Chapter 1

From Microscopic to Macroscopic Behavior

We explore the fundamental differences between microscopic and macroscopic systems, note that bouncing balls come to rest and hot objects cool, and discuss how the behavior of macroscopic systems is related to the behavior of their microscopic constituents. Computer simulations are introduced to demonstrate the general qualitative behavior of macroscopic systems.

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 coin, and a rubber band – examples of a gas, liquid, solid, and polymer, respectively. Less familiar macroscopic systems include superconductors, cell membranes, the brain, the stock market, and neutron stars.

   We will find that the type of questions we ask about macroscopic systems differ in important ways from the questions we ask about systems that we treat microscopically. For example, consider the air in your room. Have you ever wondered about the trajectory of a particular molecule in the air? Would knowing that trajectory be helpful in understanding the properties of air? Instead of questions such as these, examples of questions that we do 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? How can we make it more efficient?

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 and why does a liquid freeze into a particular crystalline structure?

6. Why does helium have a superfluid phase at very low temperatures? Why do some materials exhibit zero resistance to electrical current at sufficiently low temperatures?

7. In general, how do the properties of a system emerge from its constituents?

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

9. What will the weather be tomorrow?

These questions can be roughly classified into three groups. Questions 1–3 are concerned with macroscopic properties such as pressure, volume, and temperature and processes 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 engines, for example, the internal combustion engine and the steam turbine.

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

Question 8 also relates to a macroscopic system, but temperature is not relevant in this case. Moreover, turbulent flow continually changes in time. Question 9 concerns macroscopic phenomena that change with time. Although there has been progress in our understanding of time-dependent phenomena such as turbulent flow and hurricanes, our understanding of such phenomena is much less advanced than our understanding of time-independent systems. For this reason we will focus our attention on systems whose macroscopic properties are independent of time and consider questions such as those in Questions 1–7.

1.2   Some Qualitative Observations

We begin our discussion of macroscopic systems by considering a glass of hot water. We know that if we place a glass of hot water into a large cold 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 sensations of hot and cold and is important in our everyday experience.

The direction or arrow of time raises many questions. Have you ever observed a glass of water at room temperature spontaneously become hotter? Why not? What other phenomena exhibit a direction of time? The direction of time 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 behaviors of macroscopic bodies and single particles are very different.

Unlike scientists 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. If we prepare two glasses of water under similar conditions, we know that the observable properties of the water in each glass are indistinguishable, even though the motion of the individual particles in the two glasses is very different.

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. Why does the ball eventually come 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 total energy. Hence, if we include the energy of the molecules of the ball and the floor, the total energy is conserved. Conservation of energy does not explain why the inverse process, where the ball rises higher and higher with each bounce, does not occur. 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 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 just a name, and it is important only to understand that energy conservation is not sufficient to understand the behavior of macroscopic systems.[1]

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, and we say that the energy is associated with one degree of freedom. After some time the energy becomes associated with the individual molecules near the surface of the ball and the floor, and we say that the energy is now distributed over many degrees of freedom. If we were to bounce the ball on the floor many times, the ball and the

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[1]We will learn that as for most concepts in physics, the meaning of entropy in the context of thermodynamics and statistical mechanics is very different from its meaning as used by nonscientists.

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 while the total energy has been conserved. Hence, we conclude that the entropy is a measure of how the energy is distributed.

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.[2]

1.3   Doing Work and the Quality of Energy

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 is conserved in these processes, 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 flame. We also know that if we rub our hands together, they will become warmer. There is no theoretical limit 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 equivalent to the raising of a weight. 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 dynamite might demolish an unwanted building, but this process cannot be done repeatedly with the same materials. 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 an open flame, we have to build an *engine* to do this conversion.

Can we convert stored energy into useful work with 100% efficiency? To answer this question we have to appeal to observation. We know that some forms of stored energy are more useful than others. For example, why do we burn coal and oil in power plants even though the atmosphere and the oceans are vast reservoirs of energy? Can we mitigate global climate change 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

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[2]Properties such as the thermal conductivity and viscosity are treated in the online supplement (see <www.compadre.org/stp> or <press.princeton.edu/titles/9375.html>).

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 (potential) 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, the transfer of 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 the second law of thermodynamics was conceived before the first law of thermodynamics. As we will learn, the first law is a statement of conservation of energy.

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. 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" and ash 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 problem.

1.4   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 of *simulating* the behavior of macroscopic systems. Although we cannot simulate a macroscopic system of 10^{23} particles on a computer, we will find that even small systems of the order of a 100 particles are sufficient to illustrate the qualitative behavior of macroscopic systems.

We first discuss how we can simulate a simple model of a gas consisting of molecules 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, and hence we need to solve Newton's second law for each particle. 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 is repulsive when their separation is small and weakly attractive when they are far apart. For convenience we
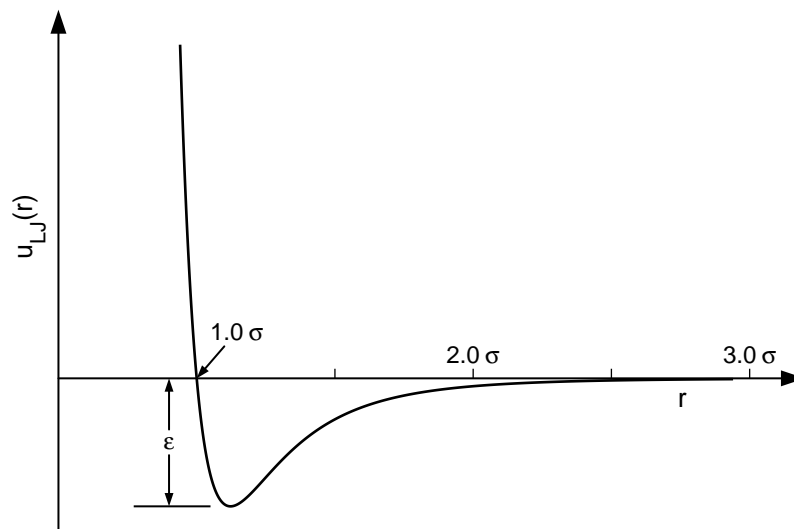
Figure 1.1: Plot of the Lennard-Jones potential $u_{\mathrm{LJ}}(r)$, where r is the distance between the particles. Note that the potential is characterized by a length σ and an energy ϵ.

will usually assume that the interaction is given by the Lennard-Jones potential given by[3]

$$u_{\mathrm{LJ}}(r) = 4\epsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6} \right], \tag{1.1}$$

where r is the distance between two particles. A plot of the Lennard-Jones potential is shown in Figure 1.1. The r^{-12} form of the repulsive part of the interaction was chosen for convenience only and has no fundamental significance. The attractive $1/r^6$ behavior at large r is the van der Waals interaction.[4] The force between any two particles is given by $f(r) = -du/dr$.

In macroscopic 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 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 macroscopic 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," reenters the box from the left side. In one dimension this boundary condition is equivalent to taking a piece of string and making it into a loop. In this way a particle moving on the wire never reaches the end (the surface).

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. We then use Newton's second law of motion to find

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[3]This potential is named after John Lennard-Jones, 1894–1954, a theoretical chemist and physicist at Cambridge University. The Lennard-Jones potential is appropriate for closed-shell systems, that is, rare gases such as Ar or Kr.

[4]The van der Waals interaction arises from an induced dipole-dipole effect. It is present in all molecules, but is important only for the heavier noble gas atoms. See for example, Brehm and Mullin.

the acceleration of each particle. Because the acceleration is the second derivative of the position, we need to solve a second-order differential equation for each particle (in each direction) given the initial position and velocity of each particle. (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 particular particle depends on the positions of all the other particles. Although we cannot solve the resultant set of coupled differential equations analytically, we can use 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.*[5]

In the following two problems 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 are written in Java and can be run on any operating system that supports Java 1.5^{+}. You may download all the programs used in this text from `<press.princeton.edu/titles/9375.html>` or `<www.compadre.org/stp>` as a single file (the STP Launcher) or as individual programs. Alternatively, you can run each simulation as an applet using a browser.

Problem 1.1. Approach to equilibrium

Suppose that we divide a box into three equal parts and place N particles in the middle third of the box.[6] The particles are placed at random with the constraint that no two particles can be closer than the length parameter 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 velocity of each particle is assigned at random and then the velocity of the center of mass is set to zero. At $t = 0$, we remove the "barriers" between the three parts and 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?

Program `ApproachToEquilibriumThreePartitions` implements this simulation.[7] Double click on the jar file to open the program, and click the `Start` button to begin the simulation. The program shows the motion of the particles in the box and plots the number of particles in the left (n_1), center (n_2), and right (n_3) part of the box as a function of time. The input parameter is N, the number of particles initially in the center cell, so that $n_1 = 0$, $n_2 = N$, and $n_3 = 0$ at $t = 0$.

Give your answers to the following questions before you do the simulation.

(a) Does the system appear to show a direction of time for $N = 6$?

(b) What is the nature of the time dependence of n_1, n_2, and n_3 as a function of the time t for $N = 27$? Does the system appear to show a direction of time? Choose various values of N that are multiples of 3 up to $N = 270$. Is the direction of time better defined for larger N?

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

[6]We have divided the box into three parts so that the effects of the toroidal boundary conditions will not be as apparent as if we had initially confined the particles to one half of the box.

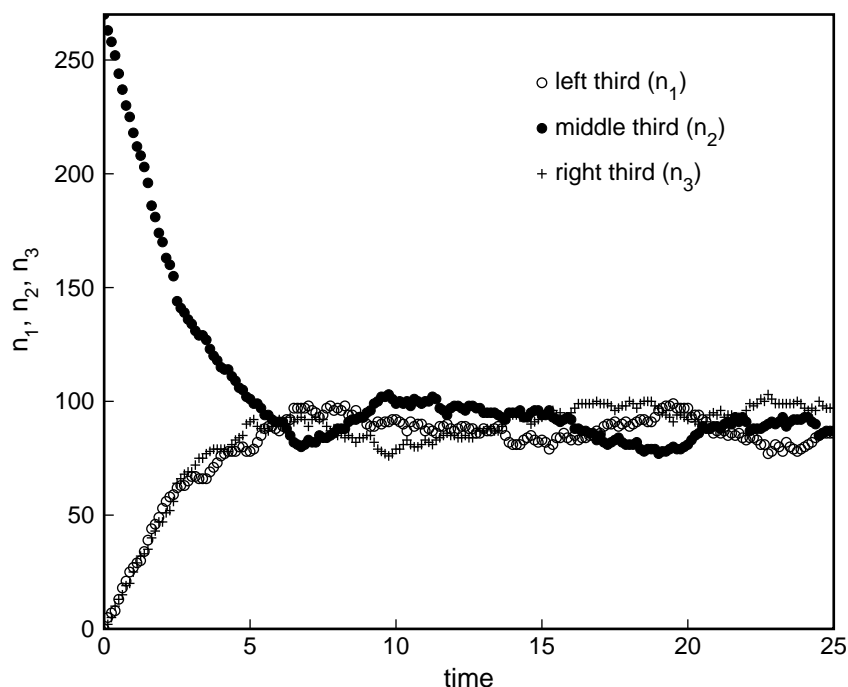[7]We will omit the prefix `stp_` whenever it will not cause confusion.

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 are assigned at random such that the center of mass velocity is zero.

(c) The time shown in the plots is in terms of $\sigma(m/\epsilon)^{1/2}$, where σ and ϵ are the length and energy parameters of the Lennard-Jones potential in (1.1) and m is the mass of a particle. Verify that this combination has units of time. For argon $\sigma = 3.4 \times 10^{-10}$ m, $\epsilon = 1.65 \times 10^{-21}$ J, and $m = 6.69 \times 10^{-26}$ kg. What is the value of $\sigma(m/\epsilon)^{1/2}$ for argon? How much real time has elapsed if the program shows that $t = 100$?

(d) To better understand the direction of time make a video[8] of the motion of the positions of 270 particles starting from $t = 0$. Run the simulation until the particles are approximately equally divided between the three regions. Run the video both forward and backward. Can you tell by just looking at the video which direction is forward? Repeat for increasing values of N. Does your conclusion about the direction of time become more certain for larger N?

(e) Repeat part (d) but start the video after the particles are distributed equally among the three regions, say at $t = 20$ as in Figure 1.2. Is the direction of time obvious now? Repeat for various values of N.

(f) *After n_1, n_2, and n_3 first become approximately equal for $N = 270$, reverse the time and

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[8]Choose Video Capture under the Tools menu. Save the video in QuickTime. The video can be run using the QuickTime Player and played forward or backward by using the command key and the right or left arrow key.

continue the simulation. Reversing the time is equivalent to letting $t \to -t$ 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 system evolve longer before the time is reversed. What happens now? Are your results consistent with the fact that Newton's equations of motion are deterministic and time reversal invariant so that reversing the velocities should exactly retrace the original particle trajectories? (See Problem 1.9 for a discussion of the extreme sensitivity of the trajectories to very small errors.)

(g) Program `ApproachToEquilibriumTwoPartitions` initially divides the box into two partitions rather than three. Run the program and verify that the simulation shows similar qualitative behavior. Explain the use of toroidal boundary conditions.   □

The results of the simulations in Problem 1.1 might not seem surprising until you think about them. Why does the system 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 why there is a direction of time, we consider a simpler model which shows similar behavior. Imagine a closed box that is divided into two parts of equal areas. The left half initially contains N identical particles and the right half is empty. We then make a small hole in the partition between the two halves. What happens? Instead of simulating this system by solving Newton's equations for each particle, we adopt a simpler approach based on a probabilistic model. We assume that the system is so dilute that the particles do not interact with one another. Hence, the probability per unit time that a particle goes through the hole in the partition is the same for all particles regardless of the number of particles in either half. We also assume that the size of the hole is such that only one particle can pass through in one unit of time.

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

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

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

3. Increase the "time" by 1.

Program `ApproachToEquilibriumPariclesInBox` implements this algorithm and plots the evolution of n.

Problem 1.2. Particles in a box

(a) Before you run the program describe what you think will be the qualitative behavior of $n(t)$, the time-dependence of the number of particles on the left side of the box.

(b) Run the program and 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?

(c) 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?

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

(e) How does $\overline{n}$, 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 the time $t = 0$. Why would such a calculation not yield the correct equilibrium average values? Use the `Zero Averages` button to reset the averages.

(f) Define the quantity σ by the relation[9]

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

What does σ measure? What would be its value if n were constant? How does σ depend on N? How does the ratio $\sigma/\overline{n}$ depend on N? We say that σ is a measure of the fluctuations of n about its mean, and $\sigma/\overline{n}$ is a measure of the relative fluctuations of n. □

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

How can we understand why the systems considered in Problems 1.1 and 1.2 exhibit a direction of time? There are two general methods. One way is to study the dynamics of the system as it approaches equilibrium.[10] 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 model 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 how long it takes the system to reach equilibrium. However, it will give us insight into why there is a direction of time.

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[9]This use of σ should not be confused with the length σ in the Lennard-Jones potential.

[10]The time dependence of the number of particles on the left half of the box in Problem 1.2 is discussed in Section 1.13.1.

microstate		n	$W(n)$	$P(n)$
L	L	2	1	1/4
L	R	1	2	1/2
R	L			
R	R	0	1	1/4

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 microstates corresponding to the macroscopic state characterized by n, the number of particles on the left-hand side. The probability $P(n)$ of macrostate n is calculated assuming that each microstate is equally likely.

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

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. Are the three possible macrostates listed in Table 1.1 equally probable?

Now let us consider $N = 4$ for which there are $2 \times 2 \times 2 \times 2 = 2^4 = 16$ microstates (see Table 1.2). Let us assume as before that all microstates are equally probable in equilibrium. We see from Table 1.2 that there is only one microstate 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 microstate. The latter microstate is "special" and is said to be nonrandom, while the microstates with $n \approx N/2$, for which the distribution of the particles is approximately uniform, are said to be "random." So we conclude that the equilibrium macrostate corresponds to the most probable state.

Problem 1.3. Counting microstates

(a) Calculate the number of possible microstates 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 microstates for each n by hand if you have enough patience, but because there are a total of $2^8 = 256$ microstates, this counting would be very tedious. An alternative is to obtain an expression for the number of ways that n particles out of N can be in the left half of the box. Motivate such an expression by enumerating the possible microstates for smaller values of N until you see a pattern.

(b) The macrostate with $n = N/2$ is much more probable than the macrostate with $n = N$. Why?   ☐

Approach to equilibrium. The macrostates that give us the least amount of information about the associated microstates are the most probable. For example, suppose that we wish to know

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

Table 1.2: The 2^4 possible microstates for $N = 4$ particles which are distributed in the two halves of a box. The quantity $W(n)$ is the number of microstates corresponding to the macroscopic state characterized by n. The probability $P(n)$ of macrostate n is calculated assuming that each microstate is equally likely.

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

We also found from the simulations in Problems 1.1 and 1.2 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. 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 microstates corresponding to a particular macrostate leads us to conclude that

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

This conclusion is independent of the nature of the dynamics. Note that the simulations in Problems 1.1 and 1.2 involved the dynamics, but our discussion of the number of microstates corresponding to each macrostate did not involve the dynamics in any way. Instead we counted (enumerated) the microstates and assigned them equal probabilities assuming that the system is isolated and in equilibrium. It is much easier to understand equilibrium systems by ignoring the dynamics 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 quantities changed besides the number of particles in each third of the box? Based on our previous discussions, we can tentatively say that the quantity that changed is the entropy. We conjecture that the entropy is associated with the number of microstates 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 such that $n_1 = n_2 = n_3 = N/3$, the mean value of $n_1 = n_2 = n_3 = N/3$ 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 look at Chapter 4, where this identification of the entropy is made explicit.

As a result of the two simulations that we have considered and our discussions, we can make some additional preliminary 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*. In equilibrium only the *average* values of the macroscopic variables are independent of time.[11] For example, in Problem 1.2 the number of particles $n(t)$ changes with t, but its average value $\overline{n}$ does not.[12] If N is large, fluctuations corresponding to a very nonuniform distribution of the particles almost never occur, and the relative fluctuations, $\sigma/\overline{n}$ [see (1.2)] become smaller as N is increased.

History independence. The properties of *equilibrium systems are independent of their history*. For example, $\overline{n}$ in Problem 1.2 would be the same whether we had started with $n(t = 0) = N$ or $n(t = 0) = 0$. In contrast, as members of the human race, we are all products of our history. One consequence of history independence is that we can ignore how a system reached equilibrium. We will find that equilibrium statistical mechanics is equivalent to counting microstates. The problem is that this counting is usually difficult to do.

Need for statistical approach. A macroscopic system can be described in detail by specifying its *microstate*. Such a description corresponds to giving all the possible information. For a system of classical particles, a microstate corresponds to specifying the position and velocity of each particle.

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

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[11] In this introductory chapter some of our general statements need to be qualified. Just because a system has time-independent macroscopic properties does not necessarily mean that it is in equilibrium. If a system is driven by external forces or currents that are time-independent, the observable macroscopic properties of the system can be time independent, and the system is said to be in a *steady state*. For example, consider a metal bar with one end in contact with a much larger system at temperature T_{hot} and the other end in contact with a large system at temperature T_{cold}. If $T_{\text{hot}} > T_{\text{cold}}$, energy will be continually transported from the "hot" end to the "cold" end and the temperature gradient will not change on the average.

[12] We have not carefully defined how to calculate the average value $\overline{n}$. One way to do so is to average $n(t)$ over some interval of time. Another way is to do an ensemble average. That is, run the same simulation many times with different sets of random number sequences and then average the results at a given time (see Section 1.8).

simpler. Suppose that we simulated a system of many particles and saved the trajectories of each particle 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? We conclude that the presence of a large number of particles motivates us to adopt a statistical approach. In Section 1.7 we will discuss another reason why a statistical 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 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 microstate was equally probable. That is, each microstate of an isolated system occurs with equal probability if the system is in equilibrium. We will make this assumption explicit 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 explored in Problem 1.4.

Problem 1.4. Different phases

(a) Program `LJ2DMD` simulates an isolated system of N particles interacting via the Lennard-Jones potential. Choose $N = 144$ and $L = 18$ so that the density $\rho = N/L^2 \approx 0.44$. The initial positions are chosen at random except that no two particles are allowed to be closer than the length σ. Run the simulation and satisfy yourself that this choice of density and resultant total energy corresponds to a gas. What are your criteria?

(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 will be able to observe "liquid-like" regions. How are they different from "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 are your criteria for a solid? Explain why the solid that we obtain in this way will not be a perfect crystalline solid.

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

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

It is remarkable that a system with the same interparticle interaction can be in different phases. At the microscopic level, the dynamics of the particles is governed by the same equations

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

1.5   Measuring the Pressure and Temperature

The obvious macroscopic quantities that we can measure in our simulations of many interacting particles include the average kinetic and potential energies, the number of particles, and the volume. We know from our everyday experience that there are at least two other macroscopic variables that are relevant for a system of particles, namely, the pressure and the temperature.

You are probably familiar with force and pressure from courses in mechanics. The idea is to determine the force needed to keep a freely moving wall stationary. This force is divided by the area A of the wall to give the pressure P:

$$P = \frac{F}{A}, \tag{1.3}$$

where the force F acts normal to the surface. The pressure is a scalar because it is the same in all directions on the average. From Newton's second law, we can rewrite (1.3) as

$$P = \frac{1}{A}\frac{d(p_x)}{dt}, \tag{1.4}$$

where p_x is the component of the momentum perpendicular to the wall. From (1.4) we see that the pressure is related to the rate of change of the momentum of all the particles that strike a wall.[13]

The number of particles that strike a wall of the box per second is huge. A pressure gauge cannot distinguish between the individual frequent impacts and measures the average force due to many impacts. We will discuss many examples of the relation of the macroscopic properties of a system to an average of some microscopic quantity.

Before we discuss the nature of temperature consider the following questions.

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) If you add energy to a pot of boiling water, does the temperature of the water change?

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

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

Although temperature and energy are related, they are not the same quantity. 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. If we placed a glass 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.

The most fundamental property of temperature is not that it has something to do with energy. More importantly, *temperature is the quantity that becomes equal when two systems are allowed to exchange energy with one another*. In Problem 1.6 we interpret the temperature from this point of view.

Problem 1.6. Identification of the temperature

(a) Consider two systems of particles A and B which interact via the Lennard-Jones potential in (1.1). Use Program `LJThermalEquilibrium`. 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. We take $N_A = 81$, $\epsilon_{AA} = 1.0$, $\sigma_{AA} = 1.0$, $N_B = 64$, $\epsilon_{BB} = 1.5$, and $\sigma_{BB} = 1.2$. Run the simulation and monitor the kinetic energy and potential energy until each system appears to reach equilibrium. 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 particles in the two systems interact with one another.[14] 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) After equilibrium has been established compare the average kinetic and potential energies of each system to their values before the two systems came into contact.

(d) We seek 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 number of particles 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 becomes the same once the two systems are in equilibrium? Do any other quantities become approximately equal? What can you conclude about the possible identification of the temperature in this system? □

From the simulations in Problem 1.6 you are likely to conclude that the temperature is proportional to the average kinetic energy per particle. You probably knew about this relation already. We will learn in Chapter 4 that the proportionality of the temperature to the average kinetic

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

energy per particle holds only for a system of particles whose kinetic energy is proportional to the square of its momentum or velocity.

How can we measure the temperature of a system? After all, in an experiment we cannot directly measure the mean kinetic energy per particle. Nevertheless, there are many kinds of thermometers. These thermometers exchange energy with the system of interest and have some physical property that changes in a way that can be calibrated to yield the temperature. In Problem 1.7 we ask you to think about the general characteristics of thermometers. We then consider a simple model thermometer that is useful in simulations. We will discuss thermometers in more detail in Chapter 2.

Problem 1.7. Thermometers

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

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

(c) What requirements must a thermometer have to be useful? □

To gain more insight into the meaning of temperature we consider a model thermometer known as a "demon." This demon is a special particle that carries a sack of energy and exchanges energy with the system of interest. If the change lowers the energy of the system, the demon puts the extra energy in its sack. If the change costs energy, the demon gives the system the needed energy with the constraint that E_d, the energy of the demon, must be nonnegative. 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 trial change.

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

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

5. Repeat steps 1–4 many times.

6. Compute the averages of the quantities of interest once the system and the demon have reached equilibrium.

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

Program `IdealThermometerIdealGas` simulates a demon that exchanges energy with an ideal gas of N particles 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 each component of its velocity by an amount chosen at random between $-\Delta$ and $+\Delta$. For simplicity, we set the initial demon energy $E_d = 0$ and the initial velocity of each particle equal to $+v_0\hat{x}$, where $v_0 = (2E_0/mN)^{1/2}$. E_0 is the desired total energy of the system, and m is the mass of the particles. We choose units such that $m = 1$; the energy and momentum are measured in dimensionless units (see Section 1.11).

(a) Run the simulation using the default parameters $N = 40$, $E = 40$, and $d = 3$. Does the mean energy of the demon approach a well-defined value after a sufficient number of energy exchanges with the system? One Monte Carlo step per particle (mcs) is equivalent to N trial changes.

(b) What is $\overline{E}_d$, the mean energy of the demon, and $\overline{E}$, the mean energy of the system? Compare the values of $\overline{E}_d$ and $\overline{E}/N$.

(c) Fix $N = 40$ and double the total energy of the system. (Remember that $E_d = 0$ initially.) Compare the values of $\overline{E}_d$ and $\overline{E}/N$. How does their ratio change? Consider other values of $N \geq 40$ and E and determine the relation between $\overline{E}_d$ and $\overline{E}/N$.[15]

(d) You probably learned in high school physics or chemistry that the mean energy of an ideal gas in three dimensions is equal to $\frac{3}{2}NkT$, where T is the temperature of the gas, N is the number of particles, and k is a constant. Use this relation to determine the temperature of the ideal gas in parts (b) and (c). Our choice of dimensionless variables implies that we have chosen units such that $k = 1$. Is $\overline{E}_d$ proportional to the temperature of the gas?

(e) 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 1). Consider various values of N and E as you did in part (c). Is the dependence of $\overline{E}_d$ on $\overline{E}/N$ the same as you found in part (d)? We will find (see Problem 4.30) that $\overline{E}_d$ is still proportional to the temperature.

(f) *After the demon and the system have reached equilibrium, we can compute the histogram $H(E_d)\Delta E_d$, the number of times that the demon has energy between E_d and $E_d + \Delta E_d$. The bin width ΔE_d is chosen by the program. This histogram is proportional to the probability $p(E_d)\Delta E$ that the demon has energy between E_d and $E_d + \Delta E$. What do you think is the nature of the dependence of $p(E_d)$ on E_d? Is the demon more likely to have zero or nonzero energy?

(g) *Verify the exponential form of $p(E_d) = Ae^{-\beta E_d}$, where A and β are parameters.[16] How does the value of $1/\beta$ compare to the value of $\overline{E}_d$? We will find that the exponential form of $p(E_d)$ is *universal*, that is, independent of the system with which the demon exchanges energy, and that $1/\beta$ is proportional to the temperature of the system.

(h) Discuss why the demon is an ideal thermometer. $\qquad\qquad\qquad\qquad\qquad\qquad\square$

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[15]Because there are finite-size effects that are order $1/N$, it is desirable to consider $N \gg 1$. The trade-off is that the simulation will take longer to run.

[16]Choose `Data Tool` under the `Tools` menu and click OK.

1.6 Work, Heating, and the First Law of Thermodynamics

As you watch the motion of the individual particles in a molecular dynamics simulation, you will 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 exhibits 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 continues to move more or less at random.

In contrast, if we squeeze a plastic container of water, we do *work* on the system, and would see the particles near the wall move *coherently*. So we can distinguish two different ways of transferring energy to the system. *Heating transfers energy incoherently and doing work transfers energy coherently.*

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

Our discussion implies that the phrase "adding heat" to a system makes no sense, because we cannot distinguish "heat energy" from potential energy and kinetic energy. Nevertheless, we frequently use the word "heat" in everyday speech. For example, we might 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 "heat" as a noun. Why do we care? Because there is no such thing as heat and the words we use affect how we think. 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 we still use it in our everyday language.

1.7 *The Fundamental Need for a Statistical Approach

In Section 1.4 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, our disinterest in the trajectory of any particular particle and the overwhelming amount of information that is generated in a simulation motivates us to develop a statistical approach.

We now discuss the 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
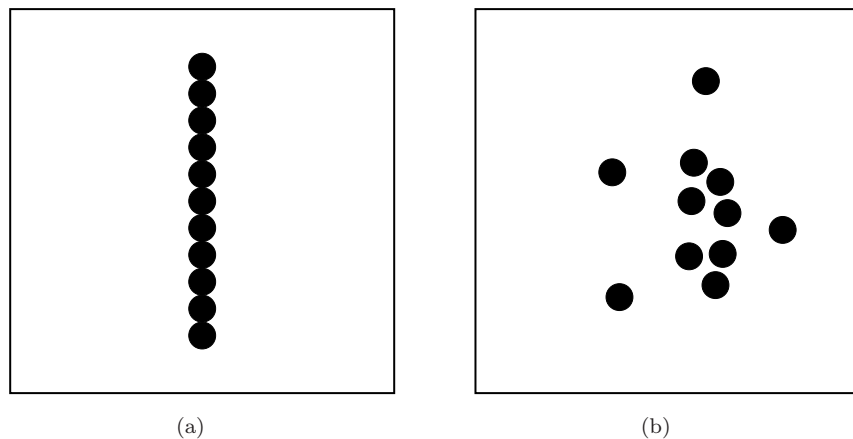
Figure 1.3: (a) A special initial condition for $N = 11$ particles such that their motion remains parallel indefinitely. (b) The positions of the particles shortly after a small change in $v_x(6)$. The only change in the initial condition from part (a) is that $v_x(6)$ was changed from 1 to 1.000001.

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 Program `SensitivityToInitialConditions`). The initial conditions are such that all particles have the same velocity $v_x(i) = 1$, $v_y(i) = 0$, and the particles are equally spaced vertically, with $x(i) = L/2$ for $i = 1, \ldots, 11$ [see Figure 1.3(a)]. Convince yourself that for these special initial conditions, the particles will continue moving indefinitely in the x-direction (using toroidal boundary conditions).

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

Problem 1.9. Irreversibility

Program `SensitivityToInitialConditions` simulates a system of $N = 11$ particles with the special initial condition described in the text. Confirm the results that we have discussed. Perturb the velocity of particle 6 and stop the simulation at time t after the change 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 particles in the system to return to their 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. For such systems we cannot predict the positions and velocities of the particles very far into the future because even the slightest error in our measurement of the initial

conditions would make our prediction entirely wrong if the elapsed time is sufficiently long. That is, we cannot answer the question "Where is a particular particle 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 the positions and velocities of the milk and coffee molecules would need to have exactly the right values to allow the milk to return to this very special state. Even the slightest error in the choice of the 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.

1.8 *Time and Ensemble Averages

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. Because of the assumption of equal probabilities for the microstates of an isolated system, all trajectories consistent with the constraints will contribute equally to the average values of macroscopic quantities. Thus, the trajectories computed in a simulation are useful even though they are very different from the exact trajectories that would be calculated with an infinite precision computer.

Solving Newton's equations numerically as we have done in our molecular dynamics simulations allows us to calculate 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. Because time is irrelevant for a system in equilibrium, we will find that it is easier to do calculations by using an *ensemble* average. In brief, an ensemble average is taken 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. We will discuss ensemble averages in Chapter 3.

It is reasonable to assume that the two ways of averaging are equivalent. This equivalence is called the *ergodic hypothesis*. 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 ergodic hypothesis.

We conclude that 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 determine these averages and give a microscopic basis for the laws of thermodynamics. In this context it is remarkable that these laws depend on the fact that the macroscopic systems we encounter in our everyday experience are chaotic.

1.9 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 approach to understanding nature is to develop models that can be understood theoretically, but that are rich enough to show the same qualitative features that are observed in nature. Some of the more common models that we will consider include the following.

1.9.1 The ideal gas

The simplest models of macroscopic systems are those for which there are no interactions between the individual constituents of the system. 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 system can be modeled as an *ideal gas*. The ideal classical gas allows us to understand much about the behavior of dilute gases, such as those in the Earth's atmosphere. The quantum versions will be useful in understanding blackbody radiation, electrons in metals, the low temperature behavior of crystalline solids, and a simple model of superfluidity.

The historical reason for the use of the term "ideal" 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?

1.9.2 Interparticle potentials

As we have mentioned, the most common form of the potential between two neutral atoms is the Lennard-Jones potential given in (1.1) and Figure 1.1. This 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 purely repulsive and is given by

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

A system of particles interacting via (1.5) is called a system of hard spheres, hard disks, or hard rods depending on whether the spatial dimension is three, two, or one, respectively. The properties of dense gases and liquids will be discussed in Chapter 8.

1.9.3 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 the moments can be neglected.

The simplest, nontrivial lattice model that includes interactions is the *Ising model*, the most important model in statistical mechanics. The model consists of magnetic moments or spins which are located on the sites of 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 point in the same direction and $+J$ if they point in opposite directions. 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. The Ising model will be discussed in Chapter 5.

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.

1.10 Importance of Simulations

Only simple models such as the ideal gas or special cases such as the one- and two-dimensional Ising model can be analyzed by analytical methods. Much of what is currently 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 might appear. How many examples of systems in classical mechanics can be solved exactly?

Statistical mechanics has grown in importance over the past several decades because powerful computers and new algorithms have made it possible to explore the behavior of more complex systems. As our models become more realistic, it is likely that they will require the computer for understanding many of their properties. Frequently the goal of a simulation is to explore the qualitative behavior of a model 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 also allow us to compute many different kinds of quantities, some of which cannot be measured in a laboratory experiment. Simulations, theory, and experiment each play an important and complementary role in understanding nature.

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.

1.11 Dimensionless Quantities

The different units used in science can be confusing. One reason is that sometimes the original measurements were done before a good theoretical understanding was achieved. For example, the calorie was created as a unit before it was understood that heat transfer was a form of energy transfer. So even today we frequently become confused using small calories, big calories, and converting each to joules.

It is frequently convenient to use dimensionless quantities. These quantities can be defined by taking the ratio of two quantities with the same units. For example, the angle θ in radians is the ratio of the arc length s on a circle subtended by the angle to the radius r of the circle: $\theta = s/r$. Similarly, the solid angle in statradians is the ratio of the surface area on a sphere subtended by a cone to the square of the radius of the sphere.

It is also useful to have another quantity with the same dimensions to set the scale. For example, for particles moving with speed v near the speed of light c, it is convenient to measure v relative to c. (You might recognize the notation $\beta \equiv v/c$.) The use of dimensionless variables makes the relevant equations simpler and make it easier to perform algebraic manipulations, thus reducing the possibility of errors. A more important reason to use dimensionless variables is to make it easier to evaluate the importance of quantities in making approximations. For example, if $\beta \ll 1$, we know that relativistic corrections are not needed in most contexts.

We will frequently consider the high and low temperature behavior of a thermal system. What characterizes high temperature? To answer this question we need to find a typical energy ϵ in the system and consider the dimensionless ratio $\tilde{T} \equiv kT/\epsilon$. For example, ϵ might be a measure of the potential energy per particle in the system. If $\tilde{T} \ll 1$, the temperature of the system is low; if $\tilde{T} \gg 1$ the system is in the high temperature regime. An important example is the behavior of electrons in metals at room temperature. We will find in Chapter 6 that the temperature of this system is low. Here ϵ is chosen to be the maximum kinetic energy of an electron at zero (absolute) temperature. In quantum mechanics no two electrons can be in the same state, and hence ϵ is nonzero.

Although $\tilde{T}$ is dimensionless, it is frequently convenient to call $\tilde{T}$ a temperature and sometimes even to denote it by T, with the understanding that T is measured in terms of ϵ. We already did so in the context of Problems 1.6 and 1.8.

Another important reason to use dimensionless quantities is that computers do not easily manipulate very small or very large numbers. Thus, it is best that all quantities be within a few orders of magnitude of one. In addition, the use of dimensionless quantities allows us to do a simulation or an analytical calculation that is valid for many systems. To find the value of a quantity for a specific system, we just multiply the dimensionless quantity by the relevant quantity that sets the scale for the system of interest.

Every measurement is a ratio and is based on a comparison to some standard. For example, if you want a certain time interval in seconds, it is given by the ratio of that interval to 9,192,631,770 periods of the radiation from a certain transition in a cesium atom. This number of periods comes from using a very accurately characterized frequency of this transition and keeping the definition of the second close to its historical definition.

1.12   Summary

The purpose of this introductory chapter is to whet your appetite. 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*.[17] 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. However, there is no unifying equation such as Newton's second law of motion in mechanics, Maxwell's equations in electrodynamics, and Schrödinger's equation in nonrelativistic quantum mechanics. The concepts are universal, but their application to particular systems is not.

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 systems of interest include high temperature superconductors, low dimensional magnets and conductors, composites, and biomaterials. Scientists are also taking a new look at more traditional condensed systems such as water and other liquids, liquid crystals, polymers, granular matter (for example, sand), and porous media such as rocks. In addition to our interest in macroscopic systems, there is growing interest is *mesoscopic* systems, systems that are neither microscopic nor macroscopic, but are in between, that is, between $\sim 10^2$ and $\sim 10^6$ 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 climate change and the development of alternative energy sources.

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, an important area of 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, and the analysis of the distribution of response times to email. Statistical physics is characterized more by its techniques than by the problems that are of interest. This universal applicability makes the techniques more difficult to understand, but also makes the journey more exciting.

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

1.13 Supplementary Notes

1.13.1 Approach to equilibrium

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

We know that, if we run the simulation once, $n(t)$ will exhibit fluctuations and not decay monotonically to equilibrium. Suppose that we do the simulation many times and average the results of each run at a given time t. As discussed in Section 1.8, this average is an ensemble average, which we will denote as $\overline{n}(t)$. If there are $\overline{n}(t)$ particles on the left side after t moves, the change in $\overline{n}$ in the time interval Δt is given by

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

where Δt is the time between moves of a single particle from one side to the other. Equation (1.6) is equivalent to assuming that the change in $\overline{n}$ in one time step is equal to the probability that a particle is removed from the left plus the probability that it is added to the right. (In the simulation we defined the time so that the time interval Δt between changes in $n(t)$ was set equal to 1.) If we treat $\overline{n}$ and t as continuous variables and take the limit $\Delta t \to 0$, we have

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

The solution of the differential equation (1.7) is

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

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

From (1.8) we can define a *relaxation time* τ as the time it takes the difference $[\overline{n}(t) - N/2]$ to decrease to $1/e$ of its initial value. Because $\tau = N/2$, $\overline{n}(t)$ for large N varies slowly, and we are justified in rewriting the difference equation (1.6) as a differential equation.

Problem 1.10. Independence of initial conditions

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

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

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

1.13.2 Mathematics refresher

As discussed in Section 1.12, there is no unifying equation in statistical mechanics such as Newton's second law of motion to be solved in a variety of contexts. For this reason we will use many mathematical tools. Section 2.24.1 summarizes the mathematics of thermodynamics which makes much use of partial derivatives. The Appendix 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 much of the mathematics that we will use in the following chapters.

Problem 1.11. Common derivatives
Calculate the derivative with respect to x of the following functions: e^x, e^{3x}, e^{ax}, $\ln x$, $\ln x^2$, $\ln 3x$, $\ln 1/x$, $\sin x$, $\cos x$, $\sin 3x$, and $\cos 2x$. ☐

Problem 1.12. Common integrals
Calculate the following integrals:

$$\int_1^2 \frac{dx}{2x^2}, \ \int_1^2 \frac{dx}{4x}, \ \int_1^2 e^{3x} dx, \ \text{and} \ \int x^{-\gamma} \, dx. \tag{1.10}$$

☐

Problem 1.13. Partial derivatives
Calculate the partial derivatives of $x^2 + xy + 3y^2$ with respect to x and y. ☐

Problem 1.14. Taylor series approximations
Calculate the first three nonzero terms of the Taylor series approximations about $x = 0$ for the following functions:

$$e^{ax}, \ln(1+x), \text{and}(1+x)^n, \tag{1.11}$$

where a and n are constants. ☐

Vocabulary

thermodynamics, statistical mechanics

macroscopic system, microstate, macrostate

specially prepared state, most probable macrostate

equilibrium, fluctuations, relative fluctuations

thermal contact, temperature

sensitivity to initial conditions, chaos

models, computer simulations, molecular dynamics

Additional Problems

Problem 1.15. The dye is cast

(a) What would 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 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 1.16. Fluid as metaphor

Why is "heat" treated as a fluid in everyday speech? After all, most people are not familiar with the caloric theory of heat. □

Problem 1.17. Do molecules really move?

Cite evidence 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. Temperature

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

Problem 1.19. Time-reversal invariance

Show that Newton's equations are time-reversal invariant. □

Problem 1.20. Properties of macroscopic systems

Summarize your present understanding of the properties of macroscopic systems. □

Problem 1.21. What's in a name?

Ask some of your friends why a ball falls when released above the Earth's surface. Then ask them what makes rolling balls come to rest. Are the answers of "gravity" and "friction" satisfactory explanations? What would be a more fundamental explanation for each phenomena? □

Problem 1.22. Randomness

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

Problem 1.23. Meaning of abstract concepts

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

Problem 1.24. Bicycle pump

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

Problem 1.25. Granular matter

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

Suggestions for Further Reading

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

John J. Brehm and William J. Mullin, *Introduction to the Structure of Matter*, John Wiley & Sons (1989).

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.

Martin Goldstein and Inge F. Goldstein, *The Refrigerator and the Universe*, Harvard University Press (1993).

Harvey Gould, Jan Tobochnik, and Wolfgang Christian, *An Introduction to Computer Simulation Methods*, third edition, Addison-Wesley (2006).

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

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

Robert H. Romer, "Heat is not a noun," Am. J. Phys. **69** (2), 107–109 (2001). See also Art Hobson, "The language of physics," Am. J. Phys. **69** (6), 634 (2001); David T. Brookes and Eugenia Etkina, "Using conceptual metaphor and functional grammar to explore how language used in physics affects student learning," Phys. Rev. ST Phys. Educ. Res. **3** (1), 010105-1–16 (2007).

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

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

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

Stephen Blundell and Katherine Blundell, *Thermal Physics*, 2nd ed., Oxford University Press (2009).

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

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

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

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

F. Reif, *Fundamentals of Statistical and Thermal Physics*, McGraw-Hill (1965). Our presentation owes a large debt to the two books by Reif on statistical physics.

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