = N f(K) = \frac{N}{2} \ln A(K) + \ln Z(K', \frac{N}{2}) \quad (9.113a)$$

$$= \frac{N}{2} \ln A(K) + \frac{N}{2} f(K'), \quad (9.113b)$$

or

$$f(K') = 2f(K) - \ln A(K). \quad (9.114)$$

We can find the form of $A(K)$ from (9.110). Recall that (9.110) holds for all values of s_1 and s_3 . We first consider the cases $s_1 = s_3 = 1$ and $s_1 = s_3 = -1$ for which

$$e^{2K} + e^{-2K} = A e^{K'}. \quad (9.115)$$

For the case $s_1 = 1$ and $s_3 = -1$ or $s_1 = -1$ and $s_3 = 1$, we have

$$2 = A e^{-K'}. \quad (9.116)$$

From (9.116) we have $A = 2e^{K'}$, and hence from (9.115), we obtain

$$e^{2K} + e^{-2K} = 2e^{2K'}, \quad (9.117)$$

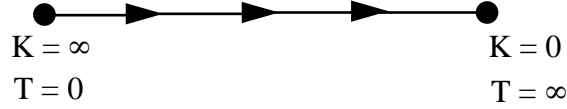


Figure 9.8: Renormalization group flow diagram for one-dimensional Ising model in zero magnetic field.

or

$$K' = R(K) = \frac{1}{2} \ln (\cosh(2K)). \quad (\text{recursion relation}) \quad (9.118)$$

From (9.116) we find that $A(K)$ is given by

$$A(K) = 2 \cosh^{1/2}(2K). \quad (9.119)$$

We can use the form of $A(K)$ in (9.119) to rewrite (9.114) as

$$f(K') = 2f(K) - \ln[2 \cosh^{1/2}(2K)]. \quad (\text{free energy per spin}) \quad (9.120)$$

Equations (9.118) and (9.120) are the essential results of the renormalization group analysis.

Because $\frac{1}{2} \ln \cosh(2K) \leq K$, the successive use of (9.118) leads to smaller values of K and smaller values of the correlation length. Thus $K = 0$ or $T = \infty$ is a trivial fixed point (see Figure 9.8). This behavior is to be expected because the Ising chain does not have a phase transition at nonzero temperature. As an example, suppose we start with $K = 10$ corresponding to a low temperature. The first iteration gives $K' = 9.65$ and further iterations lead to $K' = 0$. Because any system with $K \neq 0$ ultimately renormalizes to $K = 0$, we conclude that every point for $K > 0$ is in the same phase. Only exactly at zero temperature is this statement not true. We say that there are two fixed points; the one at $T = 0$ is unstable because any perturbation away from $T = 0$ is amplified. The fixed point at $T = \infty$ is stable. The renormalization group flows go from the unstable fixed point to the stable fixed point as shown in Figure 9.8.

Because a nontrivial fixed point of (9.118) between $T = 0$ and $T = \infty$ does not exist, the recursion relation is reversible, and we can follow the transformation backwards starting from $K \approx 0$ ($T = \infty$) and going to $K = \infty$ ($T = 0$). The advantage of starting from $T \approx \infty$ is that we can start with the exact solution for $K = 0$ ($T = \infty$) and iterate the equation to higher values of K . To find the corresponding recursion relation that works in this direction we solve (9.118) for K in terms of K' . Similarly, we solve (9.120) to find $f(K)$ in terms of $f(K')$. The result is

$$K = \frac{1}{2} \cosh^{-1}(e^{2K'}), \quad (9.121)$$

$$f(K) = \frac{1}{2} \ln 2 + \frac{1}{2} K' + \frac{1}{2} f(K'). \quad (9.122)$$

The relations (9.121) and (9.122) can be used to calculate $f(K)$. Suppose we begin with $K' = 0.01$. Because this value of K' is close to zero, the effect of the spin-spin interactions is very small, and we can take $Z(K' = 0.01, N) \approx Z(K' = 0, N) = 2^N$. From (9.112) we have

$$f(K' = 0.01) \approx \ln 2 \approx 0.693147. \quad (9.123)$$

K'	K	$f(K')$	$f(K)$
0.01	0.100334	0.693147	0.698147
0.100334	0.327447	0.698147	0.745814

Table 9.5: Summary of the first few steps of the calculation of f , the free energy per spin, for the $d = 1$ Ising model from the recursion relations (9.121) and (9.122). The function f is related to the partition function Z by $\ln Z = Nf$ (see (9.112)).

Given $K' = 0.01$, we calculate K from (9.121) and obtain the result $K = 0.100334$. The value of $f(K)$ for this value of K is found from (9.122) to be 0.698147. This calculation of $f(K)$ and K is the first step in an iterative procedure that can be repeated indefinitely with K' chosen to be the value of K from the prior iteration and $f(K')$ chosen to be the value of $f(K)$ from the previous iteration. The first few iterations are shown in Table 9.5.

Problem 9.15. Extend the calculation of $f(k)$ in Table 9.5 to larger values of K by doing several more iterations of (9.121) and (9.122). Also calculate the exact value of the free energy for the calculated values of K using (5.28) and compare your results to $f(K)$. Because the recursion relations (9.121) and (9.122) are exact, the only source of error is the first value of f . Does the error increase or decrease as the calculation proceeds?

***Problem 9.16.** For nonzero magnetic field show that the function $A(K, B)$ satisfies the relation:

$$2e^{B(s_1+s_3)/2} \cosh[K(s_1+s_3)+B] = A(K, B) e^{2f+K's_1s_3+\frac{1}{2}B'(s_1+s_3)}, \quad (9.124)$$

Show that the recursion relations for nonzero magnetic field are

$$K' = \frac{1}{4} \ln \frac{\cosh(2K+B) \cosh(2K-B)}{\cosh^2 B}, \quad (9.125a)$$

$$B' = B + \frac{1}{2} \ln \frac{\cosh(2K+B)}{\cosh(2K-B)}, \quad (9.125b)$$

and

$$f(K, B) = \frac{1}{8} \ln [16 \cosh(2K+B) \cosh(2K-B) \cosh^2 B] \quad (9.125c)$$

The recursion relations (9.125) have a line of trivial fixed points satisfying $K^* = 0$ and arbitrary B^* , corresponding to the paramagnetic phase, and an unstable ferromagnetic fixed point at $K^* = 0, B^* = 0$.

Justify the relation

$$Z(K, B, N) = e^{Nf(K, B)} Z(K', B', \frac{1}{2}N). \quad (9.126)$$

***Problem 9.17. Transfer matrix method.** As shown in Section 5.4.4, the partition function for the N -spin Ising chain can be written as the trace of the N th power of the transfer matrix \mathbf{T} . We can reduce the number of degrees of freedom by describing the system in terms of two-spin cells. We write Z as

$$Z = \text{trace } \mathbf{T}^N = \text{trace } (\mathbf{T}^2)^{N/2} = \text{trace } \mathbf{T}'^{N/2}. \quad (9.127)$$

The transfer matrix for two-spin cells, \mathbf{T}^2 , can be written as

$$\mathbf{T}^2 = \mathbf{T}\mathbf{T} = \begin{pmatrix} e^{2K+2B} + e^{-2K} & e^B + e^{-B} \\ e^{-B} + e^B & e^{2K-2B} + e^{-2K} \end{pmatrix} \quad (9.128)$$

In (9.128) we have written $K = \beta J$ and B represents the product βB as we did earlier. We require that \mathbf{T}' have the same form as \mathbf{T} :

$$\mathbf{T}' = C \begin{pmatrix} e^{K'+B'} & e^{-K'} \\ e^{-K'} & e^{K'-B'} \end{pmatrix} \quad (9.129)$$

A parameter C must be introduced because matching (9.128) with (9.129) requires matching three matrix elements, which in general is impossible with only two variables, K' and B' . We have three unknowns to satisfy the three conditions:

$$C e^{K'} e^{B'} = e^{-2K} + e^{2K} e^{2B} \quad (9.130a)$$

$$C e^{-K'} = e^{-B} + e^{-B} \quad (9.130b)$$

$$C e^{K'} e^{-B'} = e^{-2K} + e^{2K} e^{-2B}. \quad (9.130c)$$

Show that the solution can be written as

$$e^{-2K'} = \frac{e^{-B} + e^B}{e^{-2K-B} + e^{2K+B}}, \quad (9.131a)$$

$$e^{-2B'} = \frac{e^{-2K} + e^{2K-2B}}{e^{-2K} + e^{2K+2B}}, \quad (9.131b)$$

$$4C = (e^{4K} + e^{-4K} + e^{-2B} + e^{2B})(2 + e^{-2B} + e^{2B}). \quad (9.131c)$$

Also show that the recursion relations in (9.131) reduce to (9.118) for $B = 0$. For $B \neq 0$, start from some initial state K_0, B_0 and calculate a typical renormalization group trajectory. To what phase (paramagnetic or ferromagnetic) does the fixed point correspond?

9.9 The Renormalization Group and the Two-Dimensional Ising Model

For simplicity, we consider $B = 0$ so that there is only one coupling constant $K = \beta J$. As pointed out by Wilson, there is no recipe for constructing a renormalization group transformation, and we will consider only one possible approach. In particular, we consider the majority rule transformation developed by Niemeijer and van Leeuwen for the ferromagnetic Ising model on the triangular lattice. This approach is known as a real-space method, because the renormalization group transformation is applied directly to the spins on the lattice.

The idea is to divide the original lattice into cells and replace the site spins $s_i = \pm 1$ by the renormalized cell spins $\mu_\alpha = \pm 1$. The Latin indices i and j denote the original lattice sites and the Greek indices α and β denote the renormalized cell spins. As shown in Figure 9.9, we take the sites of the original triangular lattice and group them into cells or blocks of three. The cells

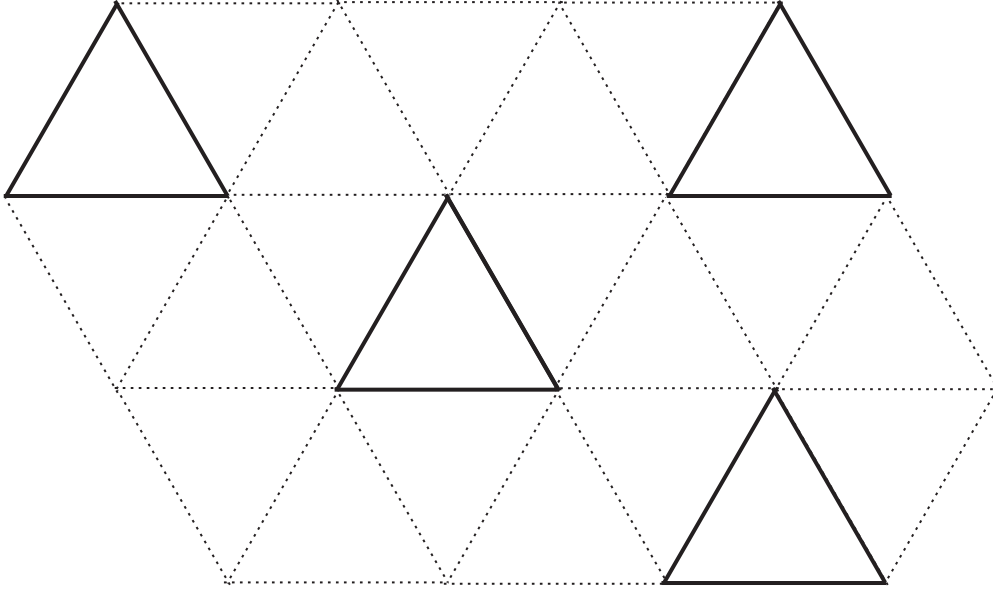


Figure 9.9: Cell spins on the triangular lattice. The solid lines indicate intracell interactions; the dotted lines show the intercell interactions.

form a triangular lattice with a lattice constant $a' = \sqrt{3}a$ so that the length rescaling parameter is $b = \sqrt{3}$.

We write the original Hamiltonian in the form

$$\mathcal{H} = \beta H = -K \sum_{\langle ij \rangle} s_i s_j, \quad (9.132)$$

and the partition function in the form

$$Z(K) = \sum_{\{s\}} e^{-\mathcal{H}(\{s\})}, \quad (9.133)$$

where $K = \beta J$. We have incorporated the factor of β into the Hamiltonian and have written $\mathcal{H} = \beta H$.

The new Hamiltonian for the renormalized lattice can be written as

$$\mathcal{H}' = \mathcal{H}_0 + \mathcal{V}, \quad (9.134)$$

where \mathcal{H}_0 represents the sum of all the interactions between spins within the same cell, and \mathcal{V} is the interaction of spins between different cells. We write

$$\mathcal{H}_0 = -K \sum_{\alpha} \sum'_{i,j \in \alpha} s_i s_j, \quad (9.135)$$

where the sum over α represents the sum over cells. The restricted sum in (9.135) (denoted by a prime) is over configurations of the original lattice that are consistent with a given set of cell spins μ . For $b = \sqrt{3}$, the Hamiltonian for cell α has the form

$$\mathcal{H}_{0,\alpha} = -K(s_{1,\alpha}s_{2,\alpha} + s_{1,\alpha}s_{3,\alpha} + s_{2,\alpha}s_{3,\alpha}). \quad (9.136)$$

We write \mathcal{V} as

$$\mathcal{V} = -K \sum_{\substack{i \subset \alpha \\ \neq}} \sum'_{i \subset \alpha} \sum'_{j \subset \beta} s_i s_j. \quad (9.137)$$

The replacement of the original site spins by cell spins leads in general to a Hamiltonian that does not have the same form as (9.132). That is, the new Hamiltonian involves interactions between cell spins that are not nearest neighbors. Nevertheless, we assume that the new Hamiltonian has the same form:

$$\mathcal{F}_r + \mathcal{H}' = -K' \sum'_{\langle \alpha \beta \rangle} \mu_\alpha \mu_\beta. \quad (9.138)$$

The term \mathcal{F}_r in (9.138) is independent of the cell spin configurations. The representation (9.134)–(9.137) is exact.

In the following, we treat the interactions of the spins within the cells exactly and the interactions between the cells approximately. We will obtain a recursion relation

$$K' = R(K), \quad (9.139)$$

and a nontrivial fixed point K^* such that

$$\lambda_K = \left. \frac{\partial K'}{\partial K} \right|_{K^*}, \quad (9.140)$$

and

$$\nu = \frac{\ln \lambda_K}{\ln b}, \quad (9.141)$$

where b is the length rescaling parameter.

The renormalized Hamiltonian is given formally by

$$e^{-\mathcal{F} - \mathcal{H}'} = \sum_{\{\mu\}} P(\mu, s) e^{-(\mathcal{H}_0 + \mathcal{V})}, \quad (9.142)$$

where the operator $P(\mu, s)$ transforms the original three spins to the cell spin and implements the majority rule so that the renormalized cell spin equals the sign of the sum of the site spins in the cell. Formally, we can write P for cell spin α as

$$P(\mu_\alpha, s) = \delta(\mu_\alpha - \text{sgn}(s_1 + s_2 + s_3)). \quad (9.143)$$

Because we need to treat the interaction between the cell spins approximately, we introduce an average over the original spin variables with respect to \mathcal{H}_0 :

$$\langle A \rangle_0 = \frac{\sum'_{\{\mu\}} A(\mu) P(\mu, s) e^{-\mathcal{H}_0(s)}}{\sum'_{\{\mu\}} P(\mu, s) e^{-\mathcal{H}_0(s)}}. \quad (9.144)$$

We write

$$e^{-\mathcal{F}} e^{-\mathcal{H}'} = \sum_{\{s\}}' P(\mu, s) e^{-(\mathcal{H}_0 + \mathcal{V})}, \quad (9.145)$$

and multiply the top and bottom of (9.145) by Z_0 , the partition function associated with \mathcal{H}_0 :

$$e^{-\mathcal{F}} e^{-\mathcal{H}'} = \sum_{\{s\}}' P(\mu, s) e^{-\mathcal{H}_0} \frac{\sum_{\{s\}}' P(\mu, s) e^{-(\mathcal{H}_0 + \mathcal{V})}}{\sum_{\{s\}}' P(\mu, s) e^{-\mathcal{H}_0}} \quad (9.146a)$$

$$= Z_0 \langle e^{-\mathcal{V}} \rangle_0. \quad (9.146b)$$

We write $Z_0 = z(\mu)^{N'}$, where $N' = N/b^d$ is the number of cells, and $z(\mu)$ is the sum over the internal spin states for one cell for a given orientation of μ . The average $\langle e^{-\mathcal{V}} \rangle_0$ is with respect to the intracell Hamiltonian \mathcal{H}_0 . We take the logarithm of both sides of (9.146b) and obtain

$$\mathcal{F}_r + \mathcal{H}' = -N' \ln z - \ln \langle e^{-\mathcal{V}} \rangle_0. \quad (9.147)$$

Then we can identify

$$f_r = \frac{\mathcal{F}_r}{N} = \frac{N'}{N} \ln z = \frac{1}{b^d} \ln z, \quad (9.148)$$

and

$$\mathcal{H}' = -\ln \langle e^{-\mathcal{V}} \rangle_0. \quad (9.149)$$

Before we evaluate the average in (9.149), we first calculate z and f_r . The sum over the spins in a given cell for $\mu = 1$ can be written as

$$z(\mu = 1) = \sum_{\{s\}}' e^{K(s_1 s_2 + s_2 s_3 + s_3 s_1)}. \quad (9.150)$$

The restricted sum over the four states $s_1, s_2, s_3 = \uparrow\uparrow\uparrow, \uparrow\uparrow\downarrow, \uparrow\downarrow\downarrow, \downarrow\uparrow\uparrow$ (see Figure 9.10) gives

$$z(\mu = 1) = e^{3K} + 3e^{-K}. \quad (9.151)$$

From (9.148) we have

$$f_r = \frac{1}{3} \ln(e^{3K} + 3e^{-K}). \quad (9.152)$$

In the absence of a magnetic field, it is clear that the sum for $\mu = -1$ gives the same value for z (see Problem 9.18).

Problem 9.18. Calculate $z(\mu = -1)$ and show that $z(\mu = +1) = z(\mu = -1)$.

The difficult part of the calculation is the evaluation of the average $\langle e^{-\mathcal{V}} \rangle_0$. Our approach will be to evaluate it approximately by keeping only the first cumulant. Because the cumulant expansion is essentially a power series in $K = \beta J$, it is reasonable to assume that the series converges given that $K_c \approx 0.275$ for the triangular lattice. We write

$$\ln \langle e^{-\mathcal{V}} \rangle_0 = \sum_{n=1}^{\infty} \frac{(-1)^n}{n!} M_n, \quad (9.153)$$

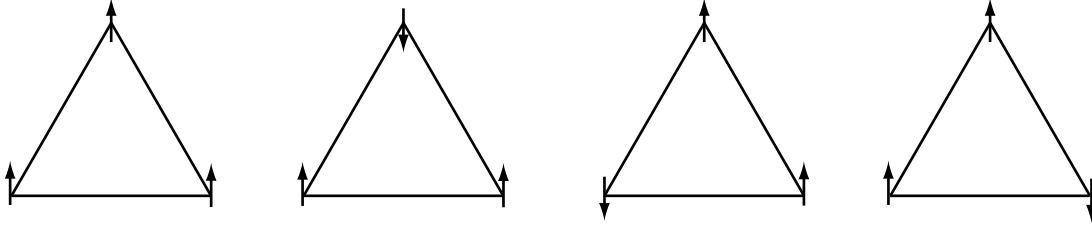


Figure 9.10: Three spin cluster on the triangular lattice.

and keep only the first cumulant

$$M_1 = \langle \mathcal{V} \rangle_0. \quad (9.154)$$

The first approximation to the intercell interaction \mathcal{V} can be written as (see Figure 9.11)

$$\mathcal{V}_{\alpha\beta} = -K s_{1,\alpha} [s_{2,\beta} + s_{3,\beta}]. \quad (9.155)$$

Note that $\mathcal{V}^{(1)}$ in (9.155) includes only the interaction of two nearest neighbor cells and that this approximation does not preserve the symmetry of the triangular lattice. However, this approximation is consistent with our assumption that the renormalized Hamiltonian has the same form as the original Hamiltonian. Because \mathcal{H}_0 does not couple different cells, we have

$$\langle \mathcal{V}_{\alpha\beta} \rangle_0 = -2K \langle s_{1,\alpha} s_{2,\beta} \rangle_0, \quad (9.156a)$$

$$= -2K \langle s_{1,\alpha} \rangle_0 \langle s_{2,\beta} \rangle_0. \quad (9.156b)$$

(The factor of 2 in (9.156) arises from the fact that $\langle s_{2,\beta} \rangle = \langle s_{3,\beta} \rangle$.)

From (9.156b) we see that we need to find $\langle s_{1,\alpha} \rangle_0$. Suppose that $\mu_\alpha = 1$. The four states consistent with this condition are shown in Figure 9.10. It is easy to see that

$$\langle s_{1,\alpha} \rangle_0 = \frac{1}{z} \sum'_{\{s\}} s_1 e^{K(s_1 s_2 + s_2 s_3 + s_3 s_1)} \quad (9.157a)$$

$$= \frac{1}{z} [+1e^{3K} + 1e^{-K} + 1e^{-K} - 1e^{-K}] \quad (9.157b)$$

$$= \frac{1}{z} [e^{3K} + e^{-K}]. \quad (\mu_\alpha = +1). \quad (9.157c)$$

Similarly, we can show that

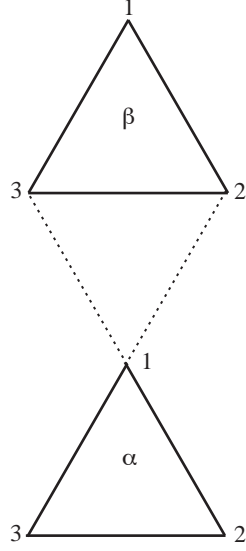
$$\langle s_{1,\alpha} \rangle_0 = \frac{1}{z} [-e^{3K} - e^{-K}] = -\frac{1}{z} [e^{3K} + e^{-K}] \quad (\mu_\alpha = -1) \quad (9.158)$$

Hence, we can write

$$\langle s_{1,\alpha} \rangle_0 = \frac{1}{z} [e^{3K} + e^{-K}] \mu_\alpha. \quad (9.159)$$

From (9.156b) and (9.159) we have

$$\langle \mathcal{V}_{\alpha\beta} \rangle_0 = -2K f(K)^2 \mu_\alpha \mu_\beta, \quad (9.160)$$

Figure 9.11: The couplings between nearest-neighbor cell spins $\mathcal{V}_{\alpha\beta}$.

where

$$f(K) = \frac{e^{3K} + e^{-K}}{e^{3K} + 3e^{-K}}. \quad (9.161)$$

We write

$$\langle \mathcal{V} \rangle_0 = \sum_{\langle \alpha\beta \rangle} \langle \mathcal{V}_{\alpha\beta} \rangle_0 = -2K f(K)^2 \sum_{\langle \alpha\beta \rangle} \mu_\alpha \mu_\beta \quad (9.162a)$$

$$= -K' \sum_{\langle \alpha\beta \rangle} \mu_\alpha \mu_\beta. \quad (9.162b)$$

Note that $\langle \mathcal{V} \rangle_0$ has the same form as the original nearest neighbor interaction with a renormalized value of the interaction. If we compare (9.160) and (9.162b), we find the recursion relation

$$K' = R(K) = 2K f(K)^2, \quad (9.163)$$

and

$$\mathcal{H}' = -K' \sum_{\langle \alpha\beta \rangle} \mu_\alpha \mu_\beta. \quad (9.164)$$

Because $f(K=0) = 1/2$ and $f(K=\infty) = 1$, it is easy to see that there are trivial fixed points at $K^* = 0$ and $K^* = \infty$. The nontrivial fixed point occurs at $f(K) = 1/\sqrt{2}$ or at

$$K^* = \frac{1}{4} \ln(2\sqrt{2} + 1) \approx 0.3356. \quad (9.165)$$

The exact answer for K_c for the triangular lattice is $K_c = \frac{1}{3} \ln 3 = 0.2747$. We also have

$$\lambda_K = \left. \frac{dK'}{dK} \right|_{K=K^*} = 1.624, \quad (9.166)$$

and hence

$$\nu = \frac{\ln 1.624}{\ln \sqrt{3}} \approx 0.882. \quad (9.167)$$

For comparison, the exact result is $\nu = 1$.

Problem 9.19. Confirm the above results for K^* , λ_K , and ν .

We can extend the renormalization group analysis by considering higher order cumulants. The second order cumulant introduces two new interactions that are not in the original Hamiltonian. That is, the cell spins interacts not only with nearest-neighbor cell spins, but also with second and third neighbor cell spins. Hence, for consistency we have to include in our original Hamiltonian second and third neighbor interactions also. Fortunately, good results can usually be found by stopping at the second cumulant. More details can be found in the references.

9.10 Vocabulary

Landau theory
 mean-field critical exponents
 Ginzburg criterion
 scaling relations, universality
 percolation, connectivity
 cluster, spanning cluster
 recursion relation
 decimation
 cell spins
 real space renormalization group approach

9.11 Additional Problems

Problem 9.20. Calculate the temperature and density dependence of the compressibility of a gas assuming that it satisfies the van der Waals equation of state (8.154).

***Problem 9.21.** We can generalize the procedure of Problem 9.3 to large lattices. Consider the seven site cell shown in Figure 9.12 and assume that the cell is occupied if the majority of its sites are occupied. Show that the recursion relation is

$$p' = R(p) = 35p^4 - 84p^5 + 70p^6 - 20p^7. \quad (9.168)$$

Show that (9.168) has a nontrivial fixed point at $p^* = 0.5$ and that the correlation length exponent is given by

$$\nu = \frac{\ln 7}{2 \ln \frac{7}{3}} \approx 1.243. \quad (9.169)$$

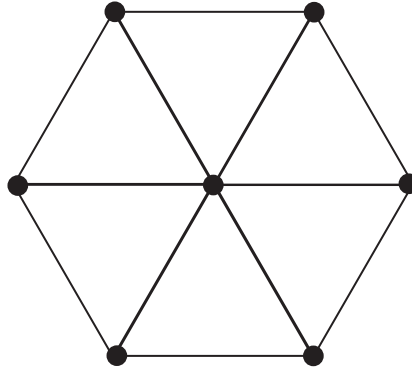


Figure 9.12: The seven site cell considered in Problem 9.21.

Problem 9.22. Apply the same approach as in Problem 9.8 to the Ising model on a triangular lattice and consider the three spin cluster, examples of which are shown in Figure 9.10. How many neighbors does each boundary spin have? Show that the effective three spin Hamiltonian can be written as

$$H_3 = -J(s_1 s_2 + s_1 s_3 + s_2 s_3) - 4mJ(s_1 + s_2 + s_3), \quad (9.170)$$

where $m = \langle s \rangle$. Then show by summing over the possible combinations of s_1 , s_2 , and s_3 that the partition function for the cluster can be written as

$$Z_3 = 2e^{3\beta J} \cosh 12\beta Jm + 6e^{-\beta J} \cosh 4\beta Jm. \quad (9.171)$$

Verify that the magnetization is given by

$$m = \frac{e^{3\beta J} \sinh 12\beta Jm + e^{-\beta J} \sinh 4\beta Jm}{e^{3\beta J} \cosh 12\beta Jm + 3e^{-\beta J} \cosh 4\beta Jm}. \quad (9.172)$$

To find the critical temperature, assume that m is small and expand (9.172) for small m . Show that the result can be written as

$$1 = 4\beta J \frac{(3e^{3\beta J} + e^{-\beta J})}{(e^{3\beta J} + 3e^{-\beta J})} = 4K \frac{(3e^{4K} + 1)}{(e^{4K} + 3)}, \quad (9.173)$$

where $K = \beta J$. Show numerically that the value of K that solves (9.173) is $K = K_c \approx 0.177$. Compare this value of $\beta_c J$ to the exact value $\beta_c H T_c = \frac{1}{3} \ln 3 \approx 0.366$ for the triangular lattice and the simple mean-field value (see Table 5.2). As an example of the fact that all mean-field approximations give the same critical exponents, show that $\beta = \frac{1}{2}$.

Problem 9.23. Another way to express the scaling hypothesis is to assume that for $B = 0$, $G(r)$ near $\epsilon = 0$ has the form

$$G(r) \sim \frac{1}{r^{d-2+\eta}} \psi_{\pm}(r/\xi), \quad (9.174)$$

where ψ_{\pm} is an unspecified scaling function. Use (9.174) and the relation (9.93) to obtain Fisher's scaling law, $\gamma = \nu(2 - \eta)$.

***Problem 9.24.** Develop an improved mean-field theory for the Ising model on a square lattice based on a four spin cluster.

***Problem 9.25.** We can apply mean-field ideas to percolation. It is easier to do so in the context of bond percolation. In bond percolation we place *bonds* between lattice sites with probability p and we call any set of sites that are connected to one another by bonds a cluster. The critical bond probability p_c occurs when there is a spanning cluster.

Let P_{∞} be the probability that a randomly chosen bond forms part of the infinite cluster. A given bond will form part of such a cluster only if it has at least one neighboring bond. That is, a bond will not form part of an infinite cluster if its neighboring bonds are themselves not part of the cluster. This requirement gives us a relation connecting the probabilities that neighboring bonds are part of the infinite cluster. If we assume that these probabilities are the same for all bonds (a mean-field assumption), we require that

$$1 - P_{\infty,i} = \prod_{j=1}^q (1 - p P_{\infty,j}), \quad (9.175)$$

where $P_{\infty,i}$ is the probability that bond i belongs to the infinite cluster. However, because we have assumed that all bonds see the same local environment, we have that $P_{\infty,i} = P_{\infty}$ and hence

$$1 - P_{\infty} = (1 - p P_{\infty})^q. \quad (9.176)$$

Work out the graphical solution of (9.176) and show that $p_c = 1/q$. If we set $P_{\infty} \sim (p - p_c)^{\beta}$, what is the mean-field value of β for percolation?

***Problem 9.26.** The method we used in Section 9.8 for the one-dimensional Ising model is an example of a *decimation* method. In this problem, we apply another decimation method to the two-dimensional Ising model on the square lattice in the absence of an external magnetic field. The Migdal-Kadanoff approximation consists of two steps that are illustrated in Figure 9.13. First the sites denoted by an \times in Figure 9.13a are removed. To compensate for this removal, the remaining bonds are doubled in strength so that the new Hamiltonian becomes

$$\beta H = -2K \sum_{\langle i,j \rangle}' s_i s_j. \quad (9.177)$$

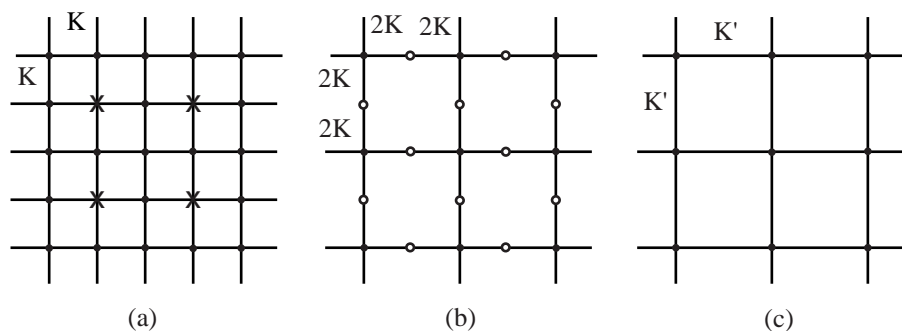


Figure 9.13: An example of the decimation of half of the spins on a square lattice.

The prime indicates that the new Hamiltonian is defined on the lattice shown in Figure 9.13b. The main virtue of this approximation is that it makes the renormalization easier. Then sum over the spins on the sites indicated by open circles in Figure 9.13b to obtain the lattice shown in Figure 9.13c. Show that the new Hamiltonian has the same form as the original Hamiltonian with the renormalized nearest neighbor interaction K' :

$$\mathcal{H}' = -K' \sum_{\langle ij \rangle} \mu_i \mu_j, \quad (9.178)$$

and that the partition function differs from the original one only by a constant factor. Let $x = 2K$ and $x' = 2K'$ and show that the resulting recursion relation can be written as

$$x' = \frac{1}{2}(x^2 + x^{-2}). \quad (9.179)$$

For the one-dimensional Ising model we found that the fixed points are the trivial ones at $K^* = 0$ and $K^* = \infty$. Show that in addition to these trivial fixed points, there is a new fixed point of (9.179) at $x = x^*$. Show that this fixed point is unstable by showing that $\lambda = dx'/dx|_{x=x^*} > 1$. What is the corresponding value of the exponent ν ? (Problem adapted from Huang, page 466.)

Suggestions for Further Reading

David Chandler, *Introduction to Modern Statistical Mechanics*, Oxford University Press (1987). Chapter 5 has a clear explanation of the renormalization group method.

R. J. Creswick, H. A. Farach, and C. P. Poole, Jr., *Introduction to Renormalization Group Methods in Physics*, John Wiley & Sons (1992).

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Leo P. Kadanoff, *Statistical Physics: Statics, Dynamics, and Renormalization*, World-Scientific (2000).

H. J. Maris and L. P. Kadanoff, *Am. J. Phys.* **46**, 652–657 (1978).

Michael Plischke and Birger Bergersen, *Equilibrium Statistical Physics*, second edition, World Scientific (1994). An excellent text for an introductory graduate level course.

Chapter 10

Introduction to Many-Body Perturbation Theory

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We introduce the language of second quantization in the context of quantum many body systems and treat the weakly interacting Bose gas at low temperatures.

10.1 Introduction

As we saw in Chapter 8, it is difficult to treat the interparticle interactions in a classical many body system of particles. As might be expected, the analysis of the analogous quantum system is even more difficult.

Just as we developed the density expansion of a classical gas by doing perturbation theory about the ideal gas, we will first treat an interacting many-body quantum system by starting from the single particle approximation. We know that the wave function $\Psi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$ for a system of N identical interacting particles can be expanded in terms of the wave function $\Phi(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N)$ of the noninteracting system. The wave function Φ is given in terms of suitably symmetrized products of the single particle eigenfunctions $\phi(\mathbf{r}_i)$. If we adopt periodic boundary conditions, $\phi_{\mathbf{k}}(\mathbf{r})$ is given by

$$\phi_{\mathbf{k}}(\mathbf{r}) = \frac{1}{L^{3/2}} e^{i\mathbf{k} \cdot \mathbf{r}}, \quad (10.1)$$

where L is the linear dimension of the system. Note that ϕ is a eigenfunction of the momentum $\mathbf{p} = \hbar\mathbf{k}$.

If the particles are bosons, the wave function Ψ and hence Φ must be symmetric with respect to the interchange of any two particles. If the particles are fermions, Ψ and Φ must be antisymmetric with respect to the interchange of any two particles. The latter condition is the generalization of the Pauli exclusion principle.

Because of the impossibility of distinguishing identical particles, it is useful to describe non-interacting quantum systems by specifying only the number of particles in each single particle state (see Section 6.5). That is, instead of working in coordinate space, we can represent the basis functions of the many-body wave functions by

$$|n_1 n_2 \dots\rangle, \quad (10.2)$$

where n_k is the number of particles in the single particle state ϕ_k . For fermions n_k equals 0 or 1; there is no restriction for bosons. For a system with a fixed number of particles N , the occupation numbers n_k satisfy the condition

$$N = \sum_k n_k. \quad (10.3)$$

We also learned in Section 6.5 that it is convenient to treat quantum mechanical systems in the grand canonical ensemble in which the number of particles in a particular single particle quantum state may vary. For this reason we next introduce a formalism that explicitly allows us to write the energy of the system in terms of operators that change the number of particles in a given state.

10.2 Occupation Number Representation

If we specify a state of the system in the occupation number representation, it is convenient to introduce the operators \hat{a}_k and \hat{a}_k^\dagger that act on states such as in (10.2). For bosons we define \hat{a}_k and \hat{a}_k^\dagger by

$$\hat{a}_k |\dots n_k \dots\rangle = \sqrt{n_k} |\dots n_k - 1 \dots\rangle, \quad (10.4a)$$

and

$$\hat{a}_k^\dagger |\dots n_k \dots\rangle = \sqrt{n_k + 1} |\dots n_k + 1 \dots\rangle \quad (10.4b)$$

From the definition (10.4a) we see that \hat{a}_k reduces the number of particles in state k and leaves the other occupation numbers unchanged. For this reason \hat{a}_k is called the *annihilation* or *destruction operator*. Similarly, from (10.4b) we see that \hat{a}_k^\dagger increases the occupation number of state k by unity and is called the *creation operator*. The factor of $\sqrt{n_k}$ is included in (10.4a) to normalize the N and $N - 1$ particle wave functions and to make the definitions consistent with the assertion that \hat{a}_k and \hat{a}_k^\dagger are Hermitian conjugates. The factor $\sqrt{1 + n_k}$ is included for the latter reason.

From the definitions in (10.4), it is easy to show that

$$\hat{a}_k \hat{a}_k^\dagger |n_k\rangle = (n_k + 1) |n_k\rangle \quad (10.5a)$$

$$\hat{a}_k^\dagger \hat{a}_k |n_k\rangle = n_k |n_k\rangle. \quad (10.5b)$$

We have written $|n_k\rangle$ for $|\dots, n_k, \dots\rangle$. By subtracting (10.5b) from (10.5a), we have

$$(\hat{a}_k \hat{a}_k^\dagger - \hat{a}_k^\dagger \hat{a}_k) |n_k\rangle = |n_k\rangle. \quad (10.6)$$

In general, we may write that

$$[\hat{a}_k, \hat{a}_k^\dagger] \equiv \hat{a}_k \hat{a}_k^\dagger - \hat{a}_k^\dagger \hat{a}_k = 1, \quad (10.7)$$

and show that

$$[\hat{a}_k, \hat{a}_k^\dagger] = \delta_{kk'}, \quad (10.8)$$

and

$$[\hat{a}_k, \hat{a}_{k'}] = [\hat{a}_k^\dagger, \hat{a}_{k'}^\dagger] = 0. \quad (10.9)$$

The commutation relations (10.8) and (10.9) define the creation and destruction operators \hat{a}_k^\dagger and \hat{a}_k .

The appropriate definition of \hat{a}_k and \hat{a}_k^\dagger is a little more tedious for fermions, and we shall simply define them by the *anticommutation* relations:

$$\{\hat{a}_k, \hat{a}_k^\dagger\} \equiv \hat{a}_k \hat{a}_k^\dagger + \hat{a}_k^\dagger \hat{a}_k = 1, \quad (10.10)$$

and

$$\{\hat{a}_k, \hat{a}_{k'}\} = \{\hat{a}_k^\dagger, \hat{a}_{k'}^\dagger\} = 0. \quad (10.11)$$

Equation (10.11) is equivalent to the statement that it is not possible to create two particles in the same single particle state.

10.3 Operators in the Second Quantization Formalism

It is easy to show that for both Bose and Fermi statistics, the number operator \hat{N}_k is given by

$$\hat{N}_k = \hat{a}_k^\dagger \hat{a}_k. \quad (10.12)$$

The eigenvalues of \hat{N}_k acting on $|n_k\rangle$ are zero or unity for fermions and either zero or any positive integer for bosons.

We now wish to write other operators in terms of \hat{a}_k and \hat{a}_k^\dagger . To do so, we note that \hat{a}_k^\dagger and \hat{a}_k are the creation and destruction operators for a free particle with momentum $\mathbf{p} = \hbar\mathbf{k}$ described by the wave function (10.1). The kinetic energy is an example of a one-particle operator

$$\hat{T} = -\frac{\hbar^2}{2m} \sum_{i=1}^N \hat{\nabla}_i^2. \quad (10.13)$$

The form (10.13) in which the momentum \mathbf{p} is expressed as an operator is an example of what is called first quantization. Note that the sum in (10.13) is over the indistinguishable particles in the system. A more convenient form for \hat{T} in the *second quantization* formalism is given by

$$\hat{T} = \sum_{\mathbf{p}} \epsilon_p \hat{a}_{\mathbf{p}}^\dagger \hat{a}_{\mathbf{p}}, \quad (10.14)$$

where $\epsilon_p = p^2/2m$ and $\mathbf{p} = \hbar\mathbf{k}$. Note that the kinetic energy is diagonal in \mathbf{p} . The form of (10.14) is suggestive and can be interpreted as the sum of the kinetic energy in state \mathbf{p} times the number of particles in this state.

The form of the two-particle potential energy operator \hat{U} can be obtained from straightforward but tedious arguments. The result can be written as

$$\hat{U} = \frac{1}{2} \sum_{\mathbf{k}'_1, \mathbf{k}'_2, \mathbf{k}_1, \mathbf{k}_2} \langle \mathbf{k}'_1 \mathbf{k}'_2 | u | \mathbf{k}_1 \mathbf{k}_2 \rangle \hat{a}_{\mathbf{k}'_1}^\dagger \hat{a}_{\mathbf{k}'_2}^\dagger \hat{a}_{\mathbf{k}_1} \hat{a}_{\mathbf{k}_2}. \quad (10.15)$$

The summation in (10.15) is over all values of the momenta (wave vectors) of a pair of particles such that the total momentum is conserved in the interaction:

$$\mathbf{k}_1 + \mathbf{k}_2 = \mathbf{k}'_1 + \mathbf{k}'_2. \quad (10.16)$$

The matrix element $\langle \mathbf{k}'_1 \mathbf{k}'_2 | u | \mathbf{k}_1 \mathbf{k}_2 \rangle$ is given by

$$\langle \mathbf{k}'_1 \mathbf{k}'_2 | u | \mathbf{k}_1 \mathbf{k}_2 \rangle = \frac{1}{V^2} \iint e^{i(\mathbf{k}'_1 - \mathbf{k}_1) \cdot \mathbf{r}_1 + i(\mathbf{k}'_2 - \mathbf{k}_2) \cdot \mathbf{r}_2} u(|\mathbf{r}_2 - \mathbf{r}_1|) d\mathbf{r}_1 d\mathbf{r}_2. \quad (10.17)$$

We next make the change of variables, $\mathbf{R} = (\mathbf{r}_1 + \mathbf{r}_2)/2$ and $\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2$, and write

$$\langle \mathbf{k}'_1 \mathbf{k}'_2 | u | \mathbf{k}_1 \mathbf{k}_2 \rangle = \frac{1}{V^2} \iint e^{i(\mathbf{k}_1 - \mathbf{k}'_1 + \mathbf{k}_2 - \mathbf{k}'_2) \cdot \mathbf{R}} e^{i(\mathbf{k}_1 - \mathbf{k}'_1 - \mathbf{k}_2 + \mathbf{k}'_2) \cdot \mathbf{r}/2} u(r) d\mathbf{R} d\mathbf{r}. \quad (10.18a)$$

Because of the homogeneity of space, the integral over \mathbf{R} can be done yielding a Dirac delta function and the condition (10.16). We thus obtain

$$\langle \mathbf{k}'_1 \mathbf{k}'_2 | u | \mathbf{k}_1 \mathbf{k}_2 \rangle = u(k) = \int e^{-i\mathbf{k} \cdot \mathbf{r}} u(r) d\mathbf{r}, \quad (10.18b)$$

where $\mathbf{k} = \mathbf{k}'_2 - \mathbf{k}_2 = -(\mathbf{k}'_1 - \mathbf{k}_1)$ is the momentum (wave vector) transferred in the interaction.

With these considerations we can write the Hamiltonian in the form

$$\hat{H} = \sum_{\mathbf{p}} \frac{p^2}{2m} \hat{a}_{\mathbf{p}}^\dagger \hat{a}_{\mathbf{p}} + \frac{1}{2V} \sum_{\mathbf{k}, \mathbf{p}_1, \mathbf{p}_2} u(k) \hat{a}_{\mathbf{p}_1 + \mathbf{k}}^\dagger \hat{a}_{\mathbf{p}_2 - \mathbf{k}}^\dagger \hat{a}_{\mathbf{p}_2} \hat{a}_{\mathbf{p}_1}. \quad (10.19)$$

We have written \mathbf{p}_1 and \mathbf{p}_2 instead of \mathbf{k}_1 and \mathbf{k}_2 in (10.19) and chosen units such that $\hbar = 1$. The order of the operators in (10.15) and (10.19) is important for fermions because the fermion operators anticommute. The order is unimportant for bosons. The form of the interaction term in (10.19) can be represented as in Figure 10.1.

10.4 Weakly Interacting Bose Gas

A calculation of the properties of the dilute Bose gas was once considered to have no direct physical relevance because the gases that exist in nature condense at low temperatures. However, such a calculation was interesting because the properties of the weakly interacting Bose gas are similar to liquid ^4He . In particular, a dilute Bose gas can be a superfluid even though an ideal Bose gas cannot. Moreover, in recent years, the dilute Bose gas at low temperatures has been created in the laboratory (see references).

The condition for a gas to be dilute is that the range of interaction σ should be small in comparison to the mean distance between the particles, $\rho^{-1/3}$, that is $\rho\sigma^3 \ll 1$. Because the gas is

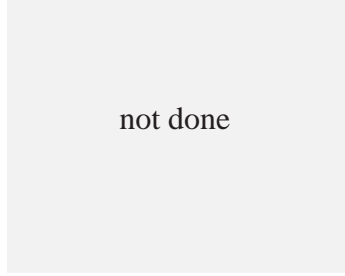


Figure 10.1: Representation of the matrix element in (10.15).

dilute, we need to consider only binary interactions between particles using quantum perturbation theory. The difficulty is that because of the rapid increase in the interparticle potential $u(r)$ at small r , ordinary perturbation theory (the Born approximation) cannot be directly applied.

We can circumvent the lack of applicability of the Born approximation by the following argument. The scattering cross section is given by $|f|^2$, where f is the scattering amplitude. In the Born approximation, f is given by

$$f(k) = -\frac{m}{4\pi\hbar^2} \int u(r) e^{-i\mathbf{k}\cdot\mathbf{r}} d\mathbf{r}, \quad (10.20)$$

where $\hbar\mathbf{k}$ is the momentum transferred in the interaction. In the limit of low temperatures, the particle momenta are small, and we can set $\mathbf{k} = 0$ in (10.20). If we set $f(k=0) = -a$, where a is the scattering amplitude, we obtain

$$a = mU_0/4\pi\hbar^2 \quad (10.21)$$

where

$$U_0 = \int u(r) d\mathbf{r}. \quad (10.22)$$

In the following, we will set $u(\mathbf{k}=0) = U_0 = 4\pi\hbar^2 a/m$, so that we will be able to mimic the result of doing a true perturbation theory calculation.¹

If we assume that $u(k) = U_0$ for all k , a constant, we can write the Hamiltonian as

$$\hat{H} = \sum_{\mathbf{p}} \frac{p^2}{2m} \hat{a}_{\mathbf{p}}^\dagger \hat{a}_{\mathbf{p}} + \frac{U_0}{2V} \sum_{\mathbf{k}, \mathbf{p}_1, \mathbf{p}_2} \hat{a}_{\mathbf{p}_1 - \mathbf{k}}^\dagger \hat{a}_{\mathbf{p}_2 + \mathbf{k}}^\dagger \hat{a}_{\mathbf{p}_2} \hat{a}_{\mathbf{p}_1}. \quad (10.23)$$

The form of (10.23) is the same for Bose or Fermi statistics. Only the commutation relations for the creation and destruction operators are different.

We now follow the approximation method developed by Bogolyubov (1947). In the limit $U_0 \rightarrow 0$, \hat{H} reduces to the Hamiltonian of the ideal Bose gas. We know that the latter has

¹In the language of quantum mechanics, we need to replace the bare interaction u by the t matrix. This replacement is the quantum mechanical generalization of replacing $-\beta u$ by the Mayer f function. Not surprisingly, this replacement can be represented by an infinite sum of ladder-type diagrams. Note that if we interpret the Mayer f function as the effective interaction between particles, the first cumulant in a high temperature expansion would yield the same result as the first term in the classical virial expansion.

a condensate, that is, there is macroscopic occupation of the zero momentum state, so that at $T = 0$, $N_0 = N$, and $N_{\mathbf{p}} = 0$ for $\mathbf{p} \neq 0$. For the weakly interacting Bose gas, we expect that the low lying states do not have zero occupation, but that $N_{\mathbf{p}}$ for $\mathbf{p} > 0$ is small so that $N_0 \approx N$. We proceed by assuming that $N - N_0$ is small and extract the $\mathbf{k} = 0$ terms in \hat{H} . For example,

$$\hat{N} = \sum_{\mathbf{p}} \hat{a}_{\mathbf{p}}^\dagger \hat{a}_{\mathbf{p}} = \hat{a}_0^\dagger \hat{a}_0 + \sum_{\mathbf{p} \neq 0} \hat{a}_{\mathbf{p}}^\dagger \hat{a}_{\mathbf{p}}. \quad (10.24)$$

Because $\hat{a}_0^\dagger \hat{a}_0 = N_0 \approx N$ is much larger than unity, it follows that $\hat{a}_0 \hat{a}_0^\dagger - \hat{a}_0^\dagger \hat{a}_0 = 1$ is small in comparison to \hat{a}_0 and \hat{a}_0^\dagger and hence \hat{a}_0 and \hat{a}_0^\dagger may be regarded as numbers (equal to $\sqrt{N_0}$), and we can ignore the fact that they do not commute.

We now expand the potential energy in (10.23) in powers of the small quantities $\hat{a}_{\mathbf{p}}$, $\hat{a}_{\mathbf{p}}^\dagger$ for $\mathbf{p} \neq 0$. The zeroth-order term is

$$\frac{U_0}{2V} a_0^\dagger a_0^\dagger a_0 a_0 = \frac{U_0}{2V} a_0^4 = \frac{U_0}{2V} N_0^2. \quad (10.25)$$

There are no first-order terms proportional to a_0^3 , because they cannot be made to satisfy conservation of momentum. The second-order contributions are proportional to $(U_0/2V)N_0$ and are given by

(a)	$\mathbf{p}_1 = \mathbf{p}_2 = 0, \mathbf{k} \neq 0$	$\hat{a}_{\mathbf{k}}^\dagger \hat{a}_{-\mathbf{k}}^\dagger$
(b)	$\mathbf{k} = -\mathbf{p}_1, \mathbf{p}_2 = 0$	$\hat{a}_{\mathbf{p}_1}^\dagger \hat{a}_{\mathbf{p}_1}$
(c)	$\mathbf{k} = \mathbf{p}_2, \mathbf{p}_1 = 0$	$\hat{a}_{\mathbf{p}_2}^\dagger \hat{a}_{\mathbf{p}_2}$
(d)	$\mathbf{p}_1 = -\mathbf{p}_2 = -\mathbf{k}$	$\hat{a}_{\mathbf{p}_1} \hat{a}_{-\mathbf{p}_1}$
(e)	$\mathbf{k} = \mathbf{p}_1 = 0, \mathbf{p}_2 \neq 0$	$\hat{a}_{\mathbf{p}_2}^\dagger \hat{a}_{\mathbf{p}_2}$
(f)	$\mathbf{k} = \mathbf{p}_2 = 0, \mathbf{p}_1 \neq 0$	$\hat{a}_{\mathbf{p}_1}^\dagger \hat{a}_{\mathbf{p}_1}$

We will ignore all higher order terms, which is equivalent to ignoring the interaction between excited particles. Hence, if we extend the above approximations to T above T_c , our approximate Hamiltonian would reduce to the Hamiltonian for the ideal gas.

The approximate Hamiltonian can now be written as

$$\hat{H} = \sum'_{\mathbf{p}} \frac{p^2}{2m} \hat{a}_{\mathbf{p}}^\dagger \hat{a}_{\mathbf{p}} + \frac{U_0}{2V} N_0^2 + \frac{U_0}{2V} N_0 \sum_{\mathbf{k}} [\hat{a}_{\mathbf{k}}^\dagger \hat{a}_{-\mathbf{k}}^\dagger + \hat{a}_{\mathbf{k}} \hat{a}_{-\mathbf{k}} + 4\hat{a}_{\mathbf{k}}^\dagger \hat{a}_{\mathbf{k}}]. \quad (10.26)$$

The notation \sum' denotes that the sum excludes terms with $\mathbf{p} = 0$ and $\mathbf{k} = 0$.

In general, we have

$$N = a_0^2 + \sum'_{\mathbf{p}} \hat{a}_{\mathbf{p}}^\dagger \hat{a}_{\mathbf{p}} = N_0 + \sum'_{\mathbf{p}} \hat{a}_{\mathbf{p}}^\dagger \hat{a}_{\mathbf{p}}. \quad (10.27)$$

For consistency, we replace N_0^2 in (10.26) by $N_0^2 = N^2 - 2N \sum'_{\mathbf{p}} \hat{a}_{\mathbf{p}}^\dagger \hat{a}_{\mathbf{p}}$. Similarly N_0 in (10.26) may be replaced by N . The result of these replacements is that

$$\hat{H} \approx \hat{H}_B = \frac{N^2}{2V} U_0 + \sum'_{\mathbf{p}} \epsilon_p \hat{a}_{\mathbf{p}}^\dagger \hat{a}_{\mathbf{p}} + \frac{N}{2V} U_0 \sum_{\mathbf{k}} [\hat{a}_{\mathbf{k}}^\dagger \hat{a}_{-\mathbf{k}}^\dagger + \hat{a}_{\mathbf{k}} \hat{a}_{-\mathbf{k}} + 2\hat{a}_{\mathbf{k}}^\dagger \hat{a}_{\mathbf{k}}]. \quad (10.28)$$

Note that H_B only allows excitation of pairs of momentum \mathbf{k} and $-\mathbf{k}$ from the condensate and re-entry of such pairs into the condensate.

The approximate Hamiltonian \hat{H}_B is bilinear in \hat{a} and \hat{a}^\dagger . This form is similar to that of a harmonic oscillator. This similarity suggests that we can diagonalize \hat{H}_B by making an appropriate linear transformation of the operators \hat{a} and \hat{a}^\dagger . If \hat{H}_B is put into diagonal form, then \hat{H}_B would have the same form as an ideal gas, and we could easily calculate the energy eigenvalues.

We define new operators \hat{b}^\dagger and \hat{b} by

$$\hat{a}_{\mathbf{k}} = u_k \hat{b}_{\mathbf{k}} + v_k \hat{b}_{-\mathbf{k}}^\dagger \quad (10.29a)$$

$$\hat{a}_{\mathbf{k}}^\dagger = u_k \hat{b}_{\mathbf{k}}^\dagger + v_k \hat{b}_{-\mathbf{k}}, \quad (10.29b)$$

and require them to satisfy the Bose commutation relations

$$\hat{b}_{\mathbf{k}} \hat{b}_{\mathbf{k}'}^\dagger - \hat{b}_{\mathbf{k}'}^\dagger \hat{b}_{\mathbf{k}} = \delta_{\mathbf{k}\mathbf{k}'} \quad \text{and} \quad \hat{b}_{\mathbf{k}} \hat{b}_{\mathbf{k}'} = \hat{b}_{\mathbf{k}'} \hat{b}_{\mathbf{k}}. \quad (10.30)$$

As shown in Problem 10.1, \hat{b}^\dagger and \hat{b} satisfy the Bose commutation relations only if the relation (10.31) between u_k and v_k is satisfied:

$$u_k^2 - v_k^2 = 1. \quad (10.31)$$

Problem 10.1. (a) Use (10.29) to express \hat{b}^\dagger and \hat{b} in terms of \hat{a}^\dagger and \hat{a} . (b) Show that the commutation relations (10.30) are satisfied only if (10.31) is satisfied.

If we substitute the above expressions for \hat{a}^\dagger and \hat{a} into (10.28), we obtain

$$\hat{H}_B = E_0 + \hat{H}_D + \hat{H}_I \quad (10.32a)$$

where

$$E_0 = \frac{N^2 U_0}{2V} + \sum_{\mathbf{k}}' \left[\left(\epsilon_p + \frac{NU_0}{V} \right) v_k^2 + \frac{NU_0}{V} u_k v_k \right] \quad (10.32b)$$

$$\hat{H}_D = \sum_{\mathbf{k}}' \left[\left(\epsilon_p + \frac{NU_0}{V} \right) (u_k^2 + v_k^2) \frac{2NU_0}{V} u_k v_k \right] \hat{b}_{\mathbf{k}}^\dagger \hat{b}_{\mathbf{k}} \quad (10.32c)$$

$$\hat{H}_I = \sum_{\mathbf{k}}' \left[\left(\epsilon_k + \frac{NU_0}{V} \right) \left(u_k v_k + \frac{1}{2} v_k (u_k^2 + v_k^2) \right) \right] (\hat{b}_{\mathbf{k}}^\dagger \hat{b}_{-\mathbf{k}}^\dagger + \hat{b}_{\mathbf{k}} \hat{b}_{-\mathbf{k}}). \quad (10.32d)$$

From the form of (10.32), we see that \hat{H}_B would be diagonal if $\hat{H}_I = 0$. This condition is satisfied if

$$2 \left(\epsilon_k + \frac{NU_0}{V} \right) (u_k v_k + v_k (u_k^2 + v_k^2)) = 0, \quad (10.33)$$

and the relation (10.31) is satisfied. Note that we have two equations for the two unknown u_k and v_k . We can satisfy the relation (10.31) automatically by letting

$$u_k = \cosh \theta_k \quad (10.34a)$$

$$v_k = \sinh \theta_k. \quad (10.34b)$$

If we use the identities $2u_kv_k = 2 \cosh \theta_k \sinh \theta_k = \sinh 2\theta_k$ and $u_k^2 + v_k^2 = \cosh 2\theta_k$, we can express (10.33) as

$$(\epsilon_k + \frac{NU_0}{V}) \sinh 2\theta_k + \frac{NU_0}{V} \cosh 2\theta_k = 0, \quad (10.35)$$

or

$$\tanh 2\theta_k = -\frac{\rho U_0}{\epsilon_k + \rho U_0}. \quad (10.36)$$

Note that (10.36) has a solution for all k only if $U_0 > 0$.

The solution (10.36) is equivalent to

$$u_k^2 + v_k^2 = \frac{\epsilon_k + \rho U_0}{E(k)} \quad (10.37)$$

and

$$2u_kv_k = -\frac{\rho U_0}{E(k)}, \quad (10.38)$$

where

$$E(k) = \sqrt{\epsilon_k(\epsilon_k + 2\rho U_0)}. \quad (10.39)$$

$$u_k^2 = \frac{1}{2} \left[\frac{\epsilon_k + \rho U_0}{E(k)} + 1 \right], \quad (10.40a)$$

$$v_k^2 = \frac{1}{2} \left[\frac{\epsilon_k + \rho U_0}{E(k)} - 1 \right]. \quad (10.40b)$$

If we substitute u_k and v_k into \hat{H}_B , we obtain

$$\hat{H}_B = \frac{1}{2} N \rho U_0 + \sum_{\mathbf{k}}' [E(k) - \epsilon_k - \rho U_0] + \sum_{\mathbf{k}}' E(k) \hat{b}_{\mathbf{k}}^\dagger \hat{b}_{\mathbf{k}}. \quad (10.41)$$

From the form of (10.41) we see that $\hat{b}_{\mathbf{k}}^\dagger$ and $\hat{b}_{\mathbf{k}}$ are the creation and destruction operators for quasiparticles or elementary excitations with energy $E(k)$ obeying Bose statistics. If we replace U_0 by $4\pi\hbar^2 a/m$, we see that the quasiparticle energy is given by

$$E(p) = \sqrt{c^2 p^2 + (p^2/2m)^2}, \quad (10.42)$$

where

$$c = \sqrt{\frac{4\pi\hbar^2 \rho a}{m^2}}. \quad (10.43)$$

Note that for small p , $E(p)$ is proportional to p and hence the excitations are phonons with velocity c .

The ground state energy E_0 is given by

$$E_0 = \frac{1}{2} N \rho U_0 + \sum_{\mathbf{k}}' [E(k) - \epsilon_k - \rho U_0]. \quad (10.44)$$

We can replace the summation over discrete values of \mathbf{k} by an integration over \mathbf{p} and multiply by $V/(2\pi\hbar)^3$. We obtain (see Huang)

$$\frac{E_0}{N} = \frac{2\pi a\rho}{m} \left[1 + \frac{128}{15} \sqrt{\frac{a^3\rho}{\pi}} \right]. \quad (10.45)$$

Problem 10.2. Show that c is equal to the sound speed using the relation (see Reif)

$$c = (\rho\kappa_S)^{-1/2}, \quad (10.46)$$

where κ_S is the adiabatic compressibility:

$$\kappa_S = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_S. \quad (10.47)$$

The above relations can be used to express c as

$$c^2 = \left(\frac{\partial \rho}{\partial P} \right)_S. \quad (10.48)$$

At $T = 0$, the pressure is given by

$$P = -\frac{\partial E_0}{\partial V}. \quad (10.49)$$

Use the above relations and (10.45) to show that the calculated speed of sound is consistent with the phonon speed (10.43) to lowest order in $(\rho a^3)^{1/2}$.

Problem 10.3. The number of quasiparticles of momentum \mathbf{p} for $T > 0$ is given by

$$\bar{n}_{\mathbf{p}} = \frac{1}{e^{\beta E(p)} - 1}. \quad (10.50)$$

Why is the chemical potential equal to zero?

Problem 10.4. The momentum distribution of the actual particles in the gas is given by

$$\bar{N}_{\mathbf{p}} = \overline{\hat{a}_{\mathbf{p}}^\dagger \hat{a}_{\mathbf{p}}}. \quad (10.51)$$

Use the relation between $\hat{a}_{\mathbf{p}}^\dagger$ and $\hat{a}_{\mathbf{p}}$ and $\hat{b}_{\mathbf{p}}^\dagger$ and $\hat{b}_{\mathbf{p}}$, and the fact that the products $\hat{b}_{\mathbf{p}}^\dagger \hat{b}_{-\mathbf{p}}^\dagger$ and $\hat{b}_{-\mathbf{p}} \hat{b}_{\mathbf{p}}$ have no diagonal matrix elements to show that

$$\bar{N}_{\mathbf{p}} = \frac{\bar{n}_{\mathbf{p}} + f_{\mathbf{p}}(\bar{n}_{\mathbf{p}} + 1)}{1 - f_{\mathbf{p}}}, \quad (10.52)$$

where

$$f_{\mathbf{p}} = \frac{m}{4\pi a\rho\hbar^2} \left[E(p) - \frac{p^2}{2m} - mc^2 \right]. \quad (10.53)$$

This result is valid only for $\mathbf{p} \neq 0$. At $T = 0$, $\bar{n}_{\mathbf{p}} = 0$ for $\mathbf{p} \neq 0$. Show that

$$\bar{N}_p = \frac{m^2 c^4}{2E(p)[E(p) + p^2/2m + mc^2]}. \quad (10.54)$$

The number of particles with zero momentum is

$$\overline{N}_0 = 1 - \sum_{\mathbf{p}}' \overline{N}_{\mathbf{p}} = 1 - V \int \frac{d^3 p}{(2\pi\hbar)^3} \overline{N}_{\mathbf{p}}. \quad (10.55)$$

Note that the interaction between the particles causes the appearance of particles with nonzero momentum even at $T = 0$. Use (10.54) to show that

$$\frac{\overline{N}_0}{N} = 1 - \frac{8}{3} \left(\frac{\rho a^3}{\pi} \right)^{1/2}. \quad (10.56)$$

Appendix A

Useful Formulae

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A.1 Physical constants

constant	symbol	magnitude
Avogadro's number	N_A	6.022×10^{23}
Boltzmann's constant	k	$1.381 \times 10^{-23} \text{ J/K}$
universal gas constant	R	8.314 J/(mol K)
Planck's constant	h	$6.626 \times 10^{-34} \text{ J s}$
	\hbar	$1.055 \times 10^{-34} \text{ J s}$
speed of light	c	$2.998 \times 10^8 \text{ m/s}$
electron charge	e	$1.602 \times 10^{-19} \text{ C}$
electron mass	m_e	$9.109 \times 10^{-31} \text{ kg}$
proton mass	m_p	$1.672 \times 10^{-27} \text{ kg}$

A.2 SI derived units

newton	$1 \text{ N} \equiv 1 \text{ kg m/s}^2$
joule	$1 \text{ J} \equiv 1 \text{ N m}$
watt	$1 \text{ W} \equiv 1 \text{ J/s}$
pascal	$1 \text{ Pa} \equiv 1 \text{ N/m}^2$

A.3 Conversion factors

1 atm	= 1.013 bar
	= 1.013×10^5 Pa
	= 760 mm Hg
1 cal	= 4.186 J
1 eV	= 1.602×10^{-19} J

A.4 Mathematical Formulae

$$\cosh x = \frac{1}{2}[e^x + e^{-x}]. \quad (\text{A.1})$$

$$\sinh x = \frac{1}{2}[e^x - e^{-x}]. \quad (\text{A.2})$$

$$\tanh x = \frac{\sinh x}{\cosh x} = \frac{e^x - e^{-x}}{e^x + e^{-x}}. \quad (\text{A.3})$$

A.5 Approximations

$$e^x = \sum_{n=0}^{\infty} \frac{x^n}{n!} \approx 1 + x + \frac{x^2}{2!} + \dots \quad (\text{A.4})$$

$$\sin x = \sum_{n=0}^{\infty} (-1)^n \frac{x^{2n+1}}{(2n+1)!} \approx x - \frac{x^3}{3!} + \frac{x^5}{5!} + \dots \quad (\text{A.5})$$

$$\cos x = \sum_{n=0}^{\infty} (-1)^n \frac{x^{2n}}{(2n)!} \approx 1 - \frac{x^2}{2!} + \frac{x^4}{4!} + \dots \quad (\text{A.6})$$

$$\frac{1}{1-x} = \sum_{n=1}^{\infty} x^{n-1} \approx 1 + x + x^2 + \dots \quad (\text{A.7})$$

$$\ln(1+x) = \sum_{n=1}^{\infty} (-1)^{n+1} \frac{x^n}{n} \approx x - \frac{x^2}{2} + \frac{1}{3}x^3 + \dots \quad (\text{A.8})$$

$$\tanh x = \sum_{n=1}^{\infty} \frac{2^{2n}(2^{2n}-1)}{(2n)!} B_{2n} x^{2n-1} \approx x - \frac{x^3}{3} + \frac{2x^5}{15} + \dots, \quad (\text{A.9})$$

where B_n are the **Bernoulli numbers** (see Sec. A.9).

A.6 Euler-Maclaurin formula

$$\sum_{i=0}^{\infty} f(x) = \int_0^{\infty} f(x) dx + \frac{1}{2}f(0) - \frac{1}{12}f'(0) + \frac{1}{720}f'''(0) + \dots \quad (\text{A.10})$$

A.7 Gaussian Integrals

$$I_n = \int_{-\infty}^{\infty} dx x^n e^{-ax^2}. \quad (n \geq 0, a > 0) \quad (\text{A.11})$$

$$I_0 = \left(\frac{\pi}{a}\right)^{1/2} \quad (\text{A.12})$$

$$I_1 = 0 \quad (\text{A.13})$$

$$I_2 = \frac{1}{2} \left(\frac{\pi}{a^3}\right)^{1/2} \quad (\text{A.14})$$

Derivation:

$$I_0 = \int_{-\infty}^{+\infty} e^{-ax^2} dx. \quad (\text{A.15})$$

We note that x in the integrand in (A.15) is a dummy variable. Hence, we may write I_0 equally well as

$$I_0 = \int_{-\infty}^{+\infty} e^{-ay^2} dy.$$

To convert the integrand to a form we can integrate, we multiply I by itself and write

$$I_0^2 = \int_{-\infty}^{+\infty} e^{-ax^2} dx \int_{-\infty}^{+\infty} e^{-ay^2} dy = \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} e^{-(x^2+y^2)} dx dy. \quad (\text{A.16})$$

The double integral in (A.16) extends over the entire xy -plane. We introduce the polar coordinates r and θ , where $r^2 = x^2 + y^2$. The element of area in polar coordinates is $r dr d\theta$. Hence, I_0^2 can be rewritten in the form

$$I_0^2 = \int_0^{2\pi} \int_0^{\infty} e^{-ar^2} r dr d\theta = 2\pi \int_0^{\infty} e^{-ar^2} r dr.$$

We let $z = ar^2$, $dz = 2ardr$, and write

$$I_0^2 = \frac{\pi}{a} \int_0^{\infty} e^{-z} dz = \frac{\pi}{a} [-e^{-z}]_0^{\infty} = \frac{\pi}{a}.$$

Hence, we obtain the desired result

$$I_0 = \int_{-\infty}^{+\infty} e^{-ax^2} dx = \left(\frac{\pi}{a}\right)^{1/2}. \quad (\text{A.17})$$

Clearly the values of I_n for n odd are zero by symmetry. For odd values of n , let us redefine I_n as

$$I_n = \int_0^{\infty} dx x^n e^{-ax^2}. \quad (n \text{ odd}) \quad (\text{A.18})$$

It is straightforward to show that

$$I_1 = \frac{1}{2a}. \quad (\text{A.19})$$

All integrals I_n for $n > 1$ can be reduced to the integrals I_0 or I_1 using the recursion relation

$$I_n = -\frac{\partial I_{n-2}}{\partial a}. \quad (\text{A.20})$$

For example,

$$I_2 = \frac{1}{2} \left(\frac{\pi}{a^3} \right)^{1/2}. \quad (\text{A.21})$$

A.8 Stirling's formula

Because $N!$ is defined as

$$N! = 1 \times 2 \times 3 \times \cdots \times N, \quad (\text{A.22})$$

we have

$$\begin{aligned} \ln N! &= \ln 1 + \ln 2 + \ln 3 + \cdots + \ln N \\ &\approx \int_1^N \ln x \, dx = [x \ln x - x]_1^N \\ &= N \ln N - N + 1. \end{aligned} \quad (\text{A.23})$$

For $N \gg 1$, we have

$$\ln N! \simeq N \ln N - N. \quad (\text{simple form of Stirling's approximation}) \quad (\text{A.24})$$

A more accurate approximation for $N!$ can be found from the integral representation:

$$N! = \int_0^\infty dx \, x^N e^{-x}. \quad (\text{A.25})$$

In the integrand $f(x) = x^N e^{-x}$, x^N is a rapidly increasing function of x for large N , and e^{-x} is a decreasing function of x . Hence $f(x)$ exhibits a sharp maximum for some value of x . To find this maximum, we let $z = x/N$, $z^N = e^{N \ln z}$, and write f as

$$f = x^N e^{-x} \rightarrow N^N z^N e^{-Nz} = N^N e^{-(z - \ln z)}. \quad (\text{A.26})$$

Because the maximum of $z - \ln z$ is at $z = 1$, we write $z = 1 + t$ and express (A.26) as

$$f = N^N e^{-N[t+1-\ln(1+t)]} = N^N e^{-N} e^{-N[t-\ln(1+t)]}.$$

We let $\ln(1+t) \approx t - \frac{1}{2}t^2$ (see (A.8)) and write

$$f \approx N^N e^{-N} e^{-Nt^2/2}. \quad (\text{A.27})$$

From (A.27) we see that f has a sharp maximum at $t = 0$ for large N , and hence

$$N! = \int_0^\infty f dx \approx N^N e^{-N} \int_{-1}^\infty N dt e^{-Nt^2/2} \quad (\text{A.28})$$

$$\begin{aligned} &= N^{N+1} e^{-N} \int_{-\infty}^\infty dt e^{-Nt^2/2} \\ &= N^N e^{-N} (2\pi N)^{1/2}, \end{aligned} \quad (\text{A.29})$$

and finally,

$$\ln N! = N \ln N - N + \frac{1}{2} \ln(2\pi N). \quad (\text{stronger form of Stirling's approximation}) \quad (\text{A.30})$$

The *Gamma function* is defined as

$$\Gamma(n) = \int_0^\infty dx x^{n-1} e^{-x}, \quad (\text{Gamma function}) \quad (\text{A.31})$$

and is useful in the context of factorials because

$$\Gamma(n+1) = n\Gamma(n) = n! \quad \text{for positive integer } n. \quad (\text{A.32})$$

(The result (A.32) can be derived by an integration by parts.) Note that $-1! = 0! = 1$ and $\Gamma(1) = \Gamma(2) = 1$.

For half integer arguments, $\Gamma(n/2)$ has the special form

$$\Gamma\left(\frac{n}{2}\right) = \frac{(n-2)!!\sqrt{\pi}}{2^{n-1}/2}, \quad (\text{A.33})$$

where the double factorial $n!! = n \times (n-2) \times \cdots \times 3 \times 1$ if n is odd and $n!! = n \times (n-2) \times \cdots \times 4 \times 2$ if n is even. We also have $-1!! = 0!! = 1$, $\Gamma(\frac{1}{2}) = \sqrt{\pi}/2$, and $\Gamma(\frac{3}{2}) = \sqrt{\pi}/2$.

A.9 Constants

The *Bernoulli numbers* are the coefficients of $x^n/n!$ in the expansion of

$$\frac{x}{e^x - 1} = \sum_{n=0} B_n \frac{x^n}{n!}. \quad (\text{A.34})$$

All the Bernoulli numbers B_n with odd n are zero except for B_1 , that is $B_{2n+1} = 0$ for $n > 0$.

$$B_0 = 1, \quad B_1 = -\frac{1}{2}, \quad B_2 = \frac{1}{6}, \quad B_4 = -1/30, \quad B_6 = \frac{1}{42}, \quad B_8 = -\frac{1}{30}. \quad (\text{A.35})$$

Euler's constant

$$\gamma = 0.577\,215\,664\,901\,5325\dots \quad (\text{A.36})$$

A.10 Probability distributions

$$P(n, N) = \frac{N!}{n! (N-n)!} p^n q^{(N-n)}. \quad (\text{binomial distribution}) \quad (\text{A.37})$$

The binomial distribution is specified by the probability $p = 1 - q$ and the number of trials N .

$$P(x) = \frac{1}{\sqrt{2\pi\sigma^2}} e^{-(x-\bar{x})^2/2\sigma^2}. \quad (\text{Gaussian distribution}) \quad (\text{A.38})$$

The Gaussian distribution is specified by \bar{x} , the mean value of x , and $\sigma^2 = \bar{x}^2 - \bar{x}^2$, the variance of x .

$$P(n) = \frac{\lambda^n}{n!} e^{-\lambda}. \quad (\text{Poisson distribution}) \quad (\text{A.39})$$

The Poisson distribution is specified only by the parameter $\lambda = \bar{n} = pN$.

A.11 Fermi integrals

The integrals that commonly occur in the context of the ideal Fermi gas have the form

$$I_n = \int_0^\infty dx \frac{x^n e^x}{(e^x + 1)^2} = n!(1 - 2^{1-n})\zeta(n). \quad (\text{A.40})$$

where the Riemann zeta function is defined by

$$\zeta(x) = \sum_{k=0}^{\infty} \frac{1}{(k+1)^x}. \quad (\text{A.41})$$

The values of the first several zeta functions are

$$\zeta\left(\frac{3}{2}\right) \approx 2.612 \quad (\text{A.42a})$$

$$\zeta(2) = \frac{\pi^2}{6} \approx 1.645 \quad (\text{A.42b})$$

$$\zeta\left(\frac{5}{2}\right) \approx 1.341 \quad (\text{A.42c})$$

$$\zeta(3) \approx 1.202 \quad (\text{A.42d})$$

$$\zeta(4) = \frac{\pi^4}{90} \approx 1.082 \quad (\text{A.42e})$$

$$\zeta(6) = \frac{\pi^6}{945} \quad (\text{A.42f})$$

A.12 Bose integrals

The integrals we need in the context of the ideal Bose gas have the form

$$I_B(n) = \int_0^\infty dx \frac{x^n}{e^x - 1} = \int_0^\infty dx \frac{x^n e^{-x}}{1 - e^{-x}} \quad (\text{A.43})$$

$$\begin{aligned} &= \int_0^\infty dx x^n \sum_{k=0}^\infty e^{-(k+1)x} \\ &= \sum_{k=0}^\infty \int_0^\infty dx x^n e^{-(k+1)x} = \sum_{k=0}^\infty \frac{1}{(k+1)^{n+1}} \int_0^\infty dy y^n e^{-y}. \end{aligned} \quad (\text{A.44})$$

If we use the definition of the Riemann zeta function in (A.40) and the definition of the Gamma function in (A.31), we obtain

$$I_B(n) = \zeta(n+1)\Gamma(n+1). \quad (\text{A.45})$$

If n is an integer, then (A.45) reduces to

$$I(n) = n!\zeta(n+1). \quad (\text{A.46})$$