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 nature of calculations in statistical mechanics.

Consider an isolated system of $N = 5$ noninteracting spins with magnetic moment $\mu$ and spin $1/2$ in a magnetic field $B$. If the total energy $E = -\mu B$, what is the mean magnetic moment of a given spin in the system? The essential steps needed to analyze this system can be summarized as follows.

1. **Specify the macrostate and accessible microstates of the system.** The macroscopic state or macrostate of the system corresponds to the information that we know. For this example the observable quantities are the total energy $E$, the magnetization $M$, the number of spins $N$, and the external magnetic field $B$. (Because the spins are noninteracting, it is redundant to specify both $M$ and $E$.)

   The most complete specification of the system corresponds to the enumeration of the microstates or configurations of the system. For $N = 5$ there are $2^5 = 32$ total microstates, each specified by the orientation of the $N$ spins. However, not all of the 32 microstates are consistent with the information that $E = -\mu B$. For example, $E = -5\mu B$ for the microstate shown in Figure 4.1(a) is not allowed, that is, such a state is inaccessible. The accessible microstates of the system are those that are consistent with the macroscopic conditions. In this example, ten of the thirty-two total microstates are accessible (see Figure 4.1(b)).
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

$$P_n = \frac{1}{\Omega},$$

where $\Omega$ represents the number of microstates of energy $E$. This assumption is equivalent to the principle of least bias or maximum uncertainty that we discussed in Section 3.4.1. For our example, we have $\Omega = 10$, and the probability that the system is in any one of its accessible microstates is $1/10$.

3. Calculate the mean values and other statistical properties. As an example of a probability calculation, we calculate the mean value of the orientation of spin 1 (see Figure 4.1(b)). Because $s_1$ assumes the value $\pm 1$, we have

$$\langle s_1 \rangle = \sum_{n=1}^{10} P_n s_n$$

$$= \frac{1}{10} \left[ (+1) + (+1) + (+1) + (-1) + (+1) + (+1) + (-1) + (+1) + (-1) + (-1) \right]$$

$$= \frac{2}{10} = \frac{1}{5}.$$ 

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 (4.2c) that the mean value of $s_1$ is $\langle s_1 \rangle = 1/5$.

**Problem 4.1.** Simple example

(a) What is the mean value of spin 2 in the above example?
(b) What is the probability \( p \) that a given spin points up?

(c) What is the probability that if spin 1 is up, then spin 2 also is up?

There is a more direct way of calculating \( \bar{s}_1 \) in this case. Because \( M = 1 \), six out of the ten spins are up. The equivalency of the spins implies that the probability of a spin being up is 6/10. Hence, \( \bar{s} = (3/5)(1) + (2/5)(-1) = 1/5 \). What is the implicit assumption that we made in the more direct method?

**Problem 4.2.** Counting microstates

Consider \( N = 4 \) noninteracting spins with magnetic moment \( \mu \) and spin \( 1/2 \) in a magnetic field \( B \).

(a) If the total energy \( E = -2\mu B \), what are the accessible microstates and the probabilities that a particular spin has a magnetic moment \( \pm \mu \)?

(b) Consider \( N = 9 \) noninteracting spins with total energy \( E = -\mu B \). What is the net number of up spins, the number of accessible microstates, and the probabilities that a particular spin has magnetic moment \( \pm \mu \)?

**Problem 4.3.** Consider a one-dimensional ideal gas consisting of \( N = 5 \) particles each of which has the same speed \( v \), but velocity \( \pm v \). The velocity of each particle is independent. What is the probability that all the particles are moving in the same direction?

The model of noninteracting spins that we have considered is an example of an isolated system. In this case the system of spins has fixed values of \( E, B, \) and \( N \). In general, an isolated system cannot exchange energy or matter with its surroundings nor do work on another system. The macrostate of such a system is specified by \( E, V, \) and \( N \) (\( B \) instead of \( V \) for a magnetic system). Our strategy will be to first understand how to treat isolated systems. Conceptually, isolated systems are simpler because all the accessible microstates have the same probability (see Section 4.5).

### 4.2 A simple example of a thermal interaction

Now that we have an idea of how we can do probability calculations for an isolated system, we next consider some model systems that can exchange energy with another system. This exchange has the effect of relaxing one of the internal constraints and, as we will see, imposing another. We will see that for nonisolated systems, the probability of each microstate is not the same.

We know what happens when we place two bodies at different temperatures into thermal contact with one another – energy is transferred from the hotter to the colder body until thermal equilibrium is reached and the two bodies have the same temperature. We now consider a simple model that illustrates how statistical concepts can help us understand the transfer of energy and the microscopic nature of thermal equilibrium.

Consider a model system of \( N \) noninteracting distinguishable particles such that the energy of each particle is restricted to integer values, that is, \( \epsilon_n = 0, 1, 2, 3, \ldots \). We can distinguish the particles by their colors, or we can assume that the particles have the same color, but are fixed on
lattice sites. For reasons that we will discuss in Section 6.12, we will refer to this model system as an Einstein solid.\footnote{These particles are equivalent to the quanta of the harmonic oscillator, which have energy $E_n = (n + \frac{1}{2})\hbar\omega$. If we measure the energies from the lowest energy state, $\frac{1}{2}\hbar\omega$, and choose units such that $\hbar\omega = 1$, we have $\epsilon_n = n$.}

Consider an Einstein solid with $N = 3$ particles (with colors red, white, and blue) in an isolated box and total energy $E = 3$. For these small values of $N$ and $E$, we can enumerate the accessible microstates by hand. The ten accessible microstates of this system are shown in Table 4.1. Because the energy is specified, the ten accessible microstates are equally probable.

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, …

<table>
<thead>
<tr>
<th>microstate</th>
<th>red</th>
<th>white</th>
<th>blue</th>
</tr>
</thead>
<tbody>
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<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>2</td>
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<td>0</td>
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</tr>
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</tr>
<tr>
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</tr>
<tr>
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<td>2</td>
<td>0</td>
</tr>
<tr>
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</tr>
<tr>
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<td>1</td>
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</tr>
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<td>0</td>
<td>3</td>
<td>0</td>
</tr>
<tr>
<td>10</td>
<td>0</td>
<td>0</td>
<td>3</td>
</tr>
</tbody>
</table>

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

$$\Omega = \frac{(E + N - 1)!}{E! (N - 1)!}.$$  \hfill (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

$$E = E_A + E_B = 5 + 1 = 6.$$  \hfill (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 $\Omega$ accessible to the composite system is

$$\Omega = \Omega_A \times \Omega_B = 6 \times 2 = 12.$$  \hfill (4.5)
Figure 4.2: Two subsystems, each with two distinguishable particles, surrounded by (a) insulating, rigid, and impermeable outer walls and (b) separated by a conducting, rigid, and impermeable wall. The other walls remain the same.

The partition is an internal constraint that prevents the transfer of energy from one subsystem to another and in this case keeps $E_A = 5$ and $E_B = 1$. (The internal constraint also keeps the volume and number of particles in each subsystem fixed.)

<table>
<thead>
<tr>
<th>$E_A$</th>
<th>accessible microstates</th>
<th>$E_B$</th>
<th>accessible microstates</th>
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<tbody>
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<td>5</td>
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<tr>
<td>3, 2</td>
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</tr>
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</table>

Table 4.2: The 12 equally probable microstates accessible to subsystems $A$ and $B$ before the removal of the internal constraint. The conditions are $N_A = 2$, $E_A = 5$, $N_B = 2$, and $E_B = 1$.

We now consider a simple example of a thermal interaction. Suppose that the insulating, rigid, impermeable partition separating subsystems $A$ and $B$ is changed to a conducting, rigid, impermeable partition (see Figure 4.2). The partition maintains the volumes $V_A$ and $V_B$, and hence the single particle energies are not changed. Because the partition is impermeable, the particles cannot penetrate the partition and go from one subsystem to the other. However, energy can be transferred from one subsystem to the other, subject only to the constraint that the total energy of subsystems $A$ and $B$ is constant, that is, $E = E_A + E_B = 6$. The microstates of subsystems $A$ and $B$ are listed in Table 4.3 for all the possible values of $E_A$ and $E_B$. The total number of microstates $\Omega(E_A, E_B)$ accessible to the composite system whose subsystems have energy $E_A$ and $E_B$ is

$$\Omega(E_A, E_B) = \Omega_A(E_A) \times \Omega_B(E_B).$$

(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 $\Omega$ 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
CHAPTER 4. STATISTICAL MECHANICS

$E_A + E_B = 6$. Hence, $\Omega$ 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

$$\Omega = (7 \times 1) + (6 \times 2) + (5 \times 3) + (4 \times 4) + (3 \times 5) + (2 \times 6) + (1 \times 7) = 84. \quad (4.8)$$

Because the composite system is isolated, its accessible microstates are equally probable, that is, the composite system is equally likely to be in any one of its 84 accessible microstates. An inspection of Table 4.3 shows that the probability that the energy of the composite system is divided such that $E_A = 2$ and $E_B = 4$ is $15/84$. Let $P_A(E_A)$ be the probability that subsystem A has energy $E_A$. Then $P_A(E_A)$ is given by

$$P_A(E_A) = \frac{\Omega_A(E_A)\Omega_B(E - E_A)}{\Omega}. \quad (4.9)$$

We show in Table 4.4 and Figure 4.3 the various values of $P_A(E_A)$.

<table>
<thead>
<tr>
<th>$E_A$ microstates</th>
<th>$\Omega_A(E_A)$</th>
<th>$E_B$ microstates</th>
<th>$\Omega_B(E_B)$</th>
<th>$\Omega_A\Omega_B$</th>
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<td>0</td>
<td>0,0</td>
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<tr>
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<td>5.0 0.5 4.1 1.4 3.2 2.3</td>
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<td>1.0 0.1</td>
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<tr>
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<td>4.0 0.4 3.1 1.3 2.2</td>
<td>5</td>
<td>2</td>
<td>2.0 0.2</td>
</tr>
<tr>
<td>3</td>
<td>3.0 0.3 2.1 1.2</td>
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<td>3</td>
<td>3.0 0.3 2.1 1.2</td>
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<td>5.0 0.5 4.1 1.4 3.2 2.3</td>
<td>6</td>
</tr>
<tr>
<td>0</td>
<td>0.0</td>
<td>1</td>
<td>6</td>
<td>6.0 0.6 5.1 1.5 4.2 2.4 3.3</td>
</tr>
</tbody>
</table>

Table 4.3: The 84 equally probable microstates accessible to the composite system consisting of subsystems $A$ and $B$ after the removal of the internal constraint. The total energy is $E = E_A + E_B = 6$ with $N_A = 2$ and $N_B = 2$.
Table 4.4: The probability \( P_A(E_A) \) that subsystem A has energy \( E_A \).

<table>
<thead>
<tr>
<th>( E_A )</th>
<th>( \Omega_A(E_A) )</th>
<th>( \Omega_B(6 - E_A) )</th>
<th>( \Omega_A\Omega_B )</th>
<th>( P_A(E_A) )</th>
</tr>
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<tr>
<td>6</td>
<td>7</td>
<td>1</td>
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<td>7/84</td>
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<td>12</td>
<td>12/84</td>
</tr>
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<td>5</td>
<td>3</td>
<td>15</td>
<td>15/84</td>
</tr>
<tr>
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<td>4</td>
<td>4</td>
<td>16</td>
<td>16/84</td>
</tr>
<tr>
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<td>6</td>
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<td>7</td>
<td>7</td>
<td>7/84</td>
</tr>
</tbody>
</table>

The mean energy of subsystem A is found by doing an ensemble average over the 84 microstates accessible to the composite system. We use the results for \( P_A(E_A) \) in Table 4.4 and find that

\[
E_A = (0 \times \frac{7}{84}) + (1 \times \frac{12}{84}) + (2 \times \frac{15}{84}) + (3 \times \frac{16}{84}) + (4 \times \frac{15}{84}) + (5 \times \frac{12}{84}) + (6 \times \frac{7}{84}) = 3. \quad (4.10)
\]

In this simple case the mean value of \( E_A \) is equal to \( \bar{E}_A \), the energy corresponding to the most probable value of \( P_A(E_A) \).

**Problem 4.5.** Use the results of Table 4.4 to find the standard deviation of the energy of subsystem A.

Note that the total number of microstates accessible to the composite system increases from 12 to 84 when the internal constraint is removed. From the microscopic point of view, it is clear that the total number of microstates must either remain the same or increase when an
internal constraint is removed. Because the number of microstates becomes a very large number for macroscopic systems, it is convenient to work with the logarithm of the number of microstates. We are thus led to define the quantity $S$ by the relation

\[ S = k \ln \Omega, \quad (4.11) \]

where $k$ is an arbitrary constant. Note the similarity of the definition (4.11) to the expression for the missing information (3.36). 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 “hottest” 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 energy goes from the hotter to the colder subsystem.

**Problem 4.6.** Consider two Einstein solids with $N_A = 3$ and $E_A = 4$ and $N_B = 4$ and $E_B = 2$ initially. The two systems are thermally isolated from one another.

(a) Use the relation (4.3) to determine the initial number of accessible microstates for the composite system.

(b) Then remove the internal constraint so that the two subsystems may exchange energy. Determine the probability $P_A(E_A)$ that system $A$ has energy $E_A$, the most probable energies $\tilde{E}_A$ and $\tilde{E}_B$, the probability that energy goes from the hotter to the colder system, and the mean and variance of the energy of each subsystem.

(c) Plot $P_A$ versus $E_A$ and discuss its qualitative energy dependence. Make a table similar to the one in Table 4.3, but do not list the microstates explicitly.

**Problem 4.7.** The applet/application at <stp.clarku.edu/simulations/EinsteinSolid> determines the number of accessible microstates of an Einstein solid using (4.3) and will help you answer the following questions. Suppose that initially system $A$ has $N_A = 4$ particles with energy $E_A = 10$ and system $B$ has $N_B = 4$ particles with energy $E_B = 2$. Initially, the two systems are thermally isolated from one another. The initial number of states accessible to subsystem $A$ is given by $\Omega_A = 13!/(10!3!) = 286$, and the initial number of states accessible to subsystem $B$ is $\Omega_B = 5!/(2!3!) = 10$. Then the internal constraint is removed so that the two subsystems may exchange energy.

(a) Determine the probability $P_A(E_A)$ that system $A$ has energy $E_A$, the most probable energies $\tilde{E}_A$ and $\tilde{E}_B$, the mean and variance of the energy of each subsystem, and the probability that energy goes from the hotter to the colder system.

(b) Discuss the qualitative energy dependence of $P_A(E_A)$. 
(c) What is the number of accessible microstates for the (composite) system after the internal constraint has been removed? What is the total entropy (choose units such that \( k = 1 \))? What is the change in the total entropy of the system?

(d) The entropy of the composite system when each subsystem is in its most probable macrostate is \( k \ln \Omega_A(E_A)\Omega_B(E - E_A) \). Compare the value of this contribution to the value of the total entropy, \( k \sum_{E_A} \ln \Omega_A(E_A)\Omega_B(E - E_A) \).

(e) Increase \( N_A, N_B \), and the total energy by a factor of ten, and discuss the qualitative changes in the various quantities of interest. Consider successively larger systems until you have satisfied yourself that you understand the qualitative behavior of the various quantities.

*Problem 4.8.* Suppose that system \( A \) is an Einstein solid with \( N_A = 8 \) particles and system \( B \) consists of \( N_B = 8 \) noninteracting spins that can be either up or down. The external magnetic field is such that \( \mu_B = 1/2 \). The magnitude of \( \mu_B \) has been chosen so that the changes in the energy of system \( B \) are the same as system \( A \), that is, \( \Delta E = \pm 1 \). The two systems are initially isolated and the initial energies are \( E_A = 4 \) and \( E_B = 4 \). What is the initial entropy of the composite system? Use the fact that \( \Omega_B = N_B!/(n!(N_B - n)!) \), where \( n \) is the number of up spins in system \( B \) (see Section 3.5). Remove the internal constraint and allow the two systems to exchange energy. Determine the probability \( P_A(E_A) \) that system \( A \) has energy \( E_A \), the mean and variance of the energy of each subsystem, the most probable energies \( \tilde{E}_A \) and \( \tilde{E}_B \), and the probability that energy goes from the hotter to the colder system. What is the change in the total entropy of the system?

From our examples, we conclude that we can identify thermal equilibrium with the most probable macrostate and the entropy with the logarithm of the number of accessible microstates. We also found that the probability \( P(E) \) that a system has energy \( E \) is approximately a Gaussian if the system is in thermal equilibrium with a much bigger system. What quantity can we identify with the temperature? The results of Problem 4.8 if you were not convinced already, that in general, this quantity is not same as the mean energy per particle of the two systems.

Let’s return to the Einstein solid and explore the energy dependence of the entropy. Consider a system with \( N_A = 3, N_B = 4 \), and total energy \( E = 10 \). The number of microstates for the two systems for the various possible values of \( E_A \) are summarized in Table 4.5. We see that that the most probable energies and hence thermal equilibrium corresponds to \( \tilde{E}_A = 4 \) and \( \tilde{E}_B = 6 \). In general, what quantity is the same for system \( A \) and \( B \) at equilibrium? From our understanding of thermal equilibrium, we know that this quantity must be the temperature. In columns 5 and 10 of Table 4.5 we show the inverse slope of the entropy \( S_A(E_A) \) and \( S_B(E_B) \) of systems \( A \) and \( B \) calculated from the central difference approximation for the slope at \( E \). For example,

\[
\frac{1}{T_A(E_A)} \approx \frac{[S_A(E_A + \Delta E_A) - S(E_A - \Delta E_A)]}{2\Delta E_A}.
\]

(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 \( S_A(E_A = 2) \),
CHAPTER 4. STATISTICAL MECHANICS

\[ \Omega_A(E_A) \ln \Omega_A(E_A) T_A^{-1} T_A \quad \Omega_B(E_B) \ln \Omega_B(E_B) T_B^{-1} T_B \quad \Omega_A \Omega_B \]

<table>
<thead>
<tr>
<th>( E_A )</th>
<th>( \Omega_A(E_A) )</th>
<th>( \ln \Omega_A(E_A) )</th>
<th>( T_A^{-1} )</th>
<th>( T_A )</th>
<th>( E_B )</th>
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<th>( \ln \Omega_B(E_B) )</th>
<th>( T_B^{-1} )</th>
<th>( T_B )</th>
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<tr>
<td>6</td>
<td>28</td>
<td>3.33</td>
<td>0.27</td>
<td>3.71</td>
<td>4</td>
<td>35</td>
<td>3.56</td>
<td>0.51</td>
<td>1.94</td>
<td>980</td>
</tr>
<tr>
<td>5</td>
<td>21</td>
<td>3.05</td>
<td>0.31</td>
<td>3.20</td>
<td>5</td>
<td>56</td>
<td>4.03</td>
<td>0.44</td>
<td>2.28</td>
<td>1176</td>
</tr>
<tr>
<td>4</td>
<td>15</td>
<td>2.71</td>
<td>0.37</td>
<td>2.70</td>
<td>6</td>
<td>84</td>
<td>4.43</td>
<td>0.38</td>
<td>2.60</td>
<td>1260</td>
</tr>
<tr>
<td>3</td>
<td>10</td>
<td>2.30</td>
<td>0.46</td>
<td>2.18</td>
<td>7</td>
<td>120</td>
<td>4.79</td>
<td>0.34</td>
<td>2.96</td>
<td>1200</td>
</tr>
<tr>
<td>2</td>
<td>6</td>
<td>1.79</td>
<td>0.60</td>
<td>1.66</td>
<td>8</td>
<td>165</td>
<td>5.11</td>
<td>0.30</td>
<td>3.30</td>
<td>990</td>
</tr>
<tr>
<td>1</td>
<td>3</td>
<td>1.10</td>
<td>0.90</td>
<td>1.11</td>
<td>9</td>
<td>220</td>
<td>5.39</td>
<td>0.28</td>
<td>3.64</td>
<td>660</td>
</tr>
<tr>
<td>0</td>
<td>1</td>
<td>0</td>
<td>na</td>
<td>na</td>
<td>10</td>
<td>286</td>
<td>5.66</td>
<td>na</td>
<td>na</td>
<td>286</td>
</tr>
</tbody>
</table>

Table 4.5: The number of states for subsystems A and B for total energy \( E = E_A + E_B = 10 \) with \( N_A = 3 \) and \( N_B = 4 \). The number of states was determined using (4.3). There are a total of 8008 microstates. The most probable energy of subsystem A is \( \tilde{E}_S = 4 \) and the fraction of microstates associated with the most probable macrostate is \( 1260/8008 \approx 0.157 \). This fraction will approach unity as the number of particles in the systems become larger.

0.60, is steeper than the slope, 0.30, of \( S_B(E_B = 8) \), which means that if energy is passed from A to B, the entropy gained by A will be greater than the entropy lost by B, and the total entropy would increase. Because we know that the entropy is a maximum in equilibrium and energy is transferred spontaneously from “hot” to “cold,” a steeper slope must correspond to a lower temperature. This reasoning suggests that the temperature is associated with the inverse slope of the energy dependence of the entropy.

**Problem 4.9.** The applet/application at [stp.clarku.edu/simulations/entropy/](http://stp.clarku.edu/simulations/entropy/) computes the entropies of two Einstein solids in thermal contact. Explore the effect of increasing the values of \( N_A, N_B, \) and the total energy \( E \). Discuss the qualitative dependence of \( S_A, S_B, \) and \( S_{\text{total}} \) 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 \( S_{\text{total}} \) have a maximum at a particular value of \( E_A \)?

You might wish to skip to Section 4.5 where we will formally develop the relations between the number of accessible microstates of an isolated system to various quantities including the entropy and the temperature.

**Boltzmann probability distribution.** We next consider the Einstein solid in another physical context. Consider an isolated Einstein solid of six particles with total energy \( E = 12 \). We focus our attention on one of the particles and consider it to be a subsystem able to exchange energy with the other five particles. This example is similar to the ones we have considered, but in this case the subsystem consists of only one particle. The quantity of interest is the mean energy of the subsystem and the probability \( P_n \) that the subsystem is in state \( n \) with energy \( \epsilon_n \). The number of ways that the subsystem can be in state \( n \) is unity because the subsystem consists of only one particle. So for this special subsystem of one particle, there is a one-to-one correspondence between the microstate of the system and the energy of the system.
### 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.

<table>
<thead>
<tr>
<th>microstate ( n )</th>
<th>( \epsilon_n )</th>
<th>( E - \epsilon_n )</th>
<th>( \Omega_B )</th>
<th>( P_n )</th>
</tr>
</thead>
<tbody>
<tr>
<td>12</td>
<td>12</td>
<td>0</td>
<td>4!/(0!4!) = 1</td>
<td>0.00016</td>
</tr>
<tr>
<td>11</td>
<td>11</td>
<td>1</td>
<td>5!/(1!4!) = 5</td>
<td>0.00081</td>
</tr>
<tr>
<td>10</td>
<td>10</td>
<td>2</td>
<td>6!/(2!4!) = 15</td>
<td>0.00242</td>
</tr>
<tr>
<td>9</td>
<td>9</td>
<td>3</td>
<td>7!/(3!4!) = 35</td>
<td>0.00566</td>
</tr>
<tr>
<td>8</td>
<td>8</td>
<td>4</td>
<td>8!/(4!4!) = 70</td>
<td>0.01131</td>
</tr>
<tr>
<td>7</td>
<td>7</td>
<td>5</td>
<td>9!/(5!4!) = 126</td>
<td>0.02036</td>
</tr>
<tr>
<td>6</td>
<td>6</td>
<td>6</td>
<td>10!/(6!4!) = 210</td>
<td>0.03394</td>
</tr>
<tr>
<td>5</td>
<td>5</td>
<td>7</td>
<td>11!/(7!4!) = 330</td>
<td>0.05333</td>
</tr>
<tr>
<td>4</td>
<td>4</td>
<td>8</td>
<td>12!/(8!4!) = 495</td>
<td>0.07999</td>
</tr>
<tr>
<td>3</td>
<td>3</td>
<td>9</td>
<td>13!/(9!4!) = 715</td>
<td>0.11555</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>10</td>
<td>14!/(10!4!) = 1001</td>
<td>0.16176</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>11</td>
<td>15!/(11!4!) = 1365</td>
<td>0.22059</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>12</td>
<td>16!/(12!4!) = 1820</td>
<td>0.29412</td>
</tr>
</tbody>
</table>

The number of accessible microstates of the composite system is shown in Table 4.6 using the relation (4.3). From Table 4.6 we can determine the mean energy of the subsystem of one particle:

\[
\tau = \frac{1}{6188} \left[ (0 \times 1820) + (1 \times 1365) + (2 \times 1001) + (3 \times 715) + (4 \times 495) + (5 \times 330) \\
+ (6 \times 210) + (7 \times 126) + (8 \times 70) + (9 \times 35) + (10 \times 15) + (11 \times 5) + (12 \times 1) \right] = 2. \tag{4.13}
\]

The probability \( P_n \) that the subsystem is in microstate \( n \) is plotted in Figure 4.4. Note that \( P_n \) decreases monotonically with increasing energy. A visual inspection of the energy dependence of \( P_n \) in Figure 4.4 indicates that \( P_n \) can be approximated by an exponential of the form

\[
P_n = \frac{1}{Z} e^{-\beta \epsilon_n}, \tag{4.14}
\]

where \( \epsilon_n = n \) in this example and \( Z \) is a normalization constant. Given the form (4.14), we can estimate the parameter \( \beta \) from the slope of \( \ln P_n \) versus \( \epsilon_n \). The result is that \( \beta \approx 0.57 \). You might wish to skip to Section 4.6 to read about the generalization of these results.

**Problem 4.10.**

Consider an Einstein solid with \( N_A = 1 \) and \( N_B = 3 \) with a total energy \( E = 6 \).

(a) Calculate the probability \( P_n \) that system \( A \) is in microstate \( n \). Is this probability the same as the probability that the system \( A \) has energy \( \epsilon_n \)?
Figure 4.4: The probability $P_n$ for the subsystem to be in state $n$ with energy $\epsilon_n = n$. The subsystem can exchange energy with a system of $N = 5$ particles. The total energy of the composite system of six particles is $E = 12$. The circles are the values of $P_n$ given in Table 4.6. The continuous line corresponds to $P_n$ calculated from (4.14) with $\beta = 0.57$.

(b) In Table 4.3 we considered a similar composite system of four particles, except that $N_A = 2$, in contrast to part a for which $N_A = 1$. Why does the probability calculated in part a differ from that calculated in part prob:4/4n.b?

Problem 4.11. From Table 4.3 determine the probability $P_n$ that system $A$ is in microstate $n$ with energy $E_n$ for the different possible energies of $A$. (The microstate $n$ corresponds to the state of system $A$.) What is the qualitative dependence of $P_n$ on $E_n$, the energy of the microstate?

Problem 4.12. Use the applet/application at <stp.clarku.edu/simulations/EinsteinSolid> to compute the probability $P_n$ that a subsystem of one particle is in microstate $n$, assuming that it can exchange energy with an Einstein solid of $N = 11$ particles. The total energy of the two systems is $E = 36$.

(a) Compare your result for $P_n$ to the form (4.14) and compute the parameter $\beta$ from a semilog plot. Also determine the mean energy of the subsystem of one particle and show that it is given by $\epsilon \approx 1/\beta$.

(b) Calculate the constant $Z$ by normalizing the probability and show that $Z$ is given approximately by $Z = (1 - e^{-\beta})^{-1}$.

We will generalize the results we have found here in Example 4.4.

Problem 4.13. Qualitative behavior of the probabilities

(a) Explain why the probability $P_n(E_n)$ that system $A$ is in microstate $n$ with energy $E_n$ is a monotonically decreasing function of $E_n$, given that the system is in thermal contact with a
much larger system. (We could equally well write \( P_n(E_n) \) as \( P_n(E_A) \), but we choose the former notation to emphasize that the system is in a particular microstate. The specification of \( E_A \) alone specifies the macrostate of the system.)

(b) Explain why the probability \( P_A(E_A) \) that system \( A \) has energy \( E_A \) has a Gaussian-like form.

**Problem 4.14.** Rapid increase in the number of states

(a) Consider an Einstein solid of \( N = 10 \) distinguishable oscillators. What is the total number of accessible microstates \( \Omega(E) \) for \( E = 10, 10^2, 10^3, \ldots \)? Is \( \Omega(E) \) a rapidly increasing function of \( E \) for fixed \( N \)?

(b) Is \( \Omega \) a rapidly increasing function of \( N \) for fixed \( E \)?

(c) Use Stirling’s approximation (3.94) to find the large \( E \) behavior of \( \Omega \) for fixed \( N \gg 1 \).

### 4.3 Counting microstates

In the examples we have considered so far, we have seen that the most time consuming task is enumerating (counting) the number of accessible microstates for a system of fixed energy and number of particles. We now discuss how to count the number of accessible microstates for several other systems of interest.

#### 4.3.1 Noninteracting spins

We first reconsider an isolated system of \( N \) noninteracting spins with spin 1/2 and magnetic moment \( \mu \) in an external magnetic field \( B \). Because we can distinguish spins at different lattice sites, a particular state or configuration of the system is specified by giving the orientation (up or down) of each of the \( N \) spins. We want to find the total number of accessible microstates \( \Omega(E, B, N) \) for particular values of \( E, B, \) and \( N \).

We know that if \( n \) spins are parallel to \( B \) and \( N - n \) spins are antiparallel to \( B \), the energy of the system is

\[
E = n(-\mu B) + (N - n)(\mu B) = -(2n - N)\mu B. \tag{4.15}
\]

For a given \( N \) and \( B \), \( n \) specifies the energy and vice versa. If we solve (4.15) for \( n \), we find

\[
n = \frac{N}{2} - \frac{E}{2\mu B}. \tag{4.16}
\]

As we found in (3.79), the total number of microstates with energy \( E \) is given by the number of ways \( n \) spins out of \( N \) can be up. This number is given by

\[
\Omega(n, N) = \frac{N!}{n!(N - n)!}. \tag{4.17}
\]

where \( n \) is related to \( E \) by (4.16). We will apply this result in Example 4.2 on page 172.
4.3.2 *One-dimensional Ising model

It is instructive to discuss the number of states for the one-dimensional Ising model. For small $N$ we can determine $\Omega(E, N)$ by counting on our fingers. For example, it is easy to verify that $\Omega(-2, 2) = 2$ and $\Omega(0, 2) = 2$ and $\Omega(-3, 3) = 2$ and $\Omega(1, 3) = 6$ using periodic boundary conditions. The general expression for $\Omega(E, N)$ for the one-dimensional Ising model for even $N$ in the absence of an external magnetic field is

$$
\Omega(E, N) = 2 \binom{N}{i} = 2 \frac{N!}{i!(N-i)!}, \quad (i = 0, 2, 4, \ldots, N)
$$

(4.18)

where $i = (E + N)/2$. The energy $E$ is measured in units of $J$ so $E$ is an integer. We will discuss the Ising model in more detail in Chapter 5.

Problem 4.15. Verify that (4.18) gives the correct answers for $N = 2$ and 4.

4.3.3 A particle in a one-dimensional box

**Classical calculation.** Consider the microstates of a single classical particle of mass $m$ confined to a one-dimensional box of length $L$. We know that the microstate of a particle is specified by its position $x$ and momentum $p$.\(^2\) We say that the microstate $(x, p)$ is a point in *phase space* (see Figure 4.5).

As in Section 4.3.1, we would like to calculate the number of microstates of the system with energy $E$. Because the values of the position and momenta of a particle are continuous variables, this question is not meaningful and instead we will determine the quantity $g(E)\Delta E$, the number of microstates between $E$ and $E + \Delta E$; the quantity $g(E)$ is the *density of states*. However, it is

\(^2\)We could equally well specify the velocity $v$ rather than $p$, but the momentum $p$ is the appropriate conjugate variable to $x$ in the formal treatment of classical mechanics.
easier to first calculate $\Gamma(E)$, the number of microstates of the system with energy less than or equal to $E$. Then the number of microstates between $E$ and $E + \Delta E$, $g(E)\Delta E$, is related to $\Gamma(E)$ by

$$g(E)\Delta E = \Gamma(E + \Delta E) - \Gamma(E) \approx \frac{d\Gamma(E)}{dE} \Delta E.$$  \hspace{1cm} (4.19)

If the energy of the particle is $E$ and the dimension of the box is $L$, then the microstates of the particle with energy less than or equal to $E$ are restricted to the rectangle shown in Figure 4.5, where $p_{\text{max}} = \sqrt{2mE}$. Because the possible values of $x$ and $p$ are continuous, there are an infinite number of microstates within the rectangle. As we discussed in Section 3.6, we have to group or bin the microstates so that we can count them, and hence we divide the rectangle in Figure 4.5 into bins or cells of area $\Delta x\Delta p$.

The area of phase space occupied by the trajectory of a particle whose position $x$ is less than or equal to $L$ and whose energy is less than or equal to $E$ is equal to $2p_{\text{max}}L$. Hence, the number of cells or microstates equals

$$\Gamma_{\text{cl}}(E) = \frac{2p_{\text{max}}L}{\Delta x\Delta p} = 2 \frac{L}{\Delta x\Delta p} (2mE)^{1/2},$$  \hspace{1cm} (4.20)

where the values of $\Delta x$ and $\Delta p$ 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

$$\lambda = 2L.$$  \hspace{1cm} (4.21)

In general, the greater the number of antinodes of the wave, the greater the energy associated with the particle. The possible wavelengths that are consistent with the boundary conditions at $x = 0$ and $x = L$ satisfy

$$\lambda_n = \frac{2L}{n}, \hspace{1cm} (n = 1, 2, 3, \ldots)$$  \hspace{1cm} (4.22)

where the index $n$ labels the quantum state of the particle and can be any nonzero, positive integer. From the de Broglie relation,

$$p = \frac{h}{\lambda},$$  \hspace{1cm} (4.23)

and the nonrelativistic relation between the energy $E$ and the momentum $p$, $E = p^2/2m$, we find that the eigenvalues of a particle in a one-dimensional box are given by

$$E_n = \frac{p_n^2}{2m} = \frac{h^2}{2m \lambda_n^2} = \frac{n^2 h^2}{8mL^2}.$$  \hspace{1cm} (4.24)
It is now straightforward to count the number of microstates with energy less than or equal to $E$. The value of $n$ for a given $E$ is (see (4.24))

$$n = \frac{2L}{\hbar} (2mE)^{1/2}. \quad (4.25)$$

Because successive microstates correspond to values of $n$ that differ by unity, the number of states with energy less than or equal to $E$ is given by

$$\Gamma_{\text{qm}}(E) = n = \frac{2L}{\hbar} (2mE)^{1/2}. \quad (4.26)$$

Unlike the classical case, the number of states $\Gamma_{\text{qm}}(E)$ for a quantum particle in a one-dimensional box has no arbitrary parameters such as $\Delta x$ and $\Delta p$. If we require that the classical and quantum enumeration of microstates agree in the semiclassical limit, we see that the number of microstates, $\Gamma_{\text{cl}}(E)$ and $\Gamma_{\text{qm}}(E)$, agrees for all $E$ if we let $2/(\Delta x \Delta p) = 1/(\pi \hbar)$. This requirement implies that the area $\Delta x \Delta p$ of a cell in phase space is given by

$$\Delta x \Delta p = \hbar. \quad (4.27)$$

We see that Planck’s constant $\hbar$ 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 $\hbar$ in phase space. This fundamental limitation implies that the subdivision of phase space into cells of volume less than $\hbar$ is physically meaningless, a result consistent with the Heisenberg uncertainty principle.

It will be convenient to introduce the wave vector $k$ by the relation $k = 2\pi/\lambda$. Then we can rewrite the de Broglie relation (4.23) as

$$p = \hbar k. \quad (4.28)$$

---

\(^3\)Note that the semiclassical limit is not equivalent to simply letting $\hbar \rightarrow 0$. 
For a particle in a one-dimensional box, we can express the condition (4.22) for a standing wave as

\[ k = \frac{\pi}{L} n. \quad (n = 1, 2, 3, \ldots) \]  

(4.29)

**Problem 4.16.** Suppose that the energy of an electron in a one-dimensional box of length \( L \) is \( E = 144 (\hbar^2 / 8mL^2) \). How many microstates are there with energy less than or equal to this value of \( E \)?

### 4.3.4 One-dimensional harmonic oscillator

The one-dimensional harmonic oscillator provides another example for which we can straightforwardly count the number of microstates in both the classical and quantum cases. The total energy of the harmonic oscillator is given by

\[ E = \frac{p^2}{2m} + \frac{1}{2} kx^2, \]  

(4.30)

where \( k \) is the spring constant and \( m \) is the mass of the particle.

**Classical calculation.** The shape of the phase space area traversed by the trajectory \( x(t), p(t) \) can be determined from (4.30) by dividing both sides by \( E \) and substituting \( \omega^2 = k/m \):

\[ \frac{x(t)^2}{2E/m\omega^2} + \frac{p(t)^2}{2mE} = 1. \]  

(4.31)

where the total energy \( E \) is a constant of the motion. From the form of (4.31) we see that the shape of phase space of a one-dimensional harmonic oscillator is an ellipse,

\[ \frac{x^2}{a^2} + \frac{p^2}{b^2} = 1, \]  

(4.32)

with \( a^2 = 2E/(m\omega^2) \) and \( b^2 = 2mE \). Hence, the area of phase space is \( \pi ab = 2\pi E/\omega \), and the number of states with energy less than or equal to \( E \) is given by

\[ \Gamma_{cl}(E) = \frac{\pi ab}{\Delta x \Delta p} = \frac{2\pi E}{\omega \Delta x \Delta p}. \]  

(4.33)

**Quantum mechanical calculation.** The energy eigenvalues of the harmonic oscillator are given by

\[ E_n = (n + \frac{1}{2}) \hbar \omega. \quad (n = 0, 1, 2, \ldots) \]  

(4.34)

Hence the number of microstates is given by

\[ \Gamma_{qm}(E) = n = \frac{E}{\hbar \omega} - \frac{1}{2} \rightarrow \frac{E}{\hbar \omega}. \]  

(4.35)

We see that \( \Gamma_{qm}(E) = \Gamma_{cl}(E) \) for all \( E \), if \( 2\pi/(\Delta x \Delta p) = \hbar \) or \( \Delta x \Delta p = \hbar \) 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 energy of the particle is given by

$$E = \frac{p^2}{2m} = \frac{1}{2m}(p_x^2 + p_y^2). \quad (4.36)$$

Because the wave function takes the form of a standing wave in two dimensions, the wave vector $k$ satisfies the conditions (see (4.29))

$$k_x = \frac{\pi}{L_x} n_x, \quad k_y = \frac{\pi}{L_y} n_y. \quad (n_x, n_y = 1, 2, 3, \ldots) \quad (4.37)$$

The corresponding eigenvalues are given by

$$E_{n_x, n_y} = \frac{\hbar^2}{8m} \left[ \frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} \right]. \quad (4.38)$$

The states of the particle are labeled by the two integers $n_x$ and $n_y$ with $n_x, n_y > 0$. The possible values of $n_x, n_y$ lie at the centers of squares of unit area as shown in Figure 4.7. For
simplicity, we assume that the box is square so that \( L_x = L_y \). The values of \((n_x, n_y)\) for a given \( E \) satisfy the condition

\[
R^2 = n_x^2 + n_y^2 = \left( \frac{2L}{\hbar} \right)^2 (2mE).
\]  

(4.39)

For large values of \( n_x \) and \( n_y \), the values of \( n_x \) and \( n_y \) that correspond to states with energy less than or equal to \( E \) lie inside the positive quadrant of a circle of radius \( R \), where

\[
R = \frac{2L}{\hbar} (2mE)^{1/2}.
\]  

(4.40)

Recall that \( n_x \) and \( n_y \) are both positive. Hence, the number of states with energy less than or equal to \( E \) is given by

\[
\Gamma(E) = \frac{1}{4} \pi R^2 = \pi \frac{L^2}{\hbar^2} (2mE).
\]  

(4.41)

Note that \( V = L^2 \) in this case.

**Problem 4.17.** The expression (4.41) for \( \Gamma(E) \) is valid only for large \( E \) because the area of a quadrant of a circle overestimates the number of lattice points \( n_x, n_y \) inside a circle of radius \( R \). 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:

```plaintext
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

\[
E = \frac{\hbar^2}{8mL^2} [n_x^2 + n_y^2 + n_z^2].
\]  

(4.42)

The values of \( n_x, n_y, \) and \( n_z \) that correspond to microstates with energy less than or equal to \( E \) lie inside the positive octant of a sphere of radius \( R \) given by

\[
R^2 = n_x^2 + n_y^2 + n_z^2 = \left( \frac{2L}{\hbar} \right)^2 (2mE).
\]  

(4.43)
Hence
\[ \Gamma(E) = \frac{1}{8} \left( \frac{4}{3} \pi R^3 \right) = \frac{\pi}{6} \left( \frac{2L}{h} \right)^3 (2mE)^{3/2} = \frac{4\pi}{3} V (2mE)^{3/2}, \quad (4.44) \]
where we have let \( V = L^3 \).

**Problem 4.18.** The expression (4.44) for \( \Gamma(E) \) is valid only for large \( E \) because the area of an octant of a sphere overestimates the number of lattice points \( n_x, n_y, n_z \). Explore how the relation \( \Gamma = \frac{\pi R^3}{6} \) 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 4.19.** Estimate the number of microstates accessible to a gas molecule at typical room temperatures and pressures. We can estimate the mean energy \( E \) of a gas molecule such as nitrogen at room temperature by using the relation \( E = \frac{3NkT}{2} \). 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 \( E \), 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
\[ E_{n_1, n_2} = \frac{\hbar^2}{8mL^2} [n_1^2 + n_2^2], \quad (4.45) \]
where the quantum numbers \( n_1 \) and \( n_2 \) are positive nonzero integers. To count the microstates correctly, we need to take into account that particles of the same species are indistinguishable, one of the fundamental principles of quantum mechanics.

As an example of how we would count the microstates of this two particle system, suppose that the total energy is such that \( n_1^2 + n_2^2 \leq 25 \). The values of \( n_1 \) and \( n_2 \) that satisfy this constraint are given in Table 4.7. However, the indistinguishability of the particles means that we cannot simply assign the quantum numbers \( n_1 \) and \( n_2 \) subject only to the constraint that \( n_1^2 + n_2^2 \leq 25 \). 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
CHAPTER 4. STATISTICAL MECHANICS

Table 4.7: The quantum numbers of two noninteracting identical particles of mass \( m \) in a one-dimensional box of length \( L \) with energies such that \( n_1^2 + n_2^2 \leq 25 \). If the two particles obey Fermi statistics, they cannot be in the same microstate, so \( n_1 = 1 \) and \( n_2 = 1 \) is not allowed for example. There is no such restriction for Bose statistics. Because the particles are identical and hence indistinguishable quantum mechanically, \( n_1 = 1, n_2 = 2 \) is indistinguishable from \( n_1 = 2, n_2 = 1 \). In the semiclassical limit, there are many many states and the possibility of both particles being in the same state is ignored. However, the particles remain indistinguishable. The number of microstates of this two particle system is \( 12/2! = 6 \) in the semiclassical limit.

<table>
<thead>
<tr>
<th>distinguishable particles</th>
<th>Bose statistics</th>
<th>Fermi statistics</th>
<th>semiclassical</th>
</tr>
</thead>
<tbody>
<tr>
<td>( n_1 )</td>
<td>( n_2 )</td>
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<td>3</td>
<td>4</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

of particles of the same species is intrinsic, the particles remain indistinguishable even as we let \( \hbar \to 0 \). 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: Semi-classical limit

We now apply these considerations to count the number of microstates of $N$ noninteracting particles in a three-dimensional box in the semiclassical limit. A simpler way to do so that yields the correct $E$ and $V$ dependence is given in Problem 4.20, but the numerical factors will not be identical to the result of the more accurate calculation that we discuss here.

The idea is to first count the microstates assuming that the $N$ particles are distinguishable and then divide by $N!$ to correct for the overcounting. We know that for one particle in a three-dimensional box, the number of microstates with energy less than or equal to $E$ is given by the volume of the positive part of the three-dimensional sphere of radius $R$ (see (4.40)). For $N$ distinguishable particles in a three-dimensional box, the number of microstates with energy less than or equal to $E$ is given by the volume of the positive part of a $3N$-dimensional hypersphere of radius $R = (2mE)^{1/2}(2L/h)$. To simplify the notation, we consider the calculation of $V_n(R)$, the volume of a $n$-dimensional hypersphere of radius $R$, and write $V_n(R)$ as

$$ V_n(R) = \int_{r_1^2 + r_2^2 + \cdots + r_n^2 < R^2} dr_1 \, dr_2 \cdots dr_n. \quad (4.46) $$

It is shown in Appendix 4A that $V_n(R)$ is given by (for integer $n$)

$$ V_n(R) = \frac{2\pi^{n/2}}{n\Gamma(n/2)} R^n, \quad (4.47) $$

where the Gamma function $\Gamma(n) = (n-1)!$, $\Gamma(n+1) = n\Gamma(n)$ if $n$ is an integer, and $\Gamma(1/2) = \sqrt{\pi}/2$. The cases $n = 2$ and $n = 3$ yield the expected results, $V_2 = 2\pi R^2/(2\Gamma(1)) = \pi R^2$ because $\Gamma(1) = 1$, and $V_3 = 2\pi^{3/2}R^3/(3\Gamma(3/2)) = \frac{4}{3}\pi R^3$ because $\Gamma(3/2) = \Gamma(1/2) = \pi^{1/2}/2$. The volume of the positive part of a $n$-dimensional sphere of radius $R$ is given by

$$ \Gamma_n(R) = \left(\frac{1}{2}\right)^n V_n(R). \quad (4.48) $$

(The volume $\Gamma_n(R)$ should not be confused with the Gamma function $\Gamma(n)$.)

We are interested in the case $n = 3N$ and $R = (2mE)^{1/2}(2L/h)$. In this case the volume $\Gamma(E, V, N)$ is given by

$$ \Gamma(E, V, N) = \left(\frac{1}{2}\right)^{3N} \frac{2\pi^{3N/2}}{3N!(3N/2 - 1)!} R^{3N/2} \quad (4.49a) $$

$$ = \left(\frac{1}{2}\right)^{3N} \frac{\pi^{3N/2}}{(3N/2)!} R^{3N/2} \quad (4.49b) $$

$$ = \left(\frac{1}{2}\right)^{3N} \frac{2L}{h} \frac{\pi^{3N/2}}{(3N/2)!} (2mE)^{3N/2} \quad (4.49c) $$

$$ = \left(\frac{V}{h^3}\right)^N \frac{(2\pi m E)^{3N/2}}{(3N/2)!}. \quad (4.49d) $$
If we include the factor of $1/N!$ to correct for the overcounting of microstates in the semiclassical limit, we obtain the desired result:

$$\Gamma(E, V, N) = \frac{1}{N!} \left( \frac{V}{\hbar^3} \right)^N \frac{(2\pi m E)^{3N/2}}{(3N/2)!}. \quad \text{(semiclassical limit)} \quad (4.50)$$

A more convenient expression for $\Gamma$ can be found by using Stirling’s approximation for $N \gg 1$. We have

$$\ln \Gamma = - \ln N! + N \ln \frac{V}{\hbar^3} + \frac{3}{2} N \ln(2\pi m E) - \ln \left( \frac{3N}{2} \right)!$$

$$= -N \ln N + N \ln V - \frac{3N}{2} \ln \hbar^2 + \frac{3}{2} N \ln(2\pi m E) - \frac{3}{2} N \ln \frac{3N}{2} + \frac{3N}{2} \quad \text{(4.51a)}$$

$$= N \ln \frac{V}{N} + \frac{3}{2} N \ln \frac{4\pi m E}{3N\hbar^2} + \frac{5}{2} N \quad \text{(4.51b)}$$

$$= N \ln \frac{V}{N} + \frac{3}{2} N \ln \frac{mE}{3N\pi\hbar^2} + \frac{5}{2} N \quad \text{(4.51c)}$$

where we have let $\hbar = 2\pi\hbar$ to obtain (4.51d) from (4.51).

**Problem 4.20.** We can obtain an equivalent expression for $\Gamma(E, V, N)$ using simpler physical considerations. We write

$$\Gamma(E, V, N) \approx \frac{1}{N!} \Gamma_1\left(\frac{E}{N}, V\right)\Gamma_1\left(\frac{E}{N}, V\right) \ldots \Gamma_1\left(\frac{E}{N}, V\right), \quad (4.52)$$

where $\Gamma_1(E, V)$ is the number of states of a single particle with energy less than $E$ in a three-dimensional box of volume $V$. We have assumed that on the average each particle has an energy $E/N$. Find the form of $\Gamma(E, V, N)$ using the relation (4.44) for $\Gamma_1$. Compare the $V$ and $E$-dependencies of $\Gamma(E, V, N)$ obtained from this simple argument to (4.50). What about the $N$-dependence?

**Problem 4.21.** Calculate $g(E, V, N)$ and verify that $\Gamma(E, V, N)$ and $g(E, V, N)$ are rapidly increasing functions of $E, V,$ and $N$.

### 4.5 The microcanonical ensemble (fixed $E$, $V$, and $N$)

So far, we have learned how to count the number of microstates of an isolated system. Such a system of particles is specified by the energy $E$, volume $V$, and number of particles $N$. All microstates that are consistent with these conditions are assumed to be equally probable. The collection of systems in different microstates and specified values of $E$, $V$, and $N$ is called the **microcanonical ensemble**. In general, the energy $E$ is a continuous variable, and the energy is specified to be in the range $E$ to $E + \Delta E$.\footnote{For a quantum system, the energy $E$ must always be specified in some range. The reason is that if the energy were specified exactly, the system would have to be in an eigenstate of the system. If it were, the system would remain in this eigenstate indefinitely, and a statistical treatment would be meaningless.}
In the following we show how the quantities that correspond to the usual thermodynamic quantities, for example, the entropy, temperature, and pressure, are related to the number of microstates. We will then use these relations to derive the ideal gas equation of state and other well known results using (4.51d) for the number of microstates of an ideal gas of \( N \) particles in a volume \( V \) with energy \( E \).

We first establish the connection between the number of accessible microstates to various thermodynamic quantities by using arguments that are similar to our treatment of the simple models that we considered in Section 4.2. Consider two isolated systems \( A \) and \( B \) that are separated by an insulating, rigid, and impermeable wall. The macrostate of each system is specified by \( E_A, V_A, N_A \) and \( E_B, V_B, N_B \), respectively, and the corresponding number of microstates is \( \Omega_A(E_A, V_A, N_A) \) and \( \Omega_B(E_B, V_B, N_B) \). Equilibrium in this context means that each accessible microstate is equally represented in our ensemble. The number of microstates of the composite system consisting of the two isolated subsystems \( A \) and \( B \) is

\[
\Omega = \Omega_A(E_A, V_A, N_A) \Omega_B(E_B, V_B, N_B).
\] (4.53)

We want a definition of the entropy that is a measure of the number of microstates and that is additive. It was assumed by Boltzmann that \( S \) is related to \( \Omega \) by the well known formula, first proposed by Planck:

\[
S = k \ln \Omega.
\] (4.54)

Note that if we substitute (4.53) in (4.54), we find that \( S = S_A + S_B \), and \( S \) is an additive function as it must be.

Next we modify the wall between \( A \) and \( B \) so that it becomes conducting, rigid, and impermeable. We say that we have relaxed the internal constraint of the composite system. The two subsystems are now in thermal contact so that the energies \( E_A \) and \( E_B \) can vary, subject to the condition that the total energy \( E = E_A + E_B \) is fixed; the volumes \( V_A \) and \( V_B \) and particle numbers \( N_A \) and \( N_B \) remain unchanged. What happens to the number of accessible microstates after we relax the internal constraint? If subsystem \( A \) has energy \( E_A \), it can be in any one of its \( \Omega(E_A) \) microstates. Similarly, subsystem \( B \) can be in any one of its \( \Omega_B(E - E_A) \) microstates. Because every possible state of \( A \) can be combined with every possible state of \( B \) to give a different state of the composite system, it follows that the number of distinct microstates accessible to the composite system when \( A \) has energy \( E_A \) is the product \( \Omega_A(E_A)\Omega_B(E - E_A) \). Hence, the total number of accessible microstates after the subsystems are in thermal equilibrium is

\[
\Omega(E) = \sum_{E_A} \Omega_A(E_A)\Omega_B(E - E_A).
\] (4.55)

The probability that system \( A \) has energy \( E_A \) is given by

\[
P(E_A) = \frac{\Omega_A(E_A)\Omega_B(E - E_A)}{\Omega(E)}. \tag{4.56}
\]

Note that the logarithm of (4.55) does not yield a sum of two functions. However, the dominant contribution to the right-hand side of (4.55) comes from the term with \( E_A = \tilde{E}_A \), where \( \tilde{E}_A \) is the most probable value of \( E_A \). With this approximation we can write

\[
\Omega \approx \Omega_A(\tilde{E}_A)\Omega_B(E - \tilde{E}_A). \tag{4.57}
\]
CHAPTER 4. STATISTICAL MECHANICS

The approximation (4.57) becomes more and more accurate as the thermodynamic limit \((N, V \to \infty, \rho = N/V = \text{constant})\) is approached and allows us to write

\[
S = k \ln \Omega = S_A + S_B
\]

before and after the constraint is removed. We see immediately that one consequence of the proposed relation between \(S\) and \(\Omega\) is that the entropy increases or remains unchanged after an internal constraint is relaxed.

The relation \(S = k \ln \Omega\) is not mysterious. It is a matter of counting the number of accessible microstates and assuming that they are all equally probable. The connection between the entropy and the probability distribution of the system’s microstates was one of the great achievements of Ludwig Boltzmann, and the equation \(S = k \ln W\) appears on his tombstone.\(^5\)

Given the definition (4.54) of \(S\) as a function of \(E, V,\) and \(N,\) it is natural to adopt the thermodynamic definitions of temperature, pressure, and chemical potential:

\[
\frac{1}{T} = \left(\frac{\partial S}{\partial E}\right)_{V,N} \\
\frac{P}{T} = \left(\frac{\partial S}{\partial V}\right)_{E,N} \\
\frac{\mu}{T} = -\left(\frac{\partial S}{\partial N}\right)_{E,V}
\]

(4.59) (4.60) (4.61)

We have made the connection between statistical mechanics and thermodynamics.

How should we generalize the relation of \(S\) to the number of microstates for a system in which the energy is a continuous variable? Three possibilities are

\[
S = k \ln g(E) \Delta E
\]

(4.62a)

\[
S = k \ln \Gamma
\]

(4.62b)

\[
S = k \ln g(E).
\]

(4.62c)

It is easy to show that in the limit \(N \to \infty,\) the three definitions yield the same result (see Problem 4.23). The reason is that \(\Gamma(E)\) and \(g(E)\) are such rapidly increasing functions of \(E\) that it makes no difference whether we include the microstates with energy less than or equal to \(E\) or just the states between \(E\) and \(E + \Delta E.\)

Example 4.1. Find the pressure and thermal equations of state of an ideal classical gas.

\textit{Solution.} If we use any of the definitions of \(S\) given in (4.62), we find that the entropy of an ideal gas in the semiclassical limit for \(N \to \infty\) is given by

\[
S(E, V, N) = N k \left[ \ln \frac{V}{N} + \frac{3}{2} \ln \frac{mE}{3N \pi \hbar^2} + \frac{5}{2} \right].
\]

(4.63)

---

\(^5\)See <en.wikipedia.org/wiki/Ludwig_Boltzmann> for a summary of Boltzmann’s life and accomplishments and a photograph of his tombstone. Boltzmann never wrote down the relation \(S = k \ln \Omega\) and referred only to \(S\) and the logarithm of the probability of a state being proportional. And the constant \(k\) was introduced by Planck, not by Boltzmann.
Problem 4.22. Compare the form of $S$ given in (4.63) with the form of $S$ determined from thermodynamic considerations in Section 2.19.

Problem 4.23. Equivalent definitions of the entropy
Verify the result (4.63) for the entropy $S$ of an ideal gas using any of the definitions of $S$ given in (4.62).

We now use the result (4.63) for $S$ to obtain the thermal equation of state of an ideal classical gas. From (4.63) we see that
\[
\frac{1}{T} = \left( \frac{\partial S}{\partial E} \right)_{V,N} = \frac{3}{2} \frac{Nk}{E},
\]
and hence we obtain the familiar result
\[
E = \frac{3}{2} NkT.
\]

The pressure equation of state follows from (4.60) and (4.63) and is given by
\[
\frac{P}{T} = \left( \frac{\partial S}{\partial V} \right)_{E,N} = \frac{Nk}{V},
\]
and hence
\[
P V = NkT.
\]

We have finally derived the equations of state of an ideal classical gas from first principles! We see that we can calculate the thermodynamic information for an isolated system by counting all the accessible microstates as a function of the total energy $E$, volume $V$, and number of particles $N$. Do the equations of state depend on $\hbar$ and the various constants in (4.50)?

Note that we originally defined the ideal gas temperature scale in Section 2.4 by assuming that $T \propto P$. We then showed that the ideal gas temperature scale is consistent with the thermodynamic temperature defined by the relation $1/T = (\partial S/\partial E)_{V,N}$. Finally, we have shown that the association of $S$ with the logarithm of the number of accessible microstates is consistent with the relation $P \propto T$ for an ideal classical gas.

Problem 4.24. Use the relations (4.63) and (4.65) to obtain $S$ as a function of $T$, $V$, and $N$ instead of $E$, $V$, and $N$. This relation is known as the Sackur-Tetrode equation.

Problem 4.25. Use (4.61) and (4.63) to derive the dependence of the chemical potential $\mu$ on $E$, $V$, and $N$ for a ideal classical gas. Then use (4.65) to determine $\mu(T,V,N)$. We will derive $\mu(T,V,N)$ for the ideal classical gas more simply in Section 6.8.

Example 4.2. Consider a system of $N$ noninteracting spins and find the dependence of its temperature $T$ on the total energy $E$. What is the probability that a given spin is up?

Solution. First we have to find the dependence of the entropy $S$ on the energy $E$ of the system. As discussed in Sec. 4.3.1, the energy $E$ for a system with $n$ spins up out of $N$ in a magnetic field $B$ is given by
\[
E = -(n-n')\mu B = -(n-(N-n))\mu B = -(2n-N)\mu B,
\]
(4.15)
where \( n' = N - n \) is the number of down spins and \( \mu \) is the magnetic moment of the spins. The corresponding number of microstates is given by (4.17):

\[
\Omega(n) = \frac{N!}{n!(N-n)!}.
\]  (4.17)

From (4.15), we find that the value of \( n \) corresponding to a given \( E \) is given by

\[
n = \frac{1}{2} \left( N - \frac{E}{\mu B} \right).
\]  (4.67)

The thermodynamic temperature \( T \) is given by

\[
\frac{1}{T} = \left( \frac{\partial S}{\partial E} \right)_{B,N} = \frac{dS(n)}{dn} \frac{dn}{dE} = -\frac{1}{2\mu B} \frac{dS}{dn}.
\]  (4.68)

To calculate \( dS/dn \), we use the approximation (3.97) for large \( n \):

\[
\frac{d}{dn} \ln n! = \ln n,
\]  (4.69)

and find

\[
\frac{dS(n)}{dn} = k[-\ln n + \ln(N - n)],
\]  (4.70)

where \( S(n) = k \ln \Omega(n) \) from (4.17). Hence

\[
\frac{1}{T} = -k \frac{1}{2\mu B} \ln \frac{N-n}{n}.
\]  (4.71)

Equation (4.71) yields \( T \) as a function of \( E \) by eliminating \( n \) using (4.67).

The natural variables in the microcanonical ensemble are \( E, V, \) and \( N \). Hence, \( T \) is a derived quantity and is found as a function of \( E \). As shown in Problem 4.26, we can rewrite this relation to express \( E \) as a function of \( T \). The result is

\[
E = -N\mu B \tanh \frac{\mu B}{kT} = -N\mu B \tanh \beta \mu B,
\]  (4.72)

where \( \beta = 1/kT \).

The probability \( p \) that a given spin is up is equal to the ratio \( n/N \). We can solve (4.71) for \( n/N \) and obtain (see Problem 4.26)

\[
p = \frac{n}{N} = \frac{1}{1 + e^{-2\mu B/kT}},
\]  (4.73a)

\[
= \frac{e^{\mu B/kT}}{e^{\mu B/kT} + e^{-\mu B/kT}} = \frac{e^{\beta \mu B}}{e^{\beta \mu B} + e^{-\beta \mu B}},
\]  (4.73b)

We have obtained the result for \( p \) that we promised in Section 3.5.
Table 4.8: Summary of the three common ensembles. Note that $\Omega$ is the number of accessible microstates in the microcanonical ensemble and the thermodynamic potential in the grand canonical ensemble.

<table>
<thead>
<tr>
<th>ensemble</th>
<th>macrostate</th>
<th>probability distribution</th>
<th>thermodynamics</th>
</tr>
</thead>
<tbody>
<tr>
<td>microcanonical</td>
<td>$E, V, N$</td>
<td>$P_n = 1/\Omega$</td>
<td>$S(E, V, N) = k \ln \Omega$</td>
</tr>
<tr>
<td>canonical</td>
<td>$T, V, N$</td>
<td>$P_n = e^{-\beta E_n}/Z$</td>
<td>$F(T, V, N) = -kT \ln Z$</td>
</tr>
<tr>
<td>grand canonical</td>
<td>$T, V, \mu$</td>
<td>$P_n = e^{-\beta(E_n - \mu N_n)}/Z$</td>
<td>$\Omega(T, V, \mu) = -kT \ln Z$</td>
</tr>
</tbody>
</table>

Note we have had to consider all $N$ spins even though the spins do not interact with each another. The reason is that the $N$ spins have a definite energy and hence we cannot assign the orientation of the spins independently. We will obtain the result (4.73) by a more straightforward method in Section 4.6.

**Problem 4.26.** Solve (4.71) for $n/N$ and verify (4.73). Then use (4.15) to solve for $E$ as a function of $T$ for a system of $N$ noninteracting spins.

Although the microcanonical ensemble is conceptually simple, it is not the most practical ensemble. The major problem is that because we must satisfy the constraint that $E$ is specified, we cannot assign energies to each particle individually, even if the particles do not interact. Another problem is that because each microstate is as important as any other, there are no obvious approximation methods that retain only the most important microstates. Moreover, isolated systems are very difficult to realize experimentally, and the temperature rather than the energy is a more natural independent variable.

Before we discuss the other common ensembles, we summarize their general features in Table 4.8. The internal energy $E$ is fixed in the microcanonical ensemble and hence only the mean temperature is specified and the temperature fluctuates. In the canonical ensemble the temperature $T$ and hence the mean energy is fixed, but the energy fluctuates. Similarly, the chemical potential and hence the mean number of particles is fixed in the grand canonical ensemble, and the number of particles fluctuates. In all of these ensembles, the volume $V$ is fixed which implies that the pressure fluctuates. We also can choose an ensemble in which the pressure is fixed and the volume fluctuates.

*Problem 4.27.** Consider a collection of $N$ distinguishable, harmonic oscillators with total energy $E$. The oscillators are distinguishable because they are localized on different lattice sites. In one dimension the energy of each particle is given by $\epsilon_n = (n + \frac{1}{2})\hbar\omega$, where $\omega$ is the angular frequency. Hence, the total energy can be written as $E = (Q + \frac{1}{2}N)\hbar\omega$, where $Q$ is the number of quanta. Calculate the dependence of the temperature $T$ on the total energy $E$ in the microcanonical ensemble using the result that the number of accessible microstates in which $N$ distinguishable oscillators can share $Q$ indistinguishable quanta is given by $\Omega = (Q + N - 1)!/Q!(N - 1)!$ (see (4.3)). Use this relation to find $E(T)$. The thermodynamics of this system is calculated much more simply in the canonical ensemble as shown in Example 4.56.
4.6 Systems in contact with a heat bath: The canonical ensemble (fixed $T$, $V$, and $N$)

We now assume that the system of interest can exchange energy with a much larger system known as a heat bath. The heat bath is sufficiently large that it is not significantly affected by the smaller system. For example, if we place a glass of cold water into a room, the temperature of the water will eventually reach the temperature of the air in the room. Because the volume of the glass is small compared to the volume of the room, the cold water does not cool the air appreciably and the air is an example of a heat bath.

The composite system, the system of interest plus the heat bath, is an isolated system. We can characterize the macrostate of the composite system by $E$, $V$, $N$. The accessible microstates of the composite system are equally probable. If the system of interest is in a microstate with energy $E_n$, then the energy of the heat bath is $E_b = E - E_n$. Because the system of interest is much smaller than the heat bath, we know that $E_n \ll E$.

For a given microstate of the system, the heat bath can be in any one of a large number of microstates such that the total energy of the composite system is $E$. The probability $P_n$ that the system is in microstate $n$ with energy $E_n$ is given by (see (4.53))

$$P_n = \frac{1 \times \Omega_b(E - E_n)}{\sum_n \Omega_b(E - E_n)}, \quad (4.74)$$

where $\Omega_b(E - E_n)$ is the number of microstates of the heat bath for a given microstate $n$ of the system of interest. As $E_n$ increases, $\Omega_b(E - E_n)$, the number of accessible microstates available to the heat bath, decreases. We conclude that $P_n$ is a decreasing function of $E_n$, because the larger the value of $E_n$, the less energy is available to the heat bath.

We can simplify the form of $P_n$ by using the fact that $E_n \ll E$. As we have seen before, we cannot approximate $\Omega_b(E - E_n)$ directly because $\Omega_b$ is a rapidly varying function of its argument. For this reason we take the logarithm of (4.74) and write

$$\ln P_n = C + \ln \Omega_b(E_b = E - E_n), \quad (4.75)$$

where $C$ is related to the denominator of (4.74) and does not depend on $E_n$. We now expand $\ln \Omega_b(E - E_n)$ and write

$$\ln P_n \approx C + \ln \Omega_b(E) - E_n \left( \frac{\partial \ln \Omega_b(E_b)}{\partial E_b} \right)_{E_b = E} \quad (4.76a)$$

$$= C + \ln \Omega_b(E) - \frac{E_n}{kT}. \quad (4.76b)$$

We have used the relation

$$\beta \equiv \frac{1}{kT} = \left( \frac{\partial \ln \Omega_b(E_b)}{\partial E_b} \right)_{N,V}, \quad (4.77)$$

Note that it is not clear how we should assign the potential energy of interaction of particles at the interface of the system and the heat bath. If the number of particles in the system of interest is large, the number of particles near the interface between the two systems is small in comparison to the number of particles in the bulk so that the potential energy of interaction of particles near the surface can be ignored. Nevertheless, these interactions are essential in order for the system to come into thermal equilibrium with the heat bath.
where \( T \) is the temperature of the heat bath. As can be seen from (4.77), \( \beta \) is proportional to the inverse temperature of the heat bath. From (4.76b) we obtain

\[
P_n = \frac{1}{Z} e^{-\beta E_n} \tag{Boltzmann distribution} \quad (4.78)
\]

The function \( Z \) is found from the normalization condition \( \sum_n P_n = 1 \) and is given by

\[
Z = \sum_n e^{-\beta E_n} \tag{partition function} \quad (4.79)
\]

The “sum over states” \( Z(T, V, N) \) is known as the \textit{partition function}. (In German \( Z \) is known as the \textit{Zustandsumme}, a more descriptive term.) Note that \( P_n \) applies to a system in equilibrium with a heat bath at temperature \( T \). The nature of the system has changed from Section 4.5.

**Problem 4.28.** Discuss the relation between the qualitative results that we obtained in Table 4.6 and the Boltzmann distribution in (4.78).

**Problem 4.29.** The hydrocarbon 2-butene, \( \text{CH}_3-\text{CH} = \text{CH}-\text{CH}_3 \) occurs in two conformations (geometrical structures) called cis- and trans. The cis (on this side) conformation of 2-butene has both \( \text{CH}_3 \) groups on the same side of the \( C = C \) double bond. In the trans (across) conformation the \( \text{CH}_3 \) groups are on opposite sides of the double bond (see Figure 4.8). The energy difference \( \Delta E \) between the two conformations is approximately \( \Delta E/k = 4180 \text{ K} \), with the trans conformation lower than the cis conformation. Determine the relative abundance of the two conformations at \( T = 300 \text{ K} \) and \( T = 1000 \text{ K} \).

In the canonical ensemble the temperature \( T \) is fixed by the heat bath, and a macrostate is specified by the temperature \( T \), volume \( V \), and the number of particles \( N \). The mean energy of the system is given by

\[
\bar{E} = \sum_n P_n E_n = \frac{1}{Z} \sum_n E_n e^{-\beta E_n}, \tag{4.80}
\]

where we have substituted the Boltzmann form (4.78) for the probability distribution. We use a trick similar to that used in Section 3.5 to obtain a simpler form for \( \bar{E} \). First we write

\[
\bar{E} = -\frac{1}{Z} \frac{\partial}{\partial \beta} \sum_n e^{-\beta E_n}, \tag{4.81}
\]
where we have used the fact that \( \frac{\partial}{\partial \beta} (e^{-\beta E_n}) = -E_n e^{-\beta E_n} \). Because

\[
\frac{\partial Z}{\partial \beta} = -\sum_n E_n e^{-\beta E_n}
\]

we can write

\[
\mathcal{E} = -\frac{1}{Z} \frac{\partial Z}{\partial \beta} = -\frac{\partial}{\partial \beta} \ln Z
\]

(4.83)

We see that \( \mathcal{E} \) 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

\[
C_V = \frac{\partial E}{\partial T} = \frac{\partial \beta}{\partial T} \frac{\partial E}{\partial \beta} = \frac{1}{kT^2} \left[ \frac{1}{Z} \frac{\partial^2 Z}{\partial \beta^2} - \frac{1}{Z^2} \left( \frac{\partial Z}{\partial \beta} \right)^2 \right]
\]

(4.85)

where \( \frac{\partial E}{\partial \beta} \) has been calculated from (4.83). Because

\[
\mathcal{E}^2 = \frac{1}{Z} \sum_n E_n^2 e^{-\beta E_n} = \frac{1}{Z} \frac{\partial^2 Z}{\partial \beta^2}
\]

(4.86)

we obtain the relation

\[
C_V = \frac{1}{kT^2} [ \mathcal{E}^2 - \mathcal{E}^2 ]
\]

(4.87)

Equation (4.87) relates the response of the system to a change in energy to the equilibrium energy fluctuations. Note that we can calculate the variance of the energy, a measure of the magnitude of the energy fluctuations, from the heat capacity. We will later find other examples of the relation of the linear response of an equilibrium system to the equilibrium fluctuations of an associated quantity.\(^7\)

\*Problem 4.30. The isothermal compressibility of a system is defined as \( \kappa = -(1/V) \left( \frac{\partial V}{\partial P} \right)_T \). Explain why \( \kappa \) is a linear response. In analogy to the relation of \( C_V \) to fluctuations in the energy, what type of fluctuations do you think are related to \( \kappa \) (at fixed \( T \), \( P \), and \( N \))?

Because the energy is restricted to a very narrow range in the microcanonical ensemble and can range anywhere between zero and infinity in the canonical ensemble, it is not obvious that the two ensembles give the same results for the thermodynamic properties of a system. One way to understand why the thermodynamic properties are independent of the choice of ensemble is to use the relation (4.87) to estimate the range of energies in the canonical ensemble that have a significant probability. Because both \( E \) and \( C_V \) are extensive quantities, they are proportional to \( N \). Hence, the relative fluctuations of the energy in the canonical ensemble is given by

\[
\frac{\sqrt{E^2 - \mathcal{E}^2}}{E} = \frac{\sqrt{kT^2 C_V}}{E} \sim \frac{N^{1/2}}{N} \sim N^{-1/2}.
\]

(4.88)

\(^7\)The relation (4.87) is important conceptually and is useful for simulations at a given temperature (see Section 4.11). However, it is almost always more convenient to calculate \( C_V \) from its definition in (4.84).
From (4.88) we see that in the limit of large \( N \), the relative fluctuations in the values of \( E \) that would be observed in the canonical ensemble are vanishingly small. For this reason the mean energy in the canonical ensemble is a well defined quantity just like it is in the microcanonical ensemble. However, the fluctuations in the energy are qualitatively different in the two ensembles (see Appendix 4B).

**Problem 4.31.** The Boltzmann probability given by (4.78) is the probability that the system is in a particular microstate with energy \( E_n \). On the basis of what you have learned so far, what do you think is the form of the probability \( p(E) \Delta E \) that the system has energy between \( E \) and \( E + \Delta E \)?

In addition to the relation of the mean energy to \( \partial \ln Z/\partial \beta \), we can express the mean pressure \( \overline{P} \) in terms of \( \partial \ln Z/\partial V \). If the system is in microstate \( n \), then a quasistatic change \( dV \) in the volume produces the energy change

\[
dE_n = \frac{dE_n}{dV} dV = -\pi_n dV. \tag{4.89}
\]

The quantity \( dE_n \) in (4.89) is the work done on the system in state \( n \) to produce the volume change \( dV \). The relation (4.89) defines the pressure \( \pi_n \) of the system in state \( n \). Hence, the mean pressure of the system is given by

\[
\overline{P} = -\sum_n \pi_n dE_n. \tag{4.90}
\]

From (4.78), (4.79), and (4.90) we can express the mean pressure as

\[
\overline{P} = kT \left( \frac{\partial \ln Z}{\partial V} \right)_{T,N}. \tag{4.91}
\]

Note that in defining the pressure, we assumed that a small change in the volume does not change the probability distribution 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 \( \overline{E} = \sum_n P_n E_n \) to write the total change in the energy as

\[
d\overline{E} = \sum_n E_n dP_n + \sum_n P_n dE_n. \tag{4.92}
\]

The second term in (4.92) can be written as

\[
\sum_n P_n dE_n = \sum_n P_n \frac{dE_n}{dV} dV. \tag{4.93}
\]

---

\[8\] We have written the pressure in microstate \( n \) as \( \pi_n \) rather than \( P_n \) or \( p_n \) to avoid confusion with the Boltzmann probability.
The identification of the second term in (4.92) with the work done on the system allows us to rewrite (4.92) as
\[ dE = \sum_n E_n dP_n - \mathcal{P} dV. \]  
(4.94)
If we use the fundamental thermodynamic relation (2.123), \( dE = TdS - P dV \) (for fixed \( N \)), we can identify the first term in (4.94) with the change in entropy of the system. Hence, we have
\[ TdS = \sum_n E_n dP_n. \]  
(4.95)
From (4.95) we see that a change in entropy of the system is related to a change in the probability distribution.

We can use (4.95) to obtain an important conceptual expression for the entropy. We rewrite \( P_n = e^{-\beta E_n}/Z \) as \( E_n = -kT(\ln Z + \ln P_n) \), and substitute this relation for \( E_n \) into (4.95):
\[ TdS = \sum_n E_n dP_n = -kT \sum_n \ln Z dP_n - kT \sum_n \ln P_n dP_n. \]  
(4.96)
The first term in (4.96) is zero because the total change in the probability must sum to zero. From (4.96) we write

\[ dS = -k \sum_n \ln P_n dP_n, \]  
(4.97a)
\[ = -k \sum_n d(P_n \ln P_n). \]  
(4.97b)
We integrate both sides of (4.97b) to obtain the desired result:
\[ S = -k \sum_n P_n \ln P_n. \]  
(4.98)
We have assumed that the constant of integration is zero (see the following). The quantity defined by (4.11) and (4.98) is known as the \textit{statistical entropy} in contrast to the thermodynamic entropy introduced in Chapter 2. Note the similarity of (4.98) to the uncertainty function defined in (3.37).

The relation (4.98) for \( S \) is also applicable to the microcanonical ensemble. If there are \( \Omega \) accessible microstates, then \( P_n = 1/\Omega \) for each state because each state is equally likely. Hence,
\[ S = -k \sum_{n=1}^\Omega \frac{1}{\Omega} \ln \frac{1}{\Omega} = -k \Omega \frac{1}{\Omega} \ln \frac{1}{\Omega} = k \ln \Omega. \]  
(4.99)
The constant of integration in going from (4.97b) to (4.98) must be set to zero so that \( S \) reduces to its form in the microcanonical ensemble. We see that we can interpret (4.98) as the generalization of its microcanonical form with the appropriate weight for each state.

It is remarkable that the statistical entropy defined by (4.11) and (4.98) is equivalent to its thermodynamic definition which can be expressed as
\[ dS = \int \frac{dQ}{T}. \]  
(4.100)
The relation (4.98) is of fundamental importance and shows that the entropy is uniquely determined by the probability distribution \( P_n \) of the different microstates. Note that complete predictability (only one accessible microstate) implies the vanishing of the entropy. Also as the number of accessible microstates increases, the greater the value of \( S \) and hence the higher the degree of unpredictability of the system.

The idea of entropy has come a long way. It was first introduced into thermodynamics as a state function to account for the irreversible behavior of macroscopic systems under certain conditions. The discovery of the connection between this quantity and the probability distribution of the system’s microstates was one of the great achievements of Ludwig Boltzmann. Since then, our understanding of entropy has been extended by Shannon and Jaynes and others to establish a link between thermodynamics and information theory (see Section 3.4.1). In this context we can say that \( S \) is a measure of the lack of information, because the greater the number of microstates that are available to a system in a given macrostate, the less we know about which microstate the system is in.

Although the relation (4.11) is of fundamental importance, we will not use it to calculate the entropy in any of the applications that we consider. The calculation of the entropy will be discussed in Section 4.7.

The third law of thermodynamics. 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 from the statistical definition of the entropy. At \( T = 0 \), the system is in the ground state which we will label by 0. From (4.98) we see that if \( P_n = 1 \) for state 0 and is zero for all other microstates, then \( S = 0 \). We conclude that \( S \to 0 \) as \( T \to 0 \) if the system has an unique ground state. This behavior is the type that we 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 \( 1/2 \), it has two quantum states for each value of its momentum. Hence, an electron in zero magnetic field has degeneracy\(^9\) \( g_n = 2 \), because its energy is independent of its spin orientation, and the ground state entropy of a system of electrons would be \( kN \ln 2 \). There are some complex systems for which \( g(0) \propto N \). In either case, we conclude that the heat capacities must go to zero as \( T \to 0 \) (see Problem 4.49).\(^10\)

Problem 4.32. Explain why the entropy associated with the ground state of a system of \( N \) electrons is \( kN \ln 2 \).

---

\(^9\)An energy level is said to be degenerate if there are two or more microstates with the same energy.

\(^10\)The simplest example of a system with a nontrivial number of ground states is the Ising antiferromagnet on the triangular lattice. We will discuss this system in Problem 5.15. In this case the system has a nonzero entropy at zero temperature.
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 (4.83) and (4.91)). We also learned in Section 2.21 that the Helmholtz free energy \(F = E - TS\) is the thermodynamic potential for the variables \(T, V,\) and \(N\). Because this set of variables corresponds to the variables specified by the canonical ensemble, it is natural to look for a connection between \(\ln Z\) and \(F\), and we define the latter as

\[
F = -kT \ln Z \quad \text{(statistical mechanics definition of the free energy)} \quad (4.101)
\]

At this stage the quantity defined in (4.101) has no obvious relation to the thermodynamic potential \(F = E - TS\) that we defined in (2.142).

We now show that \(F\) as defined by (4.101) is equivalent to the thermodynamic definition \(F = E - TS\). This equivalence and the relation (4.101) gives the fundamental relation between statistical mechanics and thermodynamics for given values of \(T, V,\) and \(N\), just as \(S = k \ln \Omega\) gives the fundamental relation between statistical mechanics and thermodynamics for given values of \(E, V,\) and \(N\) (see Table 4.8).

We write the total change in the quantity \(\beta F = -\ln Z\) as

\[
d(\beta F) = -\frac{1}{Z} \frac{\partial Z}{\partial \beta} d\beta - \frac{1}{Z} \frac{\partial Z}{\partial V} dV
= E d\beta - \beta P dV, \quad (4.102)
\]

where we have used (4.83) and (4.90). We add and subtract \(\beta dE\) to the right-hand side of (4.102) to find

\[
d(\beta F) = E d\beta + \beta dE - \beta dE - \beta P dV
= d(\beta E) - \beta (dE + P dV). \quad (4.103)
\]

Hence, we can write

\[
d(\beta F - \beta E) = -\beta (dE + P dV). \quad (4.104)
\]

From the thermodynamic relation \(dE = TdS - PdV\) (for fixed \(N\)), we can rewrite (4.104) as

\[
d(\beta F - \beta E) = -\beta (dE + P dV) = -\beta TdS = -dS/k. \quad (4.105)
\]

If we integrate (4.105), we find

\[
S/k = \beta(\overline{E} - F) + \text{constant}, \quad (4.106)
\]

or

\[
F = \overline{E} - TS + \text{constant}. \quad (4.107)
\]

If we make the additional assumption that the free energy should equal the internal energy of the system at \(T = 0\), we can set the constant in (4.107) equal to zero, and we obtain

\[
F = \overline{E} - TS. \quad (4.108)
\]
Equation (4.108) is equivalent to the thermodynamic definition of the Helmholtz free energy with $E$ replaced by $E$. In the following, we will write $E$ instead of $E$ 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

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

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

$$\mu = \left(\frac{\partial F}{\partial N}\right)_{T,V}.$$ (4.111)

These relations still hold with $F = -kT\ln Z$.

We have found that if we start with the statistical mechanical relation $F = -kT\ln Z$ (see (4.101)), we obtain the thermodynamic relation $F = E - TS$ (see (4.108)). It is instructive to start with the latter and show that it implies that $F = -kT\ln Z$. We substitute $E = -\partial \ln Z / \partial \beta$ and the relation $S = k\beta^2 (\partial F / \partial \beta)$ (see (4.109)) and find

$$F = E - TS = -\frac{\partial \ln Z}{\partial \beta} - \beta \left(\frac{\partial F}{\partial \beta}\right)_{V,N}.$$ (4.112)

We rewrite (4.112) as

$$F + \beta \left(\frac{\partial F}{\partial \beta}\right)_{V,N} = -\frac{\partial \ln Z}{\partial \beta} = \left(\frac{\partial F}{\partial \beta}\right)_{V,N}.$$ (4.113)

If we integrate both sides of (4.113), we find (up to a constant) that

$$F = -kT\ln Z.$$ (4.114)

### 4.8 Simple applications of the canonical ensemble

To gain experience with the canonical ensemble, we consider some relatively simple examples. In all of these examples, the goal is to calculate the partition function. Then we calculate the free energy using (4.101), the entropy from (4.109), and the mean energy from (4.83). (In these simple examples, the volume of the system will not be relevant, so we will not calculate the pressure.) In principle, we can follow this “recipe” for any physical system. We will later find that summing over the microstates to evaluate the partition function is usually a formidable task and can be done exactly in only a few cases.

**Example 4.3.** Consider a system consisting of two distinguishable particles. Each particle has two states with single particle energies 0 and $\Delta$. The quantity $\Delta$ 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?
CHAPTER 4. STATISTICAL MECHANICS

Solution. The states of this two-particle system are \((0, 0), (0, \Delta), (\Delta, 0),\) and \((\Delta, \Delta)\). The partition function \(Z_2\) is given by

\[
Z_2 = \sum_{n=1}^{4} e^{-\beta E_n} = 1 + 2e^{-\beta \Delta} + e^{-2\beta \Delta} \tag{4.115a}
\]

\[
= (1 + e^{-\beta \Delta})^2. \tag{4.115b}
\]

We see that we can express \(Z_2\) in terms of \(Z_1\), the partition function for one particle:

\[
Z_1 = \sum_{n=1}^{2} e^{-\beta \epsilon_n} = 1 + e^{-\beta \Delta}. \tag{4.116}
\]

By comparing the forms of (4.115c) and (4.116), we find that

\[
Z_2 = Z_1^2. \tag{4.117}
\]

What do you expect the relation is between \(Z_N\), the partition function for \(N\) noninteracting distinguishable particles, and \(Z_1\)?

Note that if the two particles were indistinguishable, there would be three microstates if the particles were bosons and one microstate if the particles are fermions, and the relation (4.117) would not hold.

Because \(Z_2\) is simply related to \(Z_1\), we can consider the statistical properties of a system consisting of one particle with \(Z_1\) given by (4.116). From (4.78) we find the probability that the system is in each of its two possible states is given by:

\[
p_1 = \frac{1}{Z_1} = \frac{1}{1 + e^{-\beta \Delta}} \tag{4.118a}
\]

\[
p_2 = \frac{e^{-\beta \Delta}}{Z_1} = \frac{e^{-\beta \Delta}}{1 + e^{-\beta \Delta}}. \tag{4.118b}
\]

The average energy is given by

\[
\bar{\epsilon} = \sum_{n=1}^{2} P_n \epsilon_n = \frac{\Delta e^{-\beta \Delta}}{1 + e^{-\beta \Delta}}. \tag{4.119}
\]

We will use a lower case symbol to denote the results for one particle.

Of course, \(\bar{\epsilon}\) could also be found from the relation \(\bar{\epsilon} = -\partial \ln Z_1 / \partial \beta\). For our example, we have

\[
Z_1 = 1 + e^{-\beta \Delta} \tag{4.120}
\]

and

\[
\frac{\partial Z}{\partial \beta} = -\Delta e^{-\beta \Delta}. \tag{4.121}
\]

Hence

\[
\bar{\epsilon} = -\frac{\partial}{\partial \beta} \ln Z_1 = -\frac{1}{Z} \frac{\partial Z}{\partial \beta} = \frac{\Delta e^{-\beta \Delta}}{1 + e^{-\beta \Delta}}. \tag{4.122}
\]
in agreement with (4.119). The energy of \( N \) noninteracting, distinguishable particles of the same type is given by \( E = N \bar{e} \).

It is easy to calculate the various thermodynamic quantities directly from the partition function in (4.115c). The free energy per particle, \( f \), is given by

\[
f = -kT \ln Z_1 = -kT \ln[1 + e^{-\beta \Delta}],
\]

and \( s \), the entropy per particle, is given by

\[
s = -\left( \frac{\partial f}{\partial T} \right)_V = k \ln[1 + e^{-\beta \Delta}] + k \frac{\beta \Delta}{1 + e^{\beta \Delta}},
\]

(4.123)

If we had not already calculated the average energy \( \bar{e} \), we could also obtain it from the relation

\[
e = f - Ts.
\]

Confirm that the various ways of determining \( e \) yield the same results as found in (4.119). The behavior of the various thermodynamic properties of this system are explored in Problem 4.53.

**Example 4.4.** Determine the thermodynamic properties of a one-dimensional harmonic oscillator in equilibrium with a heat bath at temperature \( T \).

**Solution.** The energy levels of a single harmonic oscillator are given by

\[
\epsilon_n = (n + \frac{1}{2})\hbar \omega. \quad (n = 0, 1, 2, \ldots)
\]

(4.125)

The corresponding partition function is

\[
Z = \sum_{n=0}^{\infty} e^{-\beta \hbar \omega (n+1/2)} = e^{-\beta \hbar \omega/2} \sum_{n=0}^{\infty} e^{-n\beta \hbar \omega}
\]

(4.126a)

\[
= e^{-\beta \hbar \omega/2} (1 + e^{-\beta \hbar \omega} + e^{-2\beta \hbar \omega} + \cdots) = e^{-\beta \hbar \omega/2} (1 + x + x^2 + \cdots),
\]

(4.126b)

where \( x = e^{-\beta \hbar \omega} \). The infinite sum in (4.126b) is a geometrical series in \( x \) and can be summed using the result that \( 1 + x + x^2 + \cdots = 1/(1-x) \) (see Appendix A). The result is

\[
Z = \frac{e^{-\beta \hbar \omega/2}}{1 - e^{-\beta \hbar \omega}},
\]

(4.127)

and

\[
\ln Z = -\frac{1}{2} \beta \hbar \omega - \ln(1 - e^{-\beta \hbar \omega}).
\]

(4.128)

**Problem 4.33.** Thermodynamics of a system of harmonic oscillators in the canonical ensemble

(a) Show that

\[
f = \frac{1}{2} \hbar \omega + kT \ln(1 - e^{-\beta \hbar \omega})
\]

(4.129)

\[
s = k \left[ \frac{\beta \hbar \omega}{e^{\beta \hbar \omega} - 1} - \ln(1 - e^{-\beta \hbar \omega}) \right]
\]

(4.130)

\[
e = \hbar \omega \left[ \frac{1}{2} + \frac{1}{e^{\beta \hbar \omega} - 1} \right].
\]

(4.131)
CHAPTER 4. STATISTICAL MECHANICS

185

Equation (4.131) is Planck’s formula for the mean energy of an oscillator at temperature $T$. The heat capacity is discussed in Problem 4.56.

(b) Given the result (4.131) what is the mean energy of a system of $N$ harmonic oscillators in equilibrium with a heat bath at temperature $T$?

(c) Compare your answer with the result for the energy of $N$ harmonic oscillators calculated in the microcanonical ensemble in Problem 4.27. Do the two ensembles give identical results?

Equation (4.79) for $Z$ is a sum over all the microstates of the system. Because the energies of the different microstates may be the same, we can group together microstates with the same energy and write (4.79) as

$$Z = \sum_{\text{levels}} g(E_n) e^{-\beta E_n},$$  \hspace{1cm} (4.132)

where $g(E_n)$ is the number of microstates of the system with energy $E_n$. The sum in (4.132) is over all the energy levels of the system.

**Example 4.5.** Consider a three level single particle system with five microstates with energies $0, \epsilon, \epsilon, \epsilon, \text{ and } 2\epsilon$. 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 (4.132))

$$Z_1 = 1 + 3e^{-\beta \epsilon} + e^{-2\beta \epsilon}.$$  \hspace{1cm} (4.133)

Hence, the mean energy of a single particle is given by

$$\bar{\epsilon} = \frac{\epsilon \cdot 3e^{-\beta \epsilon} + 2e^{-2\beta \epsilon}}{1 + 3e^{-\beta \epsilon} + e^{-2\beta \epsilon}}.$$  \hspace{1cm} (4.134)

What is the energy of $N$ such particles?

**Problem 4.34.** In Section 4.3.2 we were given the number of states with energy $E$ for the one-dimensional Ising model. Use the result (4.18) to calculate the free energy of the one-dimensional Ising model for $N = 2$ and 4.

4.9 **Example of a simple thermometer**

Consider a system of one particle which we will call a _demon_ that can exchange energy with another system (see page 16). 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, $\Delta E$. 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 $\Delta E$. If a trial change is not accepted, the existing microstate is counted in the averages. In either case the total energy of the system plus the demon remains constant.

3. Repeat step 2 many times choosing particles (or spins) at random.

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

The demon can trade energy with the system as long as its energy remains greater than its lower bound, which we have chosen to be zero. The demon is a facilitator that allows the particles in the system to indirectly trade energy with one another.

In Problems 4.35 and 4.37 we use the demon algorithm to determine the probability that the demon is in a particular microstate.

**Problem 4.35.** The demon and the ideal gas

Consider a demon that exchanges energy with an ideal classical gas of $N$ identical particles of mass $m$ in one dimension. Because the energy of a particle depends only on its speed, the positions of the particles are irrelevant in this case. The demon chooses a particle at random and change its velocity by an amount, $\delta$, chosen at random between $-\Delta$ and $\Delta$. 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 $\Delta$ is chosen so that the percentage of accepted changes is between 30% to 50%. The applet/application at <http://stp.clarku.edu/simulations/demon.html> implements this algorithm. The applet chooses the special microstate for which all the velocities of the particles in the system are identical so that the system has the desired initial energy. The initial demon energy is set to zero for simplicity.

(a) The demon can be considered to be a small system in equilibrium with a much larger system. Before you do the simulation, sketch the energy-dependence of the probability $p(E_d)dE_d$ that the demon has an energy between $E_d$ and $E_d + dE_d$.

(b) Consider a small number of particles, say $N = 10$. After the demon and the system have reached equilibrium, what is $\bar{E}_d$, the mean energy of the demon, and $\bar{E}/N$, the mean energy per particle of the system? Fix $N = 20$ and increase the total energy of the system. How does the ratio of $\bar{E}_d/(\bar{E}/N)$ depend on the total energy?

(c) Compare the initial mean velocity of the particles in the system to the mean value after equilibrium has been established. Would your results be different if the demon had a nonzero initial energy if the total energy of the demon plus the system was the same as before?

(d) Run for a sufficient number of trials so that the form of $p(E_d)$ is well defined. Use the Enable log scale button in the Views menu to verify the exponential form of $p(E_d)$. Fit your results to the form $p(E_d) \propto \exp(-\beta E_d)$, where $\beta$ is a parameter. Given the form of $p(E_d)$, determine analytically the dependence of the mean demon energy on $\beta$ (see Problem 4.36) and compare your prediction with your numerical results. Estimate $T$ from the inverse slope of $\ln p(E_d)$ versus $E_d$. (The units are such that the Boltzmann constant $k = 1$.)
(e) What is the relation of the mean energy per particle in the system to the temperature? Use the results that you found in parts (b) and (d) to explain the relation between $E_d$ and $E/N$.

(f) How do your results change for an ideal gas in two and three dimensions?

Problem 4.36. Temperature dependence of the mean demon energy I
A demon exchanges energy with an ideal classical gas of $N$ particles in one dimension (see Problem 4.35). What is the mean energy of the demon?

In this case the demon energy is a continuous variable. Hence,

$$E_d = \int_{0}^{\infty} E_d e^{-\beta E_d} \, \frac{1}{\int_{0}^{\infty} e^{-\beta E_d}}. \tag{4.135}$$

(a) Explain why the relation (4.135) for the demon energy is reasonable and determine the temperature dependence of $E_d$.

(b) Would this temperature dependence be different if the gas were two- or three-dimensional? Would the temperature dependence change if the particles in the gas interacted with one another?

Problem 4.37. The demon and the Einstein solid
Consider a demon that exchanges energy with an Einstein solid of $N$ particles. The demon chooses a particle at random and randomly increases or decreases its energy by one unit consistent with the constraint that $E_d \geq 0$. In this case the energy of the particle chosen also must remain nonnegative. If a trial change is not accepted, the existing microstate is counted in all averages. Use the applet/application at <stp.clarku.edu/simulations/demonsolid.html>.

(a) Choose $N = 20$ and $E = 40$. Does $E_d$ eventually reach a well defined average value? If so, what is the mean energy of the demon after equilibrium between the demon and the system has been established? Compare the values of $E_d$ and $E/N$, the mean energy per particle of the system.

(b) Compute the probability $P(E_d)$ that the demon has the energy $E_d$. Fit your results to the form $P(E_d) \propto \exp(-\beta E_d)$, where $\beta$ is a parameter. Then increase $E$ to $E = 80$. How do the various averages change? If time permits, increase $E$ and $N$ and determine any changes in $P(E_d)$ and the ratio $E_d/E/N$.

(c) Is there a simple relation between $E_d$ and $E/N$?

Problem 4.38. Temperature dependence of the mean demon energy II
A demon exchanges energy with a system of an Einstein solid of $N$ particles (see Problem 4.37). What is the mean energy of the demon?

(a) Explain why the energy of the demon is restricted to integer values.

(b) Explain why the demon’s mean energy is given by

$$E_d = \frac{\sum_{n=0}^{\infty} ne^{-\beta n}}{\sum_{n=0}^{\infty} e^{-\beta n}}. \tag{4.136}$$
(c) Do the sums in (4.136) to determine the temperature dependence of \( E_d \). (It is necessary to only do the sum in the denominator of (4.136).)

(d) Why is the temperature dependence of \( E_d \) different if the demon exchanges energy with an ideal gas rather than an Einstein solid?

(e) In what limit does the temperature dependence become the same?

4.10 Simulations of the microcanonical ensemble

How can we implement the microcanonical ensemble on a computer? One way to do so for a classical system of particles is to use the method of molecular dynamics (see Section 1.5). In this method we choose initial conditions for the positions and velocities of each particle that are consistent with the desired values of \( E \), \( V \), and \( N \). The numerical solution of Newton’s equations generates a trajectory in \( 3N \)-dimensional phase space. Each point on the trajectory represents a microstate of the microcanonical ensemble with the additional condition that the momentum of the center of mass is fixed. The averages over the phase space trajectory represent a time average.

To do such a simulation we need to be careful to choose a representative initial condition. For example, suppose that we started with the particles in one corner of the box. Even though a microstate with all the particles in one corner is as likely to occur as other microstates with the same energy, there are many more microstates for which the particles are spread throughout the box than there are those with particles in one corner.

As we will justify further in Section 6.3, we can identify the temperature of a system of interacting particles with the kinetic energy per particle using the relation (4.65). (For the ideal gas the total energy is simply the kinetic energy.) If we were to do a molecular dynamics simulation, we would find that the total energy is (approximately) constant, but the kinetic energy and hence the temperature fluctuates. The mean temperature of the system becomes well defined if the system is in equilibrium, the number of particles in the system is sufficiently large, and the simulation is done for a sufficiently long time.

Our assumption that a molecular dynamics simulation generates microstates consistent with the microcanonical ensemble is valid as long as a representative sample of the accessible microstates can be reached during the duration of the simulation. Such a system is said to be quasi-ergodic.

What if we have a system of fixed total energy for which Newton’s equations of motion is not applicable? For example, there is no dynamics for Einstein solid in which the particles have only integer values of the energy. Another general way of generating representative microstates is to use a Monte Carlo method. As an example, consider a system of \( N \) noninteracting distinguishable particles whose single particle energies are 0, 1, 2, ... For this model the relevant variables are the quantum numbers of each particle such that their sum equals the desired total energy \( E \). Given a set of quantum numbers, how do we generate another set of quantum numbers with the same energy? Because we want to generate a representative sample of the accessible states, we need to make all changes at random. One possibility is to choose a particle at random and make a trial change in its energy by ±1. However, such a trial change would change the total energy of the system and hence not be acceptable. (For this simple example of noninteracting particles, we could
choose two particles at random and make trial changes, some of which would leave the total energy unchanged.)

A more interesting example is the Ising model in which the spins interact with their nearest neighbors with an energy $+J$ if the spins are parallel and energy $-J$ if the spins are antiparallel (see Section 1.10.3). We will discuss the Ising model in some detail in Chapter 5. Here it is sufficient to understand that the individual spins interact with one another.

The condition that the total energy be fixed makes sampling the accessible microstates of the Ising model difficult. If we choose a spin at random and flip it, the change will change the energy of the system in general. This difficulty is analogous to the difficulty that we have already found doing calculations in the microcanonical ensemble. We can circumvent this difficulty by relaxing the condition that the total energy be fixed by adding to the system of $N$ particles an extra degree of freedom called the demon, as we discussed in Section 4.9. The total energy of the demon plus the original system is fixed. Because the demon is one particle out of $N + 1$, the fluctuations in the energy of the original system are order $1/N$, which goes to zero as $N \rightarrow \infty$.

4.11 Simulations of the canonical ensemble

Suppose that we wish to simulate a system that is in equilibrium with a heat bath at temperature $T$. One way to do so is to start with an arbitrary microstate of energy $E$ and weight it by its relative probability $e^{-\beta E}$. For example, for the Einstein solid considered in Section 4.10, we could generate another microstate by choosing a particle at random and changing its energy by $\pm 1$ at random. A new microstate would be generated and the mean energy of the system would be estimated by

$$E(T) = \frac{\sum_{n=1}^{M} E_n e^{-\beta E_n}}{\sum_{n=1}^{M} e^{-\beta E_n}},$$

(4.137)

where $E_n$ is the energy of microstate $n$ and the sum is over the $M$ states that have been generated in this way. However, this procedure would be very inefficient because the $M$ states would include many states whose weight in averages such as (4.137) would be very small.

To make the sampling procedure effective, we need to generate microstates with probabilities proportional to their weight, that is, proportional to $e^{-\beta E_n}$. In this way we would generate states with the highest probability. Such a sampling procedure is known as importance sampling. The simplest and most common method of importance sampling in statistical mechanics is known as the Metropolis algorithm. The method is based on the fact that the ratio of the probability that the system is in state $j$ with energy $E_j$ to the probability of being in state $i$ with energy $E_i$ is

$$p_j/p_i = e^{-\beta(E_j - E_i)} = e^{-\beta \Delta E},$$

where $\Delta E = E_j - E_i$. We interpret this ratio as the probability of making a transition from state $i$ to state $j$. If $\Delta E < 0$, the quantity $e^{-\beta \Delta E}$ is greater than unity, and the probability is unity. The Metropolis algorithm can be summarized as follows:

1. Choose an initial microstate, for example, choose random initial energies for each particle in an Einstein solid or random positions in a system of particles interacting via the Lennard-Jones potential.

2. Make a trial change in the microstate. For the Einstein solid, choose a particle at random and increase or decrease its energy by unity. For a system of particles, change the position
CHAPTER 4. STATISTICAL MECHANICS

of a particle by a small random amount. Compute the change in energy of the system, \( \Delta E \), corresponding to this change. If \( \Delta E < 0 \), then accept the change. If \( \Delta E > 0 \), accept the change with probability \( w = e^{-\beta \Delta E} \). To do so, generate a random number \( r \) uniformly distributed in the unit interval. If \( r \leq w \), accept the new microstate; otherwise, retain the previous microstate.

3. Repeat step 2 many times.

4. Compute the averages of the quantities of interest once the system has reached equilibrium.

Problem 4.39. Simulation of the Einstein solid in equilibrium with a heat bath

Use the Metropolis algorithm to simulate an Einstein solid of \( N \) particles at a temperature \( T \). The applet/application at <stp.clarku.edu/simulations/MetropolisEinsteinSolid.html> implements the Metropolis algorithm by choosing a particle at random and randomly increasing or decreasing its energy by one unit. If the energy is decreased, the change is accepted. If the energy is increased, the program generates a number \( r \) at random in the unit interval and accepts the change if \( r \leq e^{-\beta} \), where \( \beta = 1/T \). (As usual, we choose units such that Boltzmann’s constant \( k = 1 \).) If a trial change is not accepted, the existing microstate is counted in all averages.

(a) Choose \( N = 20 \) and \( \beta = 1 \). Does the energy of the system eventually reach a well defined average? If so, vary \( \beta \) and determine \( E(T) \).

(b) Compare your results to the analytical results you found in Example 4.4.

4.12 Grand canonical ensemble (fixed \( T, V, \) and \( \mu \))

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 \( T \) and a particle reservoir with chemical potential \( \mu \). 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 (4.74))

\[
P_n = \frac{1 \times \Omega_b(E - E_n, N - N_n)}{\sum_n \Omega_b(E - E_n, N - N_n)}. \tag{4.138}
\]

The difference between (4.74) and (4.138) is that we have allowed both the energy and the number of particles of the system of interest to vary. As before, we take the logarithm of both sides of (4.138) and exploit the fact that \( E_n \ll E \) and \( N_n \ll N \). We have

\[
\ln P_n \approx \text{constant} - E_n \frac{\partial \ln \Omega_b(E)}{\partial E} - N_n \frac{\partial \ln \Omega_b(N)}{\partial N}. \tag{4.139}
\]
The derivatives in (4.139) are evaluated at $E_{bath} = E$ and $N_{reservoir} = N$, respectively. If we substitute $\beta = \partial \ln \Omega_b / \partial E$ (see (4.77)) and $\beta \mu = -\partial \ln \Omega_b / \partial N$ (see (2.116)), we obtain
\[
\ln P_n = \text{constant} - \frac{E_n}{kT} + \frac{\mu N_n}{kT},
\]
(4.140)
or
\[
P_n = \frac{1}{Z} e^{-\beta(E_n - \mu N_n)} \quad \text{Gibbs distribution}
\]
(4.141)
Equation (4.141) is the Gibbs probability distribution for a variable number of particles. This distribution gives the probability that the system is in state $n$ with energy $E_n$ and $N_n$ particles. The grand partition function $Z$ in (4.141) is found from the normalization condition
\[
\sum_n P_n = 1.
\]
(4.142)
Hence, we obtain
\[
Z = \sum_n e^{-\beta(E_n - \mu N_n)}
\]
(4.143)
In analogy to the relations we found in the canonical ensemble, we expect that there is a simple relation between the Landau potential defined in (2.157) and the grand partition function. Because the derivation of this relation proceeds as in Sec. 4.6, we simply give the relation:
\[
\Omega = -kT \ln Z
\]
(4.144)
Example 4.6. Many impurity atoms in a semiconductor exchange energy and electrons with the electrons in the conduction band. Consider the impurity atoms to be in thermal and chemical equilibrium with the conduction band, which can be considered to be an energy and particle reservoir. Assume that $\Delta$ is the ionization energy of the impurity atom. Find the probability that an 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.

<table>
<thead>
<tr>
<th>state $n$</th>
<th>description</th>
<th>$N$</th>
<th>$\epsilon_n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>electron detached</td>
<td>0</td>
<td>$-\Delta$</td>
</tr>
<tr>
<td>2</td>
<td>electron attached, spin $\uparrow$</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>electron attached, spin $\downarrow$</td>
<td>1</td>
<td>0</td>
</tr>
</tbody>
</table>

The grand partition function of the impurity atom is given by
\[
Z = e^{\beta \Delta} + 2e^{\beta \mu}.
\]
(4.145)
Hence, the probability that an atom is ionized (state 1) is given by
\[
P(\text{ionized}) = \frac{e^{\beta \Delta}}{e^{\beta \Delta} + 2e^{\beta \mu}} = \frac{1}{1 + e^{-\beta(\Delta - \mu)}},
\]
(4.146)
4.13 Entropy and disorder

Many texts and articles for the scientifically literate refer to entropy as a measure of “disorder” or “randomness.” This interpretation is justified by the relation, $S = k \ln \Omega$. The argument is that an increase in the disorder in a system corresponds to an increase in $\Omega$. Usually a reference is made to a situation such as the tendency of students’ rooms to become messy. There are two problems with this interpretation—it adds nothing to our understanding of entropy and is inconsistent with our naive understanding of structural disorder.

We have already discussed the interpretation of the entropy as a measure of the uncertainty or lack of information. Thus, we already have a precise definition of entropy and can describe a student’s messy room as having a high entropy because of our lack of information about the location of a particular paper or article of clothing. We could define disorder as lack of information, but such a definition does not help us to understand entropy any better because it would not provide an independent understanding of disorder.

The other problem with introducing the term disorder to describe entropy is that it can lead to incorrect conclusions. In the following we will describe two examples where the crystalline phase of a given material has a higher entropy than the liquid phase. Yet you would probably agree that a crystal is more ordered than a liquid. So how can a crystal have a higher entropy?

Suppose that you are going on a short trip and need to pack your suitcase with only a few articles. In this case the volume of the suitcase is much greater than the total volume of the articles you wish to pack, and you would probably just randomly throw the articles into the suitcase. Placing the articles in an ordered arrangement would require extra time and the ordered arrangement would probably be destroyed during transport. In statistical mechanics terms we say that there are many more ways in which the suitcase can be packed in a disordered arrangement than the ordered one. Hence, we could include that the disordered state has a higher entropy than the ordered state. This low density case is consistent with the usual association of entropy and disorder.

Now suppose that you are going on a long trip and need to pack many articles in the same suitcase, that is, the total volume of the articles to be packed is comparable to the volume of the suitcase. In this high density case you probably know from experience that randomly throwing the articles into the suitcase won’t allow you to shut the suitcase. Such a configuration is incompatible with the volume constraints of the suitcase. If you randomly throw the articles in the suitcase many times, you might find a few configurations that would allow you to close the suitcase. In contrast, if you pack the articles in a neat and ordered arrangement, the suitcase can be closed. Also there are many such configurations that would satisfy the constraints. We conclude that the number of ordered arrangements (of the articles in the suitcase) is greater than the number of corresponding disordered arrangements. Therefore an ordered arrangement in the high density suitcase has a higher entropy than a structurally disordered state. The association of disorder with entropy is not helpful here.

The suitcase example is an example of an entropy-driven transition because energy did not enter into our considerations at all. Another example of an entropy-driven transition is a system of hard spheres or hard disks. In this seemingly simple model the interaction between two particles

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11 This example is due to Laird (see the references).
is given by
\[ u(r) = \begin{cases} 
\infty & r < \sigma \\
0 & r \geq \sigma.
\end{cases} \tag{4.147} \]

For this model only non-overlapping configurations are allowed and so the potential energy is zero. Hence, the internal energy is solely kinetic and the associated contribution of the energy to the free energy is the ideal gas part which depends only on the temperature and the density. Hence, the difference in the free energy \( \Delta F = \Delta E - T \Delta S \) between a hard sphere crystal and a hard sphere fluid at the same density and temperature must equal \(-T \Delta S\).

In the following problem we will do an exploratory simulation of a system of hard disks that suggests that there is a transition from a fluid at low density to a crystal at high density (at fixed temperature). Thus at some density \( \Delta F \) must become negative, which can occur only if \( \Delta S = S_{\text{crystal}} - S_{\text{fluid}} \) is positive. We conclude that at high density the entropy of the crystal must be greater than that of a fluid at equal temperature and density for a fluid-solid (freezing) transition to exist.

**Problem 4.40.** Simulation of hard disks

The dynamics of a system of hard disks are straightforward in principle because the particles move in straight lines in between collisions. The applet/application at [stp.clarku.edu/simulations/HardDisks.html](http://stp.clarku.edu/simulations/HardDisks.html) finds when the next two particles are going to collide and moves the particles accordingly.

(a) Run the simulation for the default parameters and record the density and the results for \( PA/NkT \) and the temperature. Is the temperature a useful quantity for hard disks? Does it fluctuate during the simulation. If not why not? Does the pressure \( P \) fluctuate?

(b) Compute \( PA/NkT \) as a function of density for a fixed number of particles. Is there any evidence of a phase transition where the slope of the pressure with respect to density changes abruptly?

**Vocabulary**

- composite system, subsystem
- equal a priori probabilities
- microcanonical ensemble, canonical ensemble, grand canonical ensemble
- Boltzmann distribution, Gibbs distribution
- entropy \( S \), Helmholtz free energy \( F \), Gibbs free energy \( G \), Landau potential \( \Omega \)
- demon algorithm, Metropolis algorithm
Appendix 4A: The volume of a hypersphere

We derive the volume of a hypersphere of $n$ dimensions given in (4.47). As in (4.46), the volume is given by

$$V_n(R) = \int_{x_1^2 + x_2^2 + \cdots + x_n^2 < R^2} dx_1 dx_2 \cdots dx_n.$$  \hspace{1cm} (4.148)

Because $V_n(R) \propto R^n$ for $n = 2$ and 3, we expect that $V_n$ is proportional to $R^n$. Hence, we write

$$V_n = C_n R^n,$$  \hspace{1cm} (4.149)

where $C_n$ is the (unknown) constant of proportionality that depends only on $n$. We rewrite the volume element $dV_n = dx_1 dx_2 \cdots dx_n$ as

$$dV_n = dx_1 dx_2 \cdots dx_n = S_n(R) dR = nC_n R^{n-1} dR,$$  \hspace{1cm} (4.150)

where $S_n = nC_n R^{n-1}$ is the surface area of the hypersphere. As an example, for $n = 3$ we have $dV_3 = 4\pi R^2 dR$ and $S_3 = 4\pi R^2$. To find $C_n$ for general $n$, consider the identity (see Appendix A)

$$I_n = \int_{-\infty}^{\infty} dx_1 \int_{-\infty}^{\infty} dx_2 \cdots \int_{-\infty}^{\infty} dx_n e^{-(x_1^2 + \cdots + x_n^2)} = \frac{1}{n!} \left( \int_{-\infty}^{\infty} dx e^{-x^2} \right)^n = \pi^{n/2}.$$  \hspace{1cm} (4.151)

The left-hand side of (4.152) can be written as

$$I_n = \int_{-\infty}^{\infty} dx_1 \cdots \int_{-\infty}^{\infty} dx_n e^{-(x_1^2 + \cdots + x_n^2)} = \int_0^{\infty} dR S_n(R) e^{-R^2}$$

$$= nC_n \int_0^{\infty} dR R^{n-1} e^{-R^2}.$$  \hspace{1cm} (4.152)

We can relate the integral in (4.152) to the Gamma function $\Gamma(n)$ defined by the relation

$$\Gamma(n) = \int_0^{\infty} dx x^{n-1} e^{-x}.$$  \hspace{1cm} (4.153)

The relation (4.153) holds for $n > -1$ and whether or not $n$ is an integer. We make the change of variables $x = R^2$ so that

$$I_n = \frac{1}{2} nC_n \int_0^{\infty} dx x^{n/2-1} e^{-x} = \frac{1}{2} nC_n \Gamma(n/2).$$  \hspace{1cm} (4.154)

A comparison of (4.154) with (4.151) yields the relation

$$C_n = \frac{2\pi^{n/2}}{n\Gamma(n/2)} = \frac{\pi^{n/2}}{(n/2)!\Gamma(n/2)}.$$  \hspace{1cm} (4.155)

It follows that

$$V_n(R) = \frac{2\pi^{n/2}}{n\Gamma(n/2)} R^n.$$  \hspace{1cm} (4.156)
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 an energy \( E \) in the range \( \Delta E \). 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

\[
P_n = \frac{g(E_n)e^{-\beta E_n}}{\sum_n g(E_n)e^{-\beta E_n}},
\]

(4.157)

where \( g(E_n) \) is the number of microstates with energy \( E_n \). In the thermodynamic limit \( N, V \to \infty \), the spacing between consecutive energy levels becomes very small and we can regard \( E \) as a continuous variable. We write \( P(E) \, dE \) for the probability that the system in the range \( E \) and \( E + dE \) and let \( g(E) \, dE \) be the number of microstates between \( E \) and \( E + dE \). (The function \( g(E) \) is the density of states and is the same function discussed in Section 4.3.) Hence, we can rewrite (4.157) as

\[
P(E) \, dE = \frac{g(E)e^{-\beta E} \, dE}{\int_0^\infty g(E)e^{-\beta E} \, dE}.
\]

(4.158)

As we did in Section 3.7, we can find an approximate form of \( P(E) \) by expanding \( P(E) \) about \( E = \bar{E} \), the most probable value of \( E \). To do so, we evaluate the derivatives \( \partial \ln P/\partial E \) and \( \partial^2 \ln P/\partial E^2 \) using (4.158):

\[
\left( \frac{\partial \ln P}{\partial E} \right)_{E = \bar{E}} = \left( \frac{\partial \ln g}{\partial E} \right)_{E = \bar{E}} - \beta = 0.
\]

(4.159)

and

\[
\left( \frac{\partial^2 \ln P}{\partial E^2} \right)_{E = \bar{E}} = \left( \frac{\partial^2 \ln g}{\partial E^2} \right)_{E = \bar{E}}.
\]

(4.160)

We have

\[
\left( \frac{\partial^2 \ln g}{\partial E^2} \right)_{E = \bar{E}} = \frac{\partial}{\partial E} \left( \frac{\partial \ln g}{\partial E} \right)_{E = \bar{E}} = \frac{\partial \beta}{\partial E}.
\]

(4.161)

Finally, we obtain

\[
\frac{\partial \beta}{\partial E} = -\frac{1}{kT^2} \frac{\partial T}{\partial E} = -\frac{1}{kT^2 C_V}.
\]

(4.162)

We can use the above results to expand \( \ln P(E) \) about \( E = \bar{E} \) through second order in \((E - \bar{E})^2\). The result is

\[
\ln P(E) = \ln P(\bar{E}) - \frac{(E - \bar{E})^2}{2kT^2 C_V} + \ldots
\]

(4.163)

or

\[
P(E) = P(\bar{E}) e^{-\frac{(E - \bar{E})^2}{2kT^2 C_V}}.
\]

(4.164)

If we compare (4.164) to the standard form of a Gaussian distribution (3.120), we see that \( \bar{E} = \bar{E} \) and \( \sigma_E^2 = kT^2 C_V \) as expected.
Additional Problems

<table>
<thead>
<tr>
<th>Problems</th>
<th>page</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.1</td>
<td>148</td>
</tr>
<tr>
<td>4.2, 4.3</td>
<td>149</td>
</tr>
<tr>
<td>4.4, 4.6, 4.7, 4.8</td>
<td>155</td>
</tr>
<tr>
<td>4.9</td>
<td>156</td>
</tr>
<tr>
<td>4.10, 4.11</td>
<td>157</td>
</tr>
<tr>
<td>4.12, 4.13, 4.14</td>
<td>159</td>
</tr>
<tr>
<td>4.15</td>
<td>160</td>
</tr>
<tr>
<td>4.16</td>
<td>163</td>
</tr>
<tr>
<td>4.17</td>
<td>165</td>
</tr>
<tr>
<td>4.18, 4.19</td>
<td>166</td>
</tr>
<tr>
<td>4.20, 4.21</td>
<td>169</td>
</tr>
<tr>
<td>4.22, 4.23, 4.24, 4.25</td>
<td>172</td>
</tr>
<tr>
<td>4.26, 4.27</td>
<td>174</td>
</tr>
<tr>
<td>4.28, 4.29</td>
<td>176</td>
</tr>
<tr>
<td>4.30, 4.31</td>
<td>177</td>
</tr>
<tr>
<td>4.32</td>
<td>180</td>
</tr>
<tr>
<td>4.33</td>
<td>184</td>
</tr>
<tr>
<td>4.34, 4.35</td>
<td>186</td>
</tr>
<tr>
<td>4.36, 4.37, 4.38</td>
<td>187</td>
</tr>
<tr>
<td>4.39</td>
<td>190</td>
</tr>
<tr>
<td>4.40</td>
<td>193</td>
</tr>
</tbody>
</table>

Table 4.9: Listing of inline problems.

**Problem 4.41.** Discuss the statistical nature of the Clausius statement of the second law that energy cannot go spontaneously from a colder to a hotter body. Under what conditions is the statement applicable? In what sense is this statement incorrect?

**Problem 4.42.** Given our discussion of the second law of thermodynamics from both the macroscopic and microscopic points of view, discuss the following quote due to Arthur Stanley Eddington:

> The law that entropy always increases, the Second Law of Thermodynamics, holds . . . the supreme position among the laws of Nature. If someone points out to you that your pet theory of the universe is in disagreement with Maxwell’s equations, then so much the worse for Maxwell’s equations . . . But if your theory is found to be against the second law of thermodynamics, I can give you no hope; there is nothing for it but to collapse in deepest humiliation.

**Problem 4.43.** Consider an isolated composite system consisting of subsystems 1 and 2 that can exchange energy with each other. Subsystem 1 consists of three noninteracting spins, each having magnetic moment $\mu$. Subsystem 2 consists of two noninteracting spins each with a magnetic moment $2\mu$. 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 $-3\mu$ and the net magnetic moment of 2 is $+4\mu$. The systems are then placed in thermal contact with one another and are allowed to exchange energy. What is the probability $P(M)$ that the net magnetic moment of system 1 has one of its possible values $M$? What is the mean value of the net magnetic moment of system 1?

**Problem 4.44.** Consider two isolated systems of noninteracting spins with $N_A = 4$ and $N_B = 16$. If their initial energies are $E_A = -2\mu B$ and $E_B = -2\mu B$, what is the total number of microstates available to the composite system? If the two systems are now allowed to exchange energy with one another, what is the probability that system 1 has energy $E_A$? What is the mean value of $E_A$ and its relative fluctuations of $E_A$? Calculate the analogous quantities for system $B$. What is the most probable macrostate for the composite system?

**Problem 4.45.** Show that the relations (4.59)–(4.61) follow from the thermodynamic relation $dE = TdS - PdV + \mu dN$ (see (2.123)).

**Problem 4.46.** Suppose that the number of states between energy $E$ and $E + \Delta E$ of an isolated system of $N$ particles in a volume $V$ is given by

$$g(E)\Delta E = c(V - bN)^N\left(E + \frac{N^2a}{V}\right)^{3N/2}\Delta E,$$

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 $\rho$? What are the units of the parameters $a$ and $b$?

**Problem 4.47.** Discuss the assumptions that are needed to derive the classical ideal gas equations of state, (4.65) and (4.66).

**Problem 4.48.** Assume that $g(E) = E^{3N/2}$ for a classical ideal gas. Plot $g(E), e^{-\beta E}$, and the product $g(E)e^{-\beta E}$ versus $E$ for $N = 6$ and $\beta = 1$. What is the qualitative behavior of the three functions? Show that the product $g(E)e^{-\beta E}$ has a maximum at $\tilde{E} = 3N/(2\beta)$. Compare this value to the mean value of $E$ given by

$$\langle E \rangle = \frac{\int_0^{\infty} g(E)e^{-\beta E}dE}{\int_0^{\infty} g(E)e^{-\beta E}dE}.$$  

**Problem 4.49.** Explain why the various heat capacities must go to zero as $T \to 0$.

**Problem 4.50.** The partition function of a hypothetical system is given by

$$\ln Z = aT^4V,$$

where $a$ is a constant. Evaluate the mean energy $E$, the pressure $P$, and the entropy $S$.

**Problem 4.51.** An analogy for the heat capacity

The following analogy might be useful for understanding the temperature dependence of the heat capacity of a two level system.
(a) Suppose that you walk into a store with little money in your pocket (and no credit card). Would you care about the prices of the articles you wished to purchase? Would you care about the prices if you had just won the lottery?

(b) Suppose that you wish to purchase a car that costs $20,000 but have no money. You then find a dollar bill on the street. Has your “capacity” for purchasing the car increased? Suppose that your uncle gives you $8000. Has your capacity for purchasing the car increased substantially? How much money would you need before you might think about buying the car?

Problem 4.52. Show that the partition function $Z_{12}$ of two independent distinguishable systems 1 and 2 both in equilibrium with a heat bath at temperature $T$ equals the product of the partition functions of the separate systems:

$$Z_{12} = Z_1 Z_2.$$ (4.168)

Problem 4.53. Qualitative temperature dependence of two level system

(a) Consider a system of $N$ noninteracting, distinguishable particles each of which can be in single particle states with energy 0 and $\Delta$ (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 $\Delta$, and discuss the limiting behavior of the probabilities for low and high temperatures. What does high and low temperature mean in this case? Sketch the $T$-dependence of the mean energy $E(T)$ and give a simple argument for its behavior. From your sketch of $E(T)$ sketch the $T$-dependence of the heat capacity $C(T)$ and describe its qualitative behavior. Give a simple physical argument why $C$ has a maximum and estimate the temperature at which the maximum occurs.

(b) Calculate $C(T)$ explicitly and verify that its behavior is consistent with the qualitative features illustrated in your sketch. The maximum in the heat capacity of a two state system is called the Schottky anomaly, but the characterization of this behavior as anomaly is a misnomer because many systems behave as two level systems at low temperatures.

Problem 4.54. Consider a system of $N$ noninteracting, distinguishable particles. Each particle can be in one of three states with energies 0, $\Delta$, and $10\Delta$. Without doing an explicit calculation, sketch the temperature dependence of the heat capacity at low temperatures.

Problem 4.55. Consider a system of one particle in equilibrium with a heat bath. The particle has two microstates of energy $\epsilon_1 = 0$ and $\epsilon_2 = \Delta$. Find the probabilities $p_1$ and $p_2$ when the mean energy of the system is 0.2$\Delta$, 0.4$\Delta$, 0.5$\Delta$, 0.6$\Delta$, and $\Delta$, respectively. What are the corresponding temperatures? (Hint: Write the mean energy as $x\Delta$ and express your answers in terms of $x$.)

Problem 4.56. Harmonic oscillators in equilibrium with a heat bath

(a) Calculate the heat capacity $C_V$ of a system of $N$ one-dimensional harmonic oscillators (see Example 4.4).

(b) Plot the $T$-dependence of the mean energy $E$ and the heat capacity $C = dE/dT$. Show that $E \to kT$ at high temperatures for which $kT \gg \hbar \omega$. This result corresponds to the classical limit and will be shown in Section 6.3 to be a consequence of the equipartition theorem. In this limit the thermal energy $kT$ is large in comparison to $\hbar \omega$, the separation between energy levels. Hint: expand the exponential function in (4.131).
CHAPTER 4. STATISTICAL MECHANICS

Figure 4.9: The two particles considered in Problem 4.58. The two distinguishable particles can each be in one of the two boxes. The energy of the system depends on which box the particles occupy.

(c) Show that at low temperatures for which $\hbar \omega \gg kT$, $E = \hbar \omega (\frac{1}{2} + e^{-\beta \hbar \omega})$. What is the value of the heat capacity? Why is the latter so much smaller than it is in the high temperature limit?

(d) Verify that $S \to 0$ as $T \to 0$ in agreement with the third law of thermodynamics, and that at high $T$, $S \to kN \ln(kT/\hbar \omega)$. The latter result implies that the effective number of microstates over which the probability is nonzero is $ekT/\hbar \omega$. This result is reasonable because the width of the Boltzmann probability distribution is $kT$, and hence the number of microstates that are occupied at high temperature is $kT/\hbar \omega$.

Problem 4.57. In the canonical ensemble the temperature is fixed and the constant volume heat capacity is related to the variance of the energy fluctuations (see (4.87)). As discussed on page 188, the temperature fluctuates in the microcanonical ensemble. Guess how the constant volume heat capacity might be expressed in the microcanonical ensemble.

Problem 4.58. Consider the system illustrated in Figure 4.9. The system consists of two distinguishable particles, each of which can be in either of two boxes. Assume that the energy of a particle is zero if it is in the left box and $r$ if it is in the right box. There is also a correlation energy term that lowers the energy by $\Delta$ 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 $\Delta$ and use your result to find the mean energy and the heat capacity. Explain your result for $C$ in simple terms.

(d) What is the probability that the system is in a particular microstate?

Problem 4.59. Consider a system in equilibrium with a heat bath at temperature $T$ and a particle reservoir at chemical potential $\mu$. 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 $\Delta$. Determine the (grand) partition function of the system.

Problem 4.60. Constant pressure ensemble

In the text we derived the form of the probability distribution for a system with fixed $T$, $V$, and $N$ (the canonical ensemble) and fixed $T$, $V$, and $\mu$ (the grand canonical ensemble). What is the form of the probability distribution for an equilibrium system with fixed $T$, $P$, and $N$? This ensemble has no generally accepted name and is not particularly useful for calculations. However, it is useful for doing simulations at a given pressure rather than for a given volume.
Problem 4.61. Demonstration of an entropy-driven transition

The following demonstration illustrates an entropy-driven transition. Get a bag of M & M’s or similar disk-shaped candy. Ball bearings work better, but they are not as tasty. You will also need a flat bottom glass dish (preferably square) that fits on an overhead projector.

Place the glass dish on the overhead projector and add a few of the candies. Shake the dish gently from side to side to simulate the effects of temperature. You should observe a two-dimensional model of a gas. Gradually add more candies while continuing to shake the dish. As the density is increased further, you will begin to notice clusters of hexagonal crystals. Do these clusters disappear if you shake the dish faster? At what density do large clusters of hexagonal crystals begin to appear? Is this density less than the maximum packing density?

Suggestions for Further Reading


W. G. V. Rosser, An Introduction to Statistical Physics, Ellis Horwood Limited (1982). As far as we know, this book was the first to introduce the Einstein solid in the context of the counting of states and the thermal interaction of simple systems.

Daniel V. Schroeder, An Introduction to Thermal Physics, Addison-Wesley (1999).