3 Interactions and Implications

In the previous chapter I argued that whenever two large systems interact, they will evolve toward whatever macrostate has the highest possible entropy. This statement is known as the second law of thermodynamics. The second law is not built into the fundamental laws of nature, though; it arises purely through the laws of probability and the mathematics of very large numbers. But since the probabilities are so overwhelming for any system large enough to see with our eyes, we might as well forget about probabilities and just treat the second law as fundamental. That's what I'll do throughout most of the rest of this book, as we explore the consequences of the second law.

The purpose of the present chapter is twofold. First, we need to figure out how entropy is related to other variables, such as temperature and pressure, that can be measured more directly. I'll derive the needed relations by considering the various ways in which two systems can interact, exchanging energy, volume, and/or particles. In each case, for the second law to apply, entropy must govern the direction of change. Second, we'll use these relations and our various formulas for entropy to predict the thermal properties of a variety of realistic systems, from the heat capacity of a solid to the pressure of a gas to the magnetization of a paramagnetic material.

3.1 Temperature

The second law says that when two objects are in thermal equilibrium, their total entropy has reached its maximum possible value. In Section 1.1, however, I gave another criterion that is met when two objects are in thermal equilibrium: I said that they are then at the same **temperature**. In fact, I *defined* temperature to be the thing that's the same for both objects when they're in thermal equilibrium. So now that we have a more precise understanding of thermal equilibrium in terms of entropy, we are in a position to figure out what temperature is, *really*.

Let's look at a specific example. Consider two Einstein solids, A and B, that are "weakly coupled" so that they can exchange energy (but with the total energy fixed). Suppose (as in Figure 2.5) that the numbers of oscillators in the two solids are $N_A = 300$ and $N_B = 200$, and that they are sharing 100 units of energy: $q_{\text{total}} = 100$. Table 3.1 lists the various macrostates and their multiplicities. Now, however, I have also included columns for the entropy of solid A, the entropy of solid B, and the total entropy (which can be obtained either by adding S_A and S_B, or by taking the logarithm of Ω_{total}).

Figure 3.1 shows a graph of S_A, S_B, and S_{total} (in units of Boltzmann's constant), for the same parameters as in the table. The equilibrium point is at $q_A = 60$, where S_{total} reaches its maximum value. At this point, the tangent to the graph of S_{total} is horizontal; that is,

$$\frac{\partial S_{\text{total}}}{\partial q_A} = 0 \qquad \text{or} \qquad \frac{\partial S_{\text{total}}}{\partial U_A} = 0 \qquad \text{at equilibrium.} \tag{3.1}$$

(Technically it's a *partial* derivative because the number of oscillators in each solid is being held fixed. The energy U_A is just q_A times a constant, the size of each unit of energy.) But the slope of the S_{total} graph is the sum of the slopes of the S_A and S_B graphs. Therefore,

$$\frac{\partial S_A}{\partial U_A} + \frac{\partial S_B}{\partial U_A} = 0 \qquad \text{at equilibrium.} \tag{3.2}$$

The second term in this equation is rather awkward, with B in the numerator and A in the denominator. But dU_A is the same thing as $-dU_B$, since adding a bit of energy to solid A is the same as subtracting the same amount from solid B.

q_A	Ω_A	S_A/k	q_B	Ω_B	S_B/k	Ω_{total}	S_{total}/k
0	1	0	100	2.8×10^{81}	187.5	2.8×10^{81}	187.5
1	300	5.7	99	9.3×10^{80}	186.4	2.8×10^{83}	192.1
2	45150	10.7	98	3.1×10^{80}	185.3	1.4×10^{85}	196.0
⋮	⋮	⋮	⋮	⋮	⋮	⋮	⋮
11	5.3×10^{19}	45.4	89	1.1×10^{76}	175.1	5.9×10^{95}	220.5
12	1.4×10^{21}	48.7	88	3.4×10^{75}	173.9	4.7×10^{96}	222.6
13	3.3×10^{22}	51.9	87	1.0×10^{75}	172.7	3.5×10^{97}	224.6
⋮	⋮	⋮	⋮	⋮	⋮	⋮	⋮
59	2.2×10^{68}	157.4	41	3.1×10^{46}	107.0	6.7×10^{114}	264.4
60	1.3×10^{69}	159.1	40	5.3×10^{45}	105.3	6.9×10^{114}	264.4
61	7.7×10^{69}	160.9	39	8.8×10^{44}	103.5	6.8×10^{114}	264.4
⋮	⋮	⋮	⋮	⋮	⋮	⋮	⋮
100	1.7×10^{96}	221.6	0	1	0	1.7×10^{96}	221.6

Table 3.1. Macrostates, multiplicities, and entropies of a system of two Einstein solids, one with 300 oscillators and the other with 200, sharing a total of 100 units of energy.
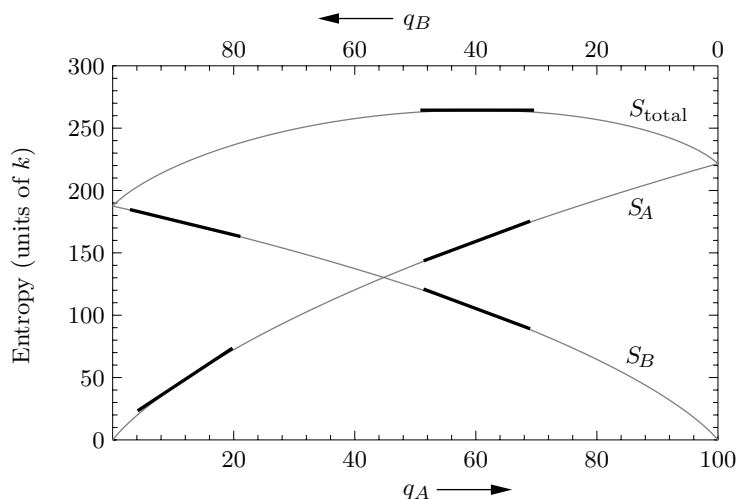
Figure 3.1. A plot of the entropies calculated in Table 3.1. At equilibrium ($q_A = 60$), the total entropy is a maximum so its graph has a horizontal tangent; therefore the slopes of the tangents to the graphs of S_A and S_B are equal in magnitude. Away from equilibrium (for instance, at $q_A = 12$), the solid whose graph has the steeper tangent line tends to gain energy spontaneously; therefore we say that it has the lower temperature.

We can therefore write

$$\frac{\partial S_A}{\partial U_A} = \frac{\partial S_B}{\partial U_B} \qquad \text{at equilibrium.} \tag{3.3}$$

In other words, the thing that's the same for both systems when they're in thermal equilibrium is the *slope* of their entropy vs. energy graphs. This slope must somehow be related to the temperature of a system.

To get a better idea of how temperature is related to the slope of the entropy vs. energy graph, let's look at a point away from equilibrium, for instance, the point $q_A = 12$ in the figure. Here the slope of the S_A graph is considerably steeper than the slope of the S_B graph. This means that if a bit of energy passes from solid B to solid A, the entropy gained by A will be greater than the entropy lost by B. The total entropy will increase, so this process will happen spontaneously, according to the second law. Apparently, the second law tells us that energy will always tend to flow *into* the object with the *steeper* S vs. U graph, and *out of* the object with the *shallower* S vs. U graph. The former really "wants" to gain energy (in order to increase its entropy), while the latter doesn't so much "mind" losing a bit of energy (since its entropy doesn't decrease by much). A steep slope must correspond to a *low* temperature, while a shallow slope must correspond to a *high* temperature.

Now let's look at units. Thanks to the factor of Boltzmann's constant in the definition of entropy, the slope $\partial S/\partial U$ of a system's entropy vs. energy graph has units of $(J/K)/J = 1/K$. If we take the reciprocal of this slope, we get something with units of kelvins, just what we want for temperature. Moreover, we have just

seen that when the slope is large the temperature must be small, and vice versa. I therefore propose the following relation:

$$T \equiv \left(\frac{\partial S}{\partial U}\right)^{-1}. \tag{3.4}$$

The **temperature** of a system is the reciprocal of the slope of its entropy vs. energy graph. The partial derivative is to be taken with the system's volume and number of particles held fixed;* more explicitly,

$$\frac{1}{T} \equiv \left(\frac{\partial S}{\partial U}\right)_{N,V}. \tag{3.5}$$

From now on I will take equation 3.5 to be the *definition* of temperature. (To verify that no further factors of 2 or other numbers are needed in equation 3.5, we need to check an example where we already know the answer. I'll do so on page 91.)

You may be wondering why I don't just turn the derivative upside down, and write equation 3.5 as

$$T = \left(\frac{\partial U}{\partial S}\right)_{N,V}. \tag{3.6}$$

The answer is that there's nothing wrong with this, but it's less convenient in practice, because rarely do you ever have a formula for energy in terms of entropy, volume, and number of particles. However, in numerical examples like in Table 3.1, this version of the formula is just fine. For instance, comparing the two lines in the table for $q_A = 11$ and $q_A = 13$ gives for solid A

$$T_A = \frac{13\epsilon - 11\epsilon}{51.9k - 45.4k} = 0.31 \ \epsilon/k, \tag{3.7}$$

where $\epsilon \ (= hf)$ is the size of each energy unit. If $\epsilon = 0.1$ eV, the temperature is about 360 K. This number is the approximate temperature at $q_A = 12$, in the middle of the small interval considered. (Technically, since a difference of one or two energy units is not infinitesimal compared to 12, the derivative is not precisely defined for this small system. For a large system, this ambiguity will never occur.) Similarly, for solid B,

$$T_B = \frac{89\epsilon - 87\epsilon}{175.1k - 172.7k} = 0.83 \ \epsilon/k. \tag{3.8}$$

As expected, solid B is hotter at this point, since it is the one that will tend to *lose* energy.

It's still not obvious that our new definition of temperature (3.5) is in complete agreement with the *operational* definition given in Section 1.1, that is, with the result that we would get by measuring the temperature with a properly calibrated

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*Volume isn't very relevant for an Einstein solid, although the *size* of the energy units can depend on volume. For some systems there can be other variables, such as magnetic field strength, that must also be held fixed in the partial derivative.

thermometer. If you're skeptical, let me say this: For most practical purposes, the two definitions *are* equivalent. However, any operational definition is of limited scope, since it depends on the physical limitations of the instruments used. In our case, any particular thermometer that you use to "define" temperature will have limitations—it may freeze or melt or something. There are even some systems for which *no* standard thermometer will work; we'll see an example in Section 3.3. So our new definition really is better than the old one, even if it isn't quite the same.

> **Problem 3.1.** Use Table 3.1 to compute the temperatures of solid A and solid B when $q_A = 1$. Then compute both temperatures when $q_A = 60$. Express your answers in terms of ϵ/k, and then in kelvins assuming that $\epsilon = 0.1$ eV.

> **Problem 3.2.** Use the definition of temperature to prove the **zeroth law of thermodynamics**, which says that if system A is in thermal equilibrium with system B, and system B is in thermal equilibrium with system C, then system A is in thermal equilibrium with system C. (If this exercise seems totally pointless to you, you're in good company: Everyone considered this "law" to be completely obvious until 1931, when Ralph Fowler pointed out that it was an unstated assumption of classical thermodynamics.)

A Silly Analogy

To get a better feel for the theoretical definition of temperature (3.5), I like to make a rather silly analogy. Imagine a world, not entirely unlike our own, in which people are constantly exchanging money in their attempts to become happier. They are not merely interested in their *own* happiness, however; each person is actually trying to maximize the *total* happiness of everyone in the community. Now some individuals become much happier when given only a little money. We might call these people "greedy," since they accept money gladly and are reluctant to give any up. Other individuals, meanwhile, become only a little happier when given more money, and only a little sadder upon losing some. These people will be quite generous, giving their money to the more greedy people in order to maximize the total happiness.

The analogy to thermodynamics is as follows. The community corresponds to an isolated system of objects, while the people correspond to the various objects in the system. Money corresponds to *energy*; it is the quantity that is constantly being exchanged, and whose total amount is conserved. Happiness corresponds to *entropy*; the community's overriding goal is to increase its total amount. Generosity corresponds to *temperature*; this is the measure of how willingly someone gives up money (energy). Here is a summary of the analogies:

$$\begin{array}{rcl} \text{money} & \leftrightarrow & \text{energy} \\ \text{happiness} & \leftrightarrow & \text{entropy} \\ \text{generosity} & \leftrightarrow & \text{temperature} \end{array}$$

One can press this analogy even further. Normally, you would expect that as people acquire more money, they become more generous. In thermodynamics, this would mean that as an object's energy increases, so does its temperature. Indeed, most objects behave in this way. Increasing temperature corresponds to a *decreasing*
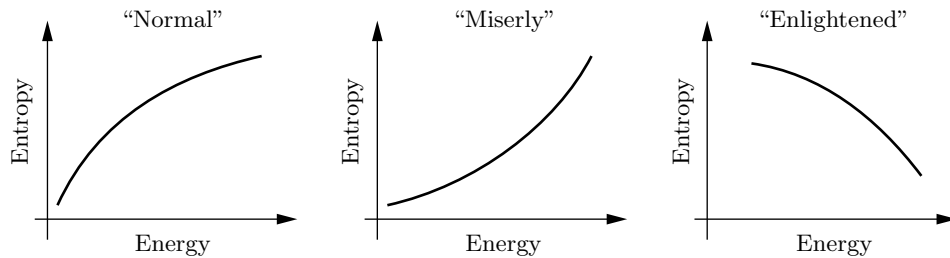
Figure 3.2. Graphs of entropy vs. energy (or happiness vs. money) for a "normal" system that becomes hotter (more generous) as it gains energy; a "miserly" system that becomes colder (less generous) as it gains energy; and an "enlightened" system that doesn't want to gain energy at all.

slope on the entropy vs. energy graph, so the graph for such an object is everywhere concave-down (see Figures 3.1 and 3.2).

However, every community seems to have a few misers who actually become *less* generous as they acquire more money. Similarly, there's no law of physics that prevents an object's temperature from *decreasing* as you add energy. Such an object would have a negative heat capacity; its entropy vs. energy graph would be concave-up. (Collections of particles that are held together by gravity, such as stars and star clusters, behave in exactly this way. Any added energy goes into *potential* energy, as the particles in the system get farther apart and actually slow down. See Problems 1.55, 3.7, and 3.15.)

Even more unusual are those enlightened individuals who become happier as they *lose* money. An analogous thermodynamic system would have an entropy-energy graph with negative slope. This situation is extremely counterintuitive, but does occur in real physical systems, as we'll see in Section 3.3. (The negative-slope portion of the total entropy graph in Figure 3.1 is not an example of "enlightened" behavior; here I'm talking about the equilibrium entropy of a *single* object as a function of its total energy.)

Problem 3.3. Figure 3.3 shows graphs of entropy vs. energy for two objects, A and B. Both graphs are on the same scale. The energies of these two objects initially have the values indicated; the objects are then brought into thermal contact with each other. Explain what happens subsequently and why, *without* using the word "temperature."
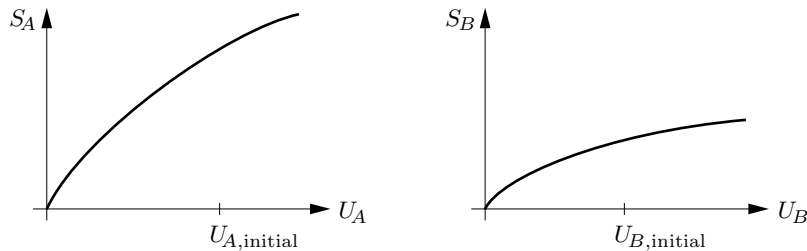

Figure 3.3. Graphs of entropy vs. energy for two objects.

Problem 3.4. Can a "miserly" system, with a concave-up entropy-energy graph, ever be in stable thermal equilibrium with another system? Explain.

Real-World Examples

The theoretical definition of temperature isn't just interesting and intuitive—it is also useful. If you have an explicit formula for the entropy of an object as a function of energy, you can easily calculate its temperature (also as a function of energy).

Perhaps the simplest realistic example is a large Einstein solid, in the limit $q \gg N$ (where N is the number of oscillators). The total energy U is just q times some constant that I'll call ϵ. I computed the entropy in equation 2.46:

$$S = Nk[\ln(q/N) + 1] = Nk \ln U - Nk \ln(\epsilon N) + Nk. \tag{3.9}$$

Therefore the temperature should be

$$T = \left(\frac{\partial S}{\partial U}\right)^{-1} = \left(\frac{Nk}{U}\right)^{-1}, \tag{3.10}$$

in other words,

$$U = NkT. \tag{3.11}$$

But this result is exactly what the equipartition theorem would predict: The total energy should be $\frac{1}{2}kT$ times the number of degrees of freedom, and an Einstein solid has two degrees of freedom for every oscillator. (This result verifies that no factors of 2 or other constants are needed in equation 3.5.)

As another example, let us compute the temperature of a monatomic ideal gas. Recall from equation 2.49 that the entropy is

$$S = Nk \ln V + Nk \ln U^{3/2} + (\text{a function of } N) \tag{3.12}$$

(where N is the number of molecules). The temperature is therefore

$$T = \left(\frac{\frac{3}{2}Nk}{U}\right)^{-1}. \tag{3.13}$$

Solving this equation for U gives $U = \frac{3}{2}NkT$, again verifying the equipartition theorem. (At this point we could reverse the logic of Section 1.2 and *derive* the ideal gas law, starting from the formula for U. Instead, however, I'll wait until Section 3.4, and derive the ideal gas law from a much more general formula for pressure.)

Problem 3.5. Starting with the result of Problem 2.17, find a formula for the temperature of an Einstein solid in the limit $q \ll N$. Solve for the energy as a function of temperature to obtain $U = N\epsilon\, e^{-\epsilon/kT}$ (where ϵ is the size of an energy unit).

Problem 3.6. In Section 2.5 I quoted a theorem on the multiplicity of any system with only quadratic degrees of freedom: In the high-temperature limit where the number of units of energy is much larger than the number of degrees of freedom, the multiplicity of any such system is proportional to $U^{Nf/2}$, where Nf is the total number of degrees of freedom. Find an expression for the energy of such a system in terms of its temperature, and comment on the result. How can you tell that this formula for Ω cannot be valid when the total energy is very small?

Problem 3.7. Use the result of Problem 2.42 to calculate the temperature of a black hole, in terms of its mass M. (The energy is Mc^2.) Evaluate the resulting expression for a one-solar-mass black hole. Also sketch the entropy as a function of energy, and discuss the implications of the shape of the graph.

3.2 Entropy and Heat

Predicting Heat Capacities

In the preceding section we saw how to calculate the temperature as a function of energy (or vice versa) for any system for which we have an explicit formula for the multiplicity. To compare these predictions to experiments, we can differentiate the function $U(T)$ to obtain the heat capacity at constant volume (or simply "energy capacity"):

$$C_V \equiv \left(\frac{\partial U}{\partial T} \right)_{N,V}. \tag{3.14}$$

For an Einstein solid with $q \gg N$ the heat capacity is

$$C_V = \frac{\partial}{\partial T}(NkT) = Nk, \tag{3.15}$$

while for a monatomic ideal gas,

$$C_V = \frac{\partial}{\partial T}(\tfrac{3}{2}NkT) = \tfrac{3}{2}Nk. \tag{3.16}$$

In both of these systems, the heat capacity is independent of the temperature and is simply equal to $k/2$ times the number of degrees of freedom. These results agree with experimental measurements of heat capacities of low-density monatomic gases and of solids at reasonably high temperatures. However, other systems can have much more complicated behavior. One example is the subject of Section 3.3; others are treated in the problems.

Before considering more complicated examples, let me pause and list the steps you have to go through in order to predict the heat capacity of a system using the tools we have developed:

1. Use quantum mechanics and some combinatorics to find an expression for the multiplicity, Ω, in terms of U, V, N, and any other relevant variables.

2. Take the logarithm to find the entropy, S.

3. Differentiate S with respect to U and take the reciprocal to find the temperature, T, as a function of U and other variables.

4. Solve for U as a function of T (and other variables).

5. Differentiate $U(T)$ to obtain a prediction for the heat capacity (with the other variables held fixed).

This procedure is rather intricate, and for most systems, you're likely to get stuck at step 1. In fact, there are very few systems for which I know how to write down an explicit formula for the multiplicity: the two-state paramagnet, the Einstein solid, the monatomic ideal gas, and a few others that are mathematically similar to these. In Chapter 6 I'll show you an alternative route to step 4, yielding a formula for $U(T)$ without the need to know the multiplicity or the entropy. Meanwhile, we can still learn plenty from the simple examples that I've already introduced.

> **Problem 3.8.** Starting with the result of Problem 3.5, calculate the heat capacity of an Einstein solid in the low-temperature limit. Sketch the predicted heat capacity as a function of temperature. (Note: Measurements of heat capacities of actual solids at low temperatures do not confirm the prediction that you will make in this problem. A more accurate model of solids at low temperatures is presented in Section 7.5.)

Measuring Entropies

Even if you can't write down a mathematical *formula* for the entropy of a system, you can still *measure* it, essentially by following steps 3–5 in reverse. According to the theoretical definition (3.5) of temperature, if you add a bit of heat Q to a system while holding its volume constant and doing no other forms of work, its entropy changes by

$$dS = \frac{dU}{T} = \frac{Q}{T} \qquad \text{(constant volume, no work).} \tag{3.17}$$

Since heat and temperature are usually pretty easy to measure, this relation allows us to compute the change in entropy for a wide variety of processes.* In Section 3.4 I'll show that the relation $dS = Q/T$ also applies when the volume *is* changing, provided that the process is quasistatic.

If the temperature of an object remains constant as heat is added to it (as during a phase change), then equation 3.17 can be applied even when Q and dS are not infinitesimal. When T is changing, however, it's usually more convenient to write the relation in terms of the heat capacity at constant volume:

$$dS = \frac{C_V \, dT}{T}. \tag{3.18}$$

Now perhaps you can see what to do if the temperature changes significantly as the heat is added. Imagine the process as a sequence of tiny steps, compute dS for

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*Equation 3.17 assumes not only fixed volume, but also fixed values of N and any other variables held fixed in equation 3.5. It also assumes that T doesn't vary *within* the system; internal temperature variations would cause internal heat flow and thus further increases in entropy.

each step, and add them up to get the total change in entropy:

$$\Delta S = S_f - S_i = \int_{T_i}^{T_f} \frac{C_V}{T}\, dT. \tag{3.19}$$

Often C_V is fairly constant over the temperature range of interest, and you can take it out of the integral. In other cases, especially at low temperatures, C_V changes quite a bit and must be left inside the integral.

Here's a quick example. Suppose you heat a cup (200 g) of water from 20°C to 100°C. By how much does its entropy increase? Well, the heat capacity of 200 g of water is 200 cal/K or about 840 J/K, and is essentially independent of temperature over this range. Therefore the increase in entropy is

$$\Delta S = (840 \text{ J/K}) \int_{293\,\text{K}}^{373\,\text{K}} \frac{1}{T}\, dT = (840 \text{ J/K}) \ln\!\left(\frac{373}{293}\right) = 200 \text{ J/K}. \tag{3.20}$$

This may not seem like a huge increase, but in fundamental units (dividing by Boltzmann's constant) it's an increase of 1.5×10^{25}. And this means that the *multiplicity* of the system increases by a *factor* of $e^{1.5 \times 10^{25}}$ (a very large number).

If you're lucky enough to know C_V all the way down to absolute zero, you can calculate a system's *total* entropy simply by taking zero as the lower limit of the integral:

$$S_f - S(0) = \int_0^{T_f} \frac{C_V}{T}\, dT. \tag{3.21}$$

But what is $S(0)$? In principle, zero. At zero temperature a system should settle into its unique lowest-energy state, so $\Omega = 1$ and $S = 0$. This fact is often called the **third law of thermodynamics**.

In practice, however, there can be several reasons why $S(0)$ is effectively nonzero. Most importantly, in some solid crystals it is possible to change the orientations of the molecules with very little change in energy. Water molecules, for example, can orient themselves in several possible ways within an ice crystal. Technically, one particular arrangement will always have a lower energy than any other, but in practice the arrangements are often random or nearly random, and you would have to wait eons for the crystal to rearrange itself into the true ground state. We then say that the solid has a frozen-in **residual entropy**, equal to k times the logarithm of the number of possible molecular arrangements.

Another form of residual entropy comes from the mixing of different nuclear isotopes of an element. Most elements have more than one stable isotope, but in natural systems these isotopes are mixed together randomly, with an associated entropy of mixing. Again, at $T = 0$ there should be a unique lowest-energy state in which the isotopes are unmixed or are distributed in some orderly way, but in practice the atoms are always stuck at their random sites in the crystal lattice.*

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*An important exception is helium, which remains a liquid at $T = 0$, allowing the two isotopes (^{3}He and ^{4}He) to arrange themselves in an orderly way.

A third type of "residual" entropy comes from the multiplicity of alignments of nuclear spins. At $T = 0$ this entropy *does* disappear as the spins align parallel or antiparallel to their neighbors. But this generally doesn't happen until the temperature is less than a tiny fraction of 1 K, far below the range of routine heat capacity measurements.

Entropies of a wide variety of substances have been computed from measured heat capacities using equation 3.21, and are tabulated in standard reference works. (A few dozen values are included at the back of this book.) By convention, tabulated entropies do include any residual entropy due to molecular orientations, but do not include any entropy of isotopic mixing or of nuclear spin orientations. (The tables are generally compiled by chemists, who don't care much about nuclei.)

You might be worried that the integral in formula 3.21 appears to *diverge* at its lower limit, because of the T in the denominator of the integrand. If it did diverge, either S_f would be infinity or $S(0)$ would be negative infinity. Entropy, however, must always be finite and positive, according to our original definition $S = k \ln \Omega$. The only way out is if C_V also goes to zero at $T = 0$:

$$C_V \to 0 \qquad \text{as} \qquad T \to 0. \tag{3.22}$$

This result is also sometimes called the **third law of thermodynamics**. Apparently, our earlier results (3.15 and 3.16) for the heat capacities of an Einstein solid and an ideal gas *cannot* be correct at very low temperatures. Instead, all degrees of freedom must "freeze out." This is what you should have found in Problem 3.8; we'll see many other examples throughout the rest of this book.

> **Problem 3.9.** In solid carbon monoxide, each CO molecule has two possible orientations: CO or OC. Assuming that these orientations are completely random (not quite true but close), calculate the residual entropy of a mole of carbon monoxide.

The Macroscopic View of Entropy

Historically, the relation $dS = Q/T$ was the original *definition* of entropy. In 1865, Rudolf Clausius defined entropy to be the thing that increases by Q/T whenever heat Q enters a system at temperature T. Although this definition tells us nothing about what entropy actually *is*, it is still sufficient for many purposes, when the microscopic makeup of a system does not concern us.

To illustrate this traditional view of entropy, consider again what happens when a hot object, A, is put in thermal contact with a cold object, B (see Figure 3.4). To be specific, suppose that $T_A = 500$ K and $T_B = 300$ K. From experience we know that heat will flow from A to B. Let's say that during some time interval the amount of heat that flows is 1500 J, and that A and B are large enough objects that their temperatures don't change significantly due to the loss or gain of this amount of energy. Then during this time interval, the entropy of A changes by

$$\Delta S_A = \frac{-1500 \text{ J}}{500 \text{ K}} = -3 \text{ J/K}. \tag{3.23}$$
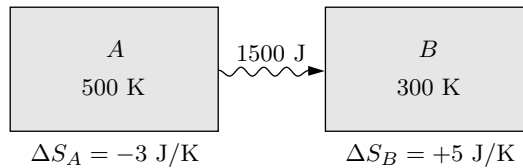
Figure 3.4. When 1500 J of heat leaves a 500 K object, its entropy decreases by 3 J/K. When this same heat enters a 300 K object, its entropy increases by 5 J/K.

Object *A* *loses* entropy, because heat is flowing *out* of it. Similarly, the entropy of *B* changes by

$$\Delta S_B = \frac{+1500 \text{ J}}{300 \text{ K}} = +5 \text{ J/K}. \tag{3.24}$$

Object *B* *gains* entropy, because heat is flowing *into* it. (Notice that the traditional entropy unit of J/K is quite convenient when we compute entropy changes in this way.)

Just as I often visualize energy as a "fluid" that can change forms and move around but never be created or destroyed, I sometimes imagine entropy, as well, to be a fluid. I imagine that, whenever energy enters or leaves a system in the form of heat, it is required (by law) to carry some entropy with it, in the amount Q/T. The weird thing about entropy, though, is that it is only half-conserved: It cannot be destroyed, but it *can* be created, and in fact, new entropy *is* created whenever heat flows between objects at different temperatures. As in the numerical example above, the entropy that is "carried by" the heat is more when it arrives at the cooler object than it was when it left the hotter object (see Figure 3.5). Only in the limit where there is no temperature difference between the two objects will no new entropy be created. In this limit, however, there is no tendency of heat to flow in the first place. It's important to remember that fundamentally, the net increase
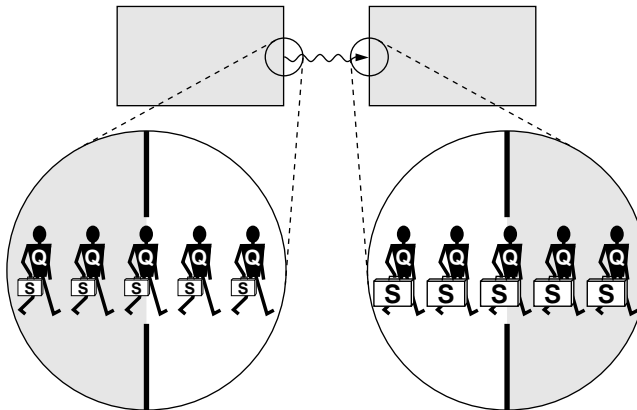

Figure 3.5. Each unit of heat energy (Q) that leaves a hot object is required to carry some entropy (Q/T) with it. When it enters a cooler object, the amount of entropy has increased.

in entropy is the driving force behind the flow of heat. Fundamentally, though, entropy isn't a fluid at all and my model is simply wrong.

Problem 3.10. An ice cube (mass 30 g) at $0°$C is left sitting on the kitchen table, where it gradually melts. The temperature in the kitchen is $25°$C.

   (a) Calculate the change in the entropy of the ice cube as it melts into water at $0°$C. (Don't worry about the fact that the volume changes somewhat.)

   (b) Calculate the change in the entropy of the water (from the melted ice) as its temperature rises from $0°$C to $25°$C.

   (c) Calculate the change in the entropy of the kitchen as it gives up heat to the melting ice/water.

   (d) Calculate the net change in the entropy of the universe during this process. Is the net change positive, negative, or zero? Is this what you would expect?

Problem 3.11. In order to take a nice warm bath, you mix 50 liters of hot water at $55°$C with 25 liters of cold water at $10°$C. How much new entropy have you created by mixing the water?

Problem 3.12. Estimate the change in the entropy of the universe due to heat escaping from your home on a cold winter day.

Problem 3.13. When the sun is high in the sky, it delivers approximately 1000 watts of power to each square meter of earth's surface. The temperature of the surface of the sun is about 6000 K, while that of the earth is about 300 K.

   (a) Estimate the entropy created in one year by the flow of solar heat onto a square meter of the earth.

   (b) Suppose you plant grass on this square meter of earth. Some people might argue that the growth of the grass (or of any other living thing) violates the second law of thermodynamics, because disorderly nutrients are converted into an orderly life form. How would you respond?

Problem 3.14. Experimental measurements of the heat capacity of aluminum at low temperatures (below about 50 K) can be fit to the formula

$$C_V = aT + bT^3,$$

where C_V is the heat capacity of one mole of aluminum, and the constants a and b are approximately $a = 0.00135$ J/K^2 and $b = 2.48 \times 10^{-5}$ J/K^4. From this data, find a formula for the entropy of a mole of aluminum as a function of temperature. Evaluate your formula at $T = 1$ K and at $T = 10$ K, expressing your answers both in conventional units (J/K) and as unitless numbers (dividing by Boltzmann's constant). [Comment: In Chapter 7 I'll explain why the heat capacity of a metal has this form. The linear term comes from energy stored in the conduction electrons, while the cubic term comes from lattice vibrations of the crystal.]

Problem 3.15. In Problem 1.55 you used the virial theorem to estimate the heat capacity of a star. Starting with that result, calculate the entropy of a star, first in terms of its average temperature and then in terms of its total energy. Sketch the entropy as a function of energy, and comment on the shape of the graph.

Problem 3.16. A **bit** of computer memory is some physical object that can be in two different states, often interpreted as 0 and 1. A **byte** is eight bits, a **kilobyte** is 1024 ($= 2^{10}$) bytes, a **megabyte** is 1024 kilobytes, and a **gigabyte** is 1024 megabytes.

(a) Suppose that your computer erases or overwrites one gigabyte of memory, keeping no record of the information that was stored. Explain why this process must create a certain minimum amount of entropy, and calculate how much.

(b) If this entropy is dumped into an environment at room temperature, how much heat must come along with it? Is this amount of heat significant?

3.3 Paramagnetism

At the beginning of the previous section I outlined a five-step procedure for predicting the thermal properties of a material, starting from a combinatoric formula for the multiplicity and applying the definitions of entropy and temperature. I also carried out this procedure for two particular model systems: a monatomic ideal gas, and an Einstein solid in the high-temperature limit ($q \gg N$). Both of these examples, however, were very simple mathematically, and merely verified the equipartition theorem. Next I would like to work out a more complicated example, where the equipartition theorem does not apply at all. This example will be more interesting mathematically, and also rather counterintuitive physically.

The system that I want to discuss is the **two-state paramagnet**, introduced briefly in Section 2.1. I'll start by reviewing the basic microscopic physics.

Notation and Microscopic Physics

The system consists of N spin-1/2 particles, immersed in a constant magnetic field $\vec{B}$ pointing in the $+z$ direction (see Figure 3.6). Each particle behaves like a little compass needle, feeling a torque that tries to align its magnetic dipole moment with the field. Because of this behavior I'll refer to the particles as **dipoles**. For simplicity I'll assume that there are *no* interactions *between* dipoles—each dipole feels only the torque from the external field. In this case we say that the system is an **ideal** paramagnet.

According to quantum mechanics, the component of a particle's dipole moment along a given axis cannot take on just any value—instead it is **quantized**, that is, limited to certain discrete values. For a spin-1/2 particle only *two* values are allowed, which I'll call simply "up" and "down" (along the z axis). The magnetic
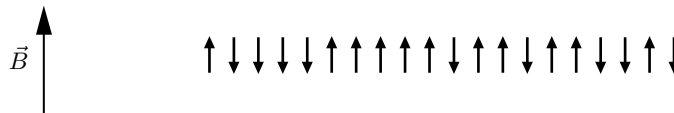

Figure 3.6. A two-state paramagnet, consisting of N microscopic magnetic dipoles, each of which is either "up" or "down" at any moment. The dipoles respond only to the influence of the external magnetic field B; they do not interact with their neighbors (except to exchange energy).

Energy

Figure 3.7. The energy levels of a single dipole in an ideal two-state paramagnet are $-\mu B$ (for the "up" state) and $+\mu B$ (for the "down" state).

$+\mu B$ ——— "Down"

0

$-\mu B$ ——— "Up"
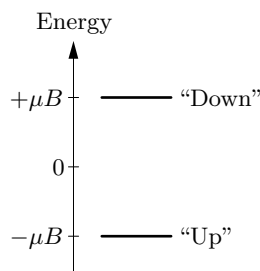
field, pointing in the $+z$ direction, gives each dipole a preference for the *up* state. To flip a single dipole from up to down we would have to add some energy; the amount of energy required is $2\mu B$, where μ is a constant related to the particle's magnetic moment (essentially the "strength" of the effective compass needle). For the sake of symmetry, I'll say that the energy of a dipole that points up is $-\mu B$, so that the energy of a dipole that points down is $+\mu B$ (see Figure 3.7).

The *total* energy of the system is

$$U = \mu B(N_\downarrow - N_\uparrow) = \mu B(N - 2N_\uparrow), \tag{3.25}$$

where $N_\uparrow$ and $N_\downarrow$ are the numbers of up and down dipoles, respectively, and $N = N_\uparrow + N_\downarrow$. I'll define the **magnetization**, M, to be the total magnetic moment of the whole system. Each "up" dipole has magnetic moment $+\mu$ and each "down" dipole has magnetic moment $-\mu$, so the magnetization can be written

$$M = \mu(N_\uparrow - N_\downarrow) = -\frac{U}{B}. \tag{3.26}$$

We would like to know how U and M depend on temperature.

Our first task is to write down a formula for the multiplicity. We will keep N fixed, and consider each different value of $N_\uparrow$ (and hence U and M) to define a different macrostate. Then this system is mathematically equivalent to a collection of N coins with $N_\uparrow$ heads, and the multiplicity is simply

$$\Omega(N_\uparrow) = \binom{N}{N_\uparrow} = \frac{N!}{N_\uparrow!N_\downarrow!}. \tag{3.27}$$

Numerical Solution

For reasonably small systems, one can just evaluate the multiplicity (3.27) directly, take the logarithm to find the entropy, and so on. Table 3.2 shows part of a computer-generated table of numbers for a paramagnet consisting of 100 elementary dipoles. There is one row in the table for each possible energy value; the rows are written in order of increasing energy, starting with the macrostate with all the dipoles pointing up.

$N_\uparrow$	$U/\mu B$	$M/N\mu$	Ω	S/k	$kT/\mu B$	C/Nk
100	-100	1.00	1	0	0	—
99	-98	.98	100	4.61	.47	.074
98	-96	.96	4950	8.51	.54	.310
97	-94	.94	1.6×10^5	11.99	.60	.365
$\vdots$	$\vdots$	$\vdots$	$\vdots$	$\vdots$	$\vdots$	$\vdots$
52	-4	.04	9.3×10^{28}	66.70	25.2	.001
51	-2	.02	9.9×10^{28}	66.76	50.5	—
50	0	0	1.0×10^{29}	66.78	∞	—
49	2	$-.02$	9.9×10^{28}	66.76	-50.5	—
48	4	$-.04$	9.3×10^{28}	66.70	-25.2	.001
$\vdots$	$\vdots$	$\vdots$	$\vdots$	$\vdots$	$\vdots$	$\vdots$
1	98	$-.98$	100	4.61	$-.47$	.074
0	100	-1.00	1	0	0	—

Table 3.2. Thermodynamic properties of a two-state paramagnet consisting of 100 elementary dipoles. Microscopic physics determines the energy U and total magnetization M in terms of the number of dipoles pointing up, $N_\uparrow$. The multiplicity Ω is calculated from the combinatoric formula 3.27, while the entropy S is $k \ln \Omega$. The last two columns show the temperature and the heat capacity, calculated by taking derivatives as explained in the text.

The behavior of the entropy as a function of energy is particularly interesting, as shown in Figure 3.8. The largest multiplicity and largest entropy occur at $U = 0$, when exactly half of the dipoles point down. As more energy is added to the system, the multiplicity and entropy actually *decrease*, since there are fewer ways to arrange the energy. This behavior is very different from that of a "normal" system such as an Einstein solid (as discussed in Section 3.1).

Let's look at this behavior in more detail. Suppose the system starts out in its minimum-energy state, with all the dipoles pointing up. Here the entropy-energy graph is very steep, so the system has a strong tendency to absorb energy from its environment. As its energy increases (but is still negative), the entropy-energy graph becomes shallower, so the tendency to absorb energy decreases, just as for an Einstein solid or any other "normal" system. However, as the energy of the paramagnet goes to zero, so does the slope of its entropy-energy graph, so its tendency to absorb more energy actually disappears. At this point, exactly half of the dipoles point down, and the system "couldn't care less" whether its energy increases a bit more or not. If we now add a bit more energy to the system, it behaves in a most unusual way. The slope of its entropy-energy graph becomes negative, so it will spontaneously give up energy to any nearby object whose entropy-energy graph has a positive slope. (Remember, any allowed process that increases the *total* entropy will happen spontaneously.)

In the preceding paragraph I have intentionally avoided any mention of "temperature." But now let's think about the temperature of this system as a function of energy. When more than half of the dipoles point up, so the total energy is
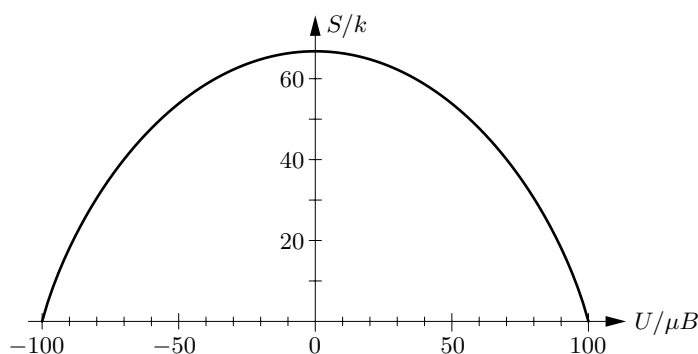
Figure 3.8. Entropy as a function of energy for a two-state paramagnet consisting of 100 elementary dipoles.

negative, this system behaves "normally": Its temperature (the reciprocal of the slope of the entropy-energy graph) increases as energy is added. In the analogy of Section 3.1, the system becomes more "generous" with increasing energy. When $U = 0$, however, the temperature is actually *infinite*, meaning that this system will gladly give up energy to *any* other system whose temperature is finite. The paramagnet is infinitely generous. At still higher energies, we would like to say that its generosity is "higher than infinity," but technically, our definition of temperature says that T is *negative* (since the slope is negative). There's nothing *wrong* with this conclusion, but we have to remember that negative temperatures behave as if they are *higher* than positive temperatures, since a system with negative temperature will give up energy to any system with positive temperature. It would be better, in this example, if we talked about $1/T$ (analogous to "greediness") instead of T. At zero energy, the system has zero greediness, while at higher energies it has negative greediness. A graph of temperature vs. energy is shown in Figure 3.9.

Negative temperatures can occur only for a system whose total energy is limited, so that the multiplicity decreases as the maximum allowed energy is approached. The best examples of such systems are *nuclear* paramagnets, in which the magnetic
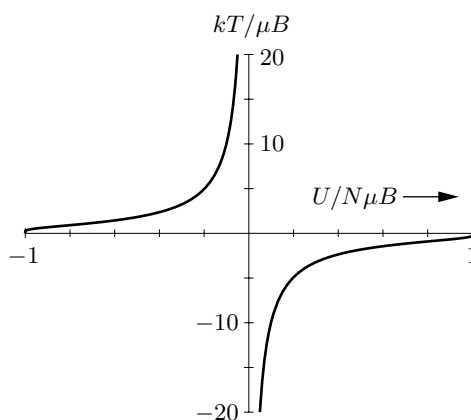
Figure 3.9. Temperature as a function of energy for a two-state paramagnet. (This graph was plotted from the analytic formulas derived later in the text; a plot of the data in Table 3.2 would look similar but less smooth.)

dipoles are the atomic nuclei rather than the electrons. In certain crystals the relaxation time for the nuclear dipoles (exchanging energy with each other) can be much shorter than the relaxation time for the nuclear dipoles to equilibrate with the crystal lattice. Therefore, on short time scales, the dipoles behave as an isolated system with only magnetic energy, no vibrational energy. To give such a system a negative temperature, all you have to do is start at any positive temperature, with most of the dipoles parallel to the magnetic field, then suddenly reverse the field so they're antiparallel. This experiment was first performed by Edward M. Purcell and R. V. Pound in 1951, using the lithium nuclei in a lithium fluoride crystal as the system of dipoles. In their original experiment the nuclear dipoles came to thermal equilibrium among themselves in only 10^{-5} seconds, but required approximately five minutes, after the field reversal, to return to equilibrium with the room-temperature crystal lattice.[*]

I like the example of the paramagnet, with its negative temperatures and other unusual behavior, because it forces us to think primarily in terms of *entropy* rather than temperature. Entropy is the more fundamental quantity, governed by the second law of thermodynamics. Temperature is less fundamental; it is merely a characterization of a system's "willingness" to give up energy, that is, of the relationship between its energy and entropy.

The sixth column of Table 3.2 lists numerical values of the temperature of this system as a function of energy. I computed each of these using the formula $T = \Delta U/\Delta S$, taking the U and S values from neighboring rows. (To be more precise, I used a "centered-difference" approximation, subtracting the values in the preceding row from those in the following row. So, for instance, the number .47 was computed as $[(-96) - (-100)]/[8.51 - 0]$.) In the last column I've taken another derivative to obtain the heat capacity, $C = \Delta U/\Delta T$. Figure 3.10 shows graphs of the heat capacity and the magnetization vs. temperature. Notice that the heat capacity of this system depends strongly on its temperature, quite unlike the constant values predicted by the equipartition theorem for more familiar systems. At zero temperature the heat capacity goes to zero, as required by the third law of thermodynamics. The heat capacity also goes to zero as T approaches infinity, since at that point only a tiny amount of energy is required to achieve a very large increase in temperature.

The behavior of the magnetization as a function of temperature is also interesting. At zero (positive) temperature the system is "saturated," with all the dipoles pointing up and maximum magnetization. As the temperature increases, random jostling tends to flip more and more dipoles. You might expect that as $T \to \infty$, the energy would be maximized with all the dipoles pointing down, but this is not the

---

[*]For a more detailed description of this experiment, see the fifth (1968) or sixth (1981) edition of *Heat and Thermodynamics* by Zemansky (with Dittman as coauthor on the sixth edition). The original (very short) letter describing the experiment is published in *Physical Review* **81**, 279 (1951). For an even more dramatic example of negative temperature, see Pertti Hakonen and Olli V. Lounasmaa, *Science* **265**, 1821–1825 (23 September, 1994).
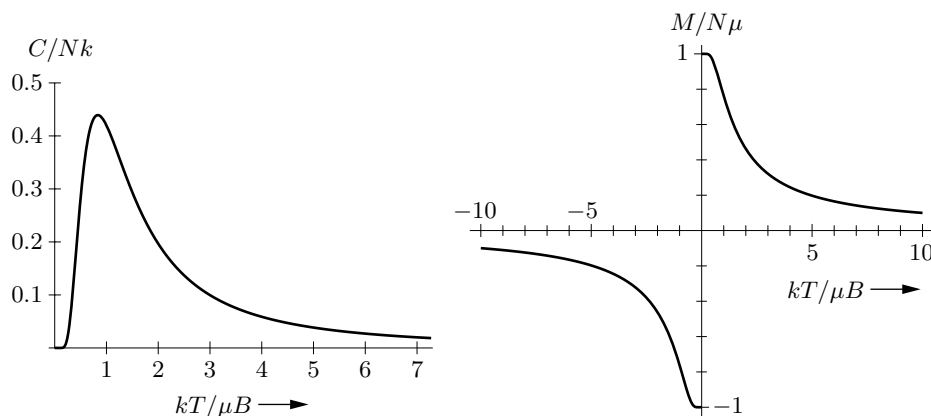
Figure 3.10. Heat capacity and magnetization of a two-state paramagnet (computed from the analytic formulas derived later in the text).

case; instead, $T = \infty$ corresponds to the state of maximum "randomness," with exactly half the dipoles pointing down. The behavior at negative temperature is essentially a mirror image of the positive-T behavior, with the magnetization again saturating, but in the opposite direction, as $T \to 0$ from below.

Problem 3.17. Verify every entry in the third line of Table 3.2 (starting with $N_\uparrow = 98$).

Problem 3.18. Use a computer to reproduce Table 3.2 and the associated graphs of entropy, temperature, heat capacity, and magnetization. (The graphs in this section are actually drawn from the analytic formulas derived below, so your numerical graphs won't be quite as smooth.)

Analytic Solution

Now that we have studied most of the physics of this system through numerical calculations, let us go back and use analytic methods to derive some more general formulas to describe these phenomena.

I will assume that the number of elementary dipoles is *large*, and also that at any given time the numbers of up and down dipoles are separately large. Then we can simplify the multiplicity function (3.27) using Stirling's approximation. Actually, it's easiest to just calculate the entropy:

$$
\begin{aligned}
S/k &= \ln N! - \ln N_\uparrow! - \ln(N - N_\uparrow)! \\
&\approx N \ln N - N - N_\uparrow \ln N_\uparrow + N_\uparrow - (N{-}N_\uparrow) \ln(N{-}N_\uparrow) + (N{-}N_\uparrow) \qquad (3.28) \\
&= N \ln N - N_\uparrow \ln N_\uparrow - (N{-}N_\uparrow) \ln(N{-}N_\uparrow).
\end{aligned}
$$

From here on the calculations are fairly straightforward but somewhat tedious. I'll outline the logic and the results, but let you fill in some of the algebraic steps (see Problem 3.19).

To find the temperature, we must differentiate S with respect to U. It is simplest to first use the chain rule and equation 3.25 to express the derivative in terms of $N_\uparrow$:

$$\frac{1}{T} = \left(\frac{\partial S}{\partial U}\right)_{N,B} = \frac{\partial N_\uparrow}{\partial U}\frac{\partial S}{\partial N_\uparrow} = -\frac{1}{2\mu B}\frac{\partial S}{\partial N_\uparrow}. \tag{3.29}$$

Now just differentiate the last line of equation 3.28 to obtain

$$\frac{1}{T} = \frac{k}{2\mu B}\ln\left(\frac{N - U/\mu B}{N + U/\mu B}\right). \tag{3.30}$$

Notice from this formula that T and U always have opposite signs.

Equation 3.30 can be solved for U to obtain

$$U = N\mu B\left(\frac{1 - e^{2\mu B/kT}}{1 + e^{2\mu B/kT}}\right) = -N\mu B\tanh\left(\frac{\mu B}{kT}\right), \tag{3.31}$$

where tanh is the hyperbolic tangent function.* The magnetization is therefore

$$M = N\mu\tanh\left(\frac{\mu B}{kT}\right). \tag{3.32}$$

The hyperbolic tangent function is plotted in Figure 3.11; it rises from the origin with a slope of 1, then flattens to an asymptotic value of 1 as its argument goes to infinity. So at very small positive temperatures the system is completely magnetized (as we saw before), while as $T \to \infty$, the magnetization goes to zero. To obtain negative temperature, all we need to do is give the system a negative magnetization, as described above.
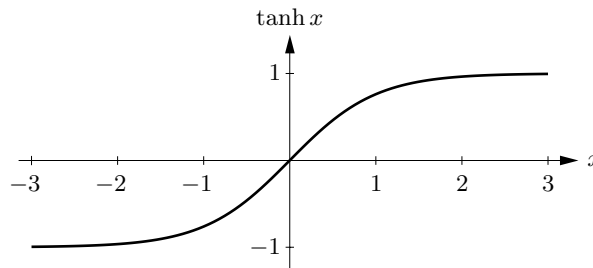

Figure 3.11. The hyperbolic tangent function. In the formulas for the energy and magnetization of a two-state paramagnet, the argument x of the hyperbolic tangent is $\mu B/kT$.

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*The definitions of the basic hyperbolic functions are $\sinh x = \frac{1}{2}(e^x - e^{-x})$, $\cosh x = \frac{1}{2}(e^x + e^{-x})$, and $\tanh x = (\sinh x)/(\cosh x)$. From these definitions you can easily show that $\frac{d}{dx}\sinh x = \cosh x$ and $\frac{d}{dx}\cosh x = \sinh x$ (with no minus sign).

To calculate the heat capacity of the paramagnet, just differentiate equation 3.31 with respect to T:

$$C_B = \left(\frac{\partial U}{\partial T}\right)_{N,B} = Nk \cdot \frac{(\mu B/kT)^2}{\cosh^2(\mu B/kT)}. \tag{3.33}$$

This function approaches zero at both low and high T, as we also saw in the numerical solution.

In a real-world paramagnet, the individual dipoles can be either electrons or atomic nuclei. Electronic paramagnetism occurs when there are electrons with angular momentum (orbital or spin) that is not compensated by other electrons; the circular currents then give rise to magnetic dipole moments. The number of possible states for each dipole is always some small integer, depending on the total angular momentum of all the electrons in an atom or molecule. The simple case considered here, with just two states, occurs when there is just one electron per atom whose spin is uncompensated. Ordinarily this electron would also have orbital angular momentum, but in some environments the orbital motion is "quenched" by the neighboring atoms, leaving only the spin angular momentum.

For an electronic two-state paramagnet the value of the constant μ is the **Bohr magneton**,

$$\mu_{\mathrm{B}} \equiv \frac{eh}{4\pi m_e} = 9.274 \times 10^{-24} \text{ J/T} = 5.788 \times 10^{-5} \text{ eV/T}. \tag{3.34}$$

(Here e is the electron's charge and m_e is its mass.) If we take $B = 1$ T (a pretty strong magnet), then $\mu B = 5.8 \times 10^{-5}$ eV. But at room temperature, $kT \approx 1/40$ eV. So at ordinary temperatures (more than a few kelvins), we can assume $\mu B/kT \ll 1$. In this limit, $\tanh x \approx x$, so the magnetization becomes

$$M \approx \frac{N\mu^2 B}{kT} \qquad \text{(when } \mu B \ll kT\text{)}. \tag{3.35}$$

The fact that $M \propto 1/T$ was discovered experimentally by Pierre Curie and is known as **Curie's law**; it holds in the high-temperature limit for all paramagnets, even those with more than two angular momentum states. In this limit the heat capacity falls off in proportion to $1/T^2$.

Figure 3.12 shows experimental values of the magnetization of a real two-state paramagnet, an organic free radical known as DPPH.* To minimize interactions *between* the elementary dipoles, the DPPH was diluted with benzene to form a 1:1 crystalline complex. Notice that the magnetization follows Curie's law very closely

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*The full name is α, α'-diphenyl-β-picrylhydrazyl, if you really want to know. This rather large molecule is paramagnetic because there is a nitrogen atom in the middle of it with an unpaired electron.
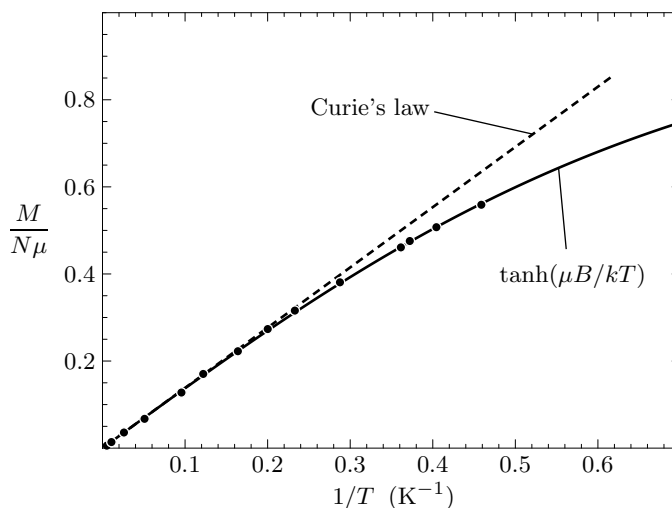
Figure 3.12. Experimental measurements of the magnetization of the organic free radical "DPPH" (in a 1:1 complex with benzene), taken at $B = 2.06$ T and temperatures ranging from 300 K down to 2.2 K. The solid curve is the prediction of equation 3.32 (with $\mu = \mu_B$), while the dashed line is the prediction of Curie's law for the high-temperature limit. (Because the effective number of elementary dipoles in this experiment was uncertain by a few percent, the vertical scale of the theoretical graphs has been adjusted to obtain the best fit.) Adapted from P. Grobet, L. Van Gerven, and A. Van den Bosch, *Journal of Chemical Physics* **68**, 5225 (1978).

down to temperatures of a few kelvins, but then deviates to follow the prediction of equation 3.32 as the total magnetization approaches its maximum possible value.*

For a *nuclear* paramagnet, a typical value of μ can be found by replacing the electron mass with the proton mass in expression 3.34 for the Bohr magneton. Since a proton is nearly 2000 times heavier than an electron, μ is typically smaller for nuclei by a factor of about 2000. This means that to achieve the same degree of magnetization you would need to either make the magnetic field 2000 times stronger, or make the temperature 2000 times lower. Laboratory magnets are

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*This data is the best I could find for a nearly ideal *two*-state paramagnet. Ideal paramagnets with *more* than two states per dipole turn out to be more common, or at least easier to prepare. The most extensively studied examples are salts in which the paramagnetic ions are either transition metals or rare earths, with unfilled inner electron shells. To minimize interactions between neighboring ions, they are diluted with large numbers of magnetically inert atoms. An example is iron ammonium alum, $Fe_2(SO_4)_3 \cdot (NH_4)_2SO_4 \cdot 24H_2O$, in which there are 23 inert atoms (not counting the very small hydrogens) for each paramagnetic Fe^{3+} ion. The magnetic behavior of this crystal has been shown to be ideal at field strengths up to 5 T and temperatures down to 1.3 K, at which the magnetization is more than 99% complete. See W. E. Henry, *Physical Review* **88**, 561 (1952). The theory of ideal multi-state paramagnets is treated in Problem 6.22.

limited to strengths of a few teslas, so in practice it takes temperatures in the millikelvin range to line up essentially all of the dipoles in a nuclear paramagnet.

Problem 3.19. Fill in the missing algebraic steps to derive equations 3.30, 3.31, and 3.33.

Problem 3.20. Consider an ideal two-state electronic paramagnet such as DPPH, with $\mu = \mu_B$. In the experiment described above, the magnetic field strength was 2.06 T and the minimum temperature was 2.2 K. Calculate the energy, magnetization, and entropy of this system, expressing each quantity as a fraction of its maximum possible value. What would the experimenters have had to do to attain 99% of the maximum possible magnetization?

Problem 3.21. In the experiment of Purcell and Pound, the maximum magnetic field strength was 0.63 T and the initial temperature was 300 K. Pretending that the lithium nuclei have only two possible spin states (in fact they have four), calculate the magnetization per particle, M/N, for this system. Take the constant μ to be 5×10^{-8} eV/T. To detect such a tiny magnetization, the experimenters used resonant absorption and emission of radio waves. Calculate the energy that a radio wave photon should have, in order to flip a single nucleus from one magnetic state to the other. What is the wavelength of such a photon?

Problem 3.22. Sketch (or use a computer to plot) a graph of the entropy of a two-state paramagnet as a function of *temperature*. Describe how this graph would change if you varied the magnetic field strength.

Problem 3.23. Show that the entropy of a two-state paramagnet, expressed as a function of temperature, is $S = Nk[\ln(2\cosh x) - x\tanh x]$, where $x = \mu B/kT$. Check that this formula has the expected behavior as $T \to 0$ and $T \to \infty$.

<div align="center">*   *   *</div>

The following two problems apply the techniques of this section to a different system, an Einstein solid (or other collection of identical harmonic oscillators) at arbitrary temperature. Both the methods and the results of these problems are extremely important. Be sure to work at least one of them, preferably both.

Problem 3.24. Use a computer to study the entropy, temperature, and heat capacity of an Einstein solid, as follows. Let the solid contain 50 oscillators (initially), and from 0 to 100 units of energy. Make a table, analogous to Table 3.2, in which each row represents a different value for the energy. Use separate columns for the energy, multiplicity, entropy, temperature, and heat capacity. To calculate the temperature, evaluate $\Delta U/\Delta S$ for two nearby rows in the table. (Recall that $U = q\epsilon$ for some constant ϵ.) The heat capacity ($\Delta U/\Delta T$) can be computed in a similar way. The first few rows of the table should look something like this:

q	Ω	S/k	kT/ϵ	C/Nk
0	1	0	0	—
1	50	3.91	.28	.12
2	1275	7.15	.33	.45

(In this table I have computed derivatives using a "centered-difference" approximation. For example, the temperature .28 is computed as $2/(7.15 - 0)$.) Make a graph of entropy vs. energy and a graph of heat capacity vs. temperature. Then change the number of oscillators to 5000 (to "dilute" the system and look at lower

temperatures), and again make a graph of heat capacity vs. temperature. Discuss your prediction for the heat capacity, and compare it to the data for lead, aluminum, and diamond shown in Figure 1.14. Estimate the numerical value of ϵ, in electron-volts, for each of those real solids.

Problem 3.25. In Problem 2.18 you showed that the multiplicity of an Einstein solid containing N oscillators and q energy units is approximately

$$\Omega(N, q) \approx \left(\frac{q+N}{q}\right)^q \left(\frac{q+N}{N}\right)^N.$$

(a) Starting with this formula, find an expression for the entropy of an Einstein solid as a function of N and q. Explain why the factors omitted from the formula have no effect on the entropy, when N and q are large.

(b) Use the result of part (a) to calculate the temperature of an Einstein solid as a function of its energy. (The energy is $U = q\epsilon$, where ϵ is a constant.) Be sure to simplify your result as much as possible.

(c) Invert the relation you found in part (b) to find the energy as a function of temperature, then differentiate to find a formula for the heat capacity.

(d) Show that, in the limit $T \to \infty$, the heat capacity is $C = Nk$. (Hint: When x is very small, $e^x \approx 1 + x$.) Is this the result you would expect? Explain.

(e) Make a graph (possibly using a computer) of the result of part (c). To avoid awkward numerical factors, plot C/Nk vs. the dimensionless variable $t = kT/\epsilon$, for t in the range from 0 to about 2. Discuss your prediction for the heat capacity at low temperature, comparing to the data for lead, aluminum, and diamond shown in Figure 1.14. Estimate the value of ϵ, in electron-volts, for each of those real solids.

(f) Derive a more accurate approximation for the heat capacity at high temperatures, by keeping terms through x^3 in the expansions of the exponentials and then carefully expanding the denominator and multiplying everything out. Throw away terms that will be smaller than $(\epsilon/kT)^2$ in the final answer. When the smoke clears, you should find $C = Nk[1 - \frac{1}{12}(\epsilon/kT)^2]$.

Problem 3.26. The results of either of the two preceding problems can also be applied to the vibrational motions of gas molecules. Looking only at the vibrational contribution to the heat capacity graph for H_2 shown in Figure 1.13, estimate the value of ϵ for the vibrational motion of an H_2 molecule.

3.4 Mechanical Equilibrium and Pressure

Next I would like to generalize the ideas of this chapter to include systems whose volumes can change as they interact. Just as the spontaneous exchange of energy between systems is governed by their temperatures, so the exchange of volume between systems is governed by their pressures. Hence, there must be a close relation between pressure and entropy, analogous to the relation $1/T = \partial S/\partial U$.

Consider, then, two systems (perhaps gases) separated by a movable partition (see Figure 3.13). The systems are free to exchange both energy and volume, but the total energy and volume are fixed. The total entropy is a function of two variables,
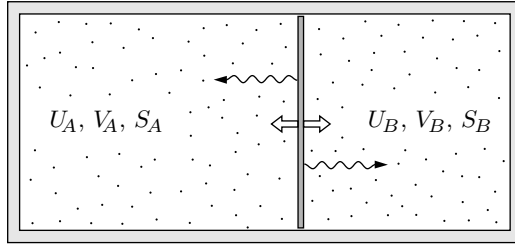
Figure 3.13. Two systems that can exchange both energy and volume with each other. The total energy and total volume are fixed.
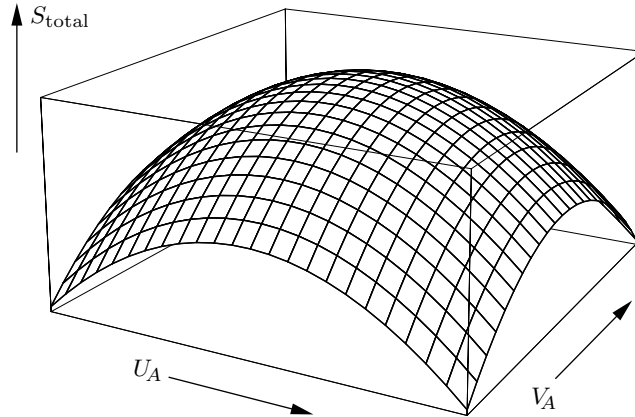

Figure 3.14. A graph of entropy vs. U_A and V_A for the system shown in Figure 3.13. The equilibrium values of U_A and V_A are where the graph reaches its highest point.

U_A and V_A, as shown in Figure 3.14. The equilibrium point is where S_{total} attains its maximum value. At this point, its partial derivatives in both directions vanish:

$$\frac{\partial S_{\text{total}}}{\partial U_A} = 0, \qquad \frac{\partial S_{\text{total}}}{\partial V_A} = 0. \tag{3.36}$$

We studied the first condition already in Section 3.1, where we concluded that this condition is equivalent to saying that the two systems are at the same temperature. Now let us study the second condition in the same way.

The manipulations are exactly analogous to those in Section 3.1:

$$0 = \frac{\partial S_{\text{total}}}{\partial V_A} = \frac{\partial S_A}{\partial V_A} + \frac{\partial S_B}{\partial V_A} = \frac{\partial S_A}{\partial V_A} - \frac{\partial S_B}{\partial V_B}. \tag{3.37}$$

The last step uses the fact that the total volume is fixed, so $dV_A = -dV_B$ (any volume added to A must be subtracted from B). Therefore we can conclude

$$\frac{\partial S_A}{\partial V_A} = \frac{\partial S_B}{\partial V_B} \qquad \text{at equilibrium.} \tag{3.38}$$

The partial derivatives are to be taken with energy (U_A or U_B) held fixed, as well as the number of particles (N_A or N_B). Note, however, that I have assumed that the systems are free to exchange energy, and in fact that they are also in *thermal* equilibrium. (If the partition is allowed to move but does not allow heat to pass through, then the energies of the systems are *not* fixed, and the equilibrium condition is more complicated.)

From experience, though, we know that when two systems are in mechanical equilibrium, their *pressures* must be equal. Therefore pressure must be some function of the derivative $\partial S/\partial V$. To figure out *what* function, let's look at units. Entropy has units of J/K, so $\partial S/\partial V$ has units of $(\text{N/m}^2)/\text{K}$, or Pa/K. To get something with units of pressure, we need to multiply by a temperature. But can we? Yes, since we've assumed already that the two systems are in thermal equilibrium, they must be at the same temperature, so the quantity $T(\partial S/\partial V)$ is *also* the same for both systems.

We should also think about whether we want $\partial S/\partial V$ to be large or small when the pressure is large. When $\partial S/\partial V$ is large, the system gains a lot of entropy upon expanding just a little. Since entropy tends to increase, this system really "wants" to expand. Yep, that's exactly what we mean when we say the pressure is large.

I therefore propose the following relation between entropy and pressure:

$$P = T\left(\frac{\partial S}{\partial V}\right)_{U,N}. \tag{3.39}$$

I won't try to call this the *definition* of pressure, but I hope you agree that this quantity has all the same qualities as pressure, and hence, that it probably is the same thing as force per unit area.

Of course, it's always reassuring to check that the formula works in a case where we already know the answer. So recall the formula for the multiplicity of a monatomic ideal gas,

$$\Omega = f(N)V^N U^{3N/2}, \tag{3.40}$$

where $f(N)$ is a complicated function of N only. Taking the logarithm gives

$$S = Nk\ln V + \tfrac{3}{2}Nk\ln U + k\ln f(N). \tag{3.41}$$

So according to formula 3.39, the pressure should be

$$P = T\,\frac{\partial}{\partial V}(Nk\ln V) = \frac{NkT}{V}, \tag{3.42}$$

that is,

$$PV = NkT. \tag{3.43}$$

Indeed. So if you already believed formula 3.39, then we've just *derived* the ideal gas law. Alternatively, you can think of this calculation as a verification of formula 3.39, and especially of the fact that no additional constant factors are needed in that formula.

The Thermodynamic Identity

There's a nice equation that summarizes both the theoretical definition of temperature and our new formula for pressure. To derive it, let's consider a process in which you change both the energy and the volume of a system by small amounts, ΔU and ΔV. Question: How much does the system's entropy change?

To answer this question, let's mentally divide the process into two steps: In step 1, the energy changes by ΔU but the volume is held fixed. Then, in step 2, the volume changes by ΔV but the energy is held fixed. These two steps are shown graphically in Figure 3.15. The total change in entropy is just the sum of the changes during steps 1 and 2:

$$\Delta S = (\Delta S)_1 + (\Delta S)_2. \tag{3.44}$$

Now multiply and divide the first term by ΔU, and multiply and divide the second term by ΔV:

$$\Delta S = \left(\frac{\Delta S}{\Delta U}\right)_V \Delta U + \left(\frac{\Delta S}{\Delta V}\right)_U \Delta V.$$

The subscripts indicate what quantity is being held fixed, as usual. Now if all of the changes are *small*, the ratios in parentheses become partial derivatives, and the change in entropy can be written

$$\begin{aligned} dS &= \left(\frac{\partial S}{\partial U}\right)_V dU + \left(\frac{\partial S}{\partial V}\right)_U dV \\ &= \frac{1}{T} dU + \frac{P}{T} dV, \end{aligned} \tag{3.45}$$

where in the second line I have used the definition of temperature and formula 3.39 for pressure to evaluate the partial derivatives. This result is called the **thermodynamic identity**. It is usually rearranged into the following form:

$$dU = T\, dS - P\, dV. \tag{3.46}$$

This equation is true for any infinitesimal change in any system, provided that T and P are well defined and no other relevant variables are changing. (For instance, I've assumed that the number of particles in the system is fixed.)

Figure 3.15. To compute the change in entropy when both U and V change, consider the process in two steps: changing U while holding V fixed, then changing V while holding U fixed.
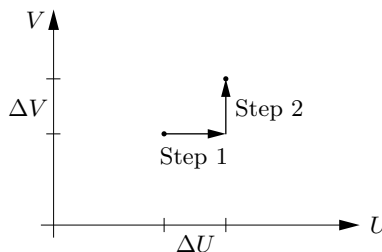
If you memorize only one formula from this chapter, make it the thermodynamic identity, because from it you can recover the formulas for both temperature and pressure as partial derivatives of the entropy. For instance, in a process that takes place at constant volume ($dV = 0$), the thermodynamic identity says $dU = T\,dS$, which can be rearranged to give the definition of temperature (equation 3.5). And for a process in which $dU = 0$, the thermodynamic identity says $T\,dS = P\,dV$, which reproduces equation 3.39 for the pressure.

> **Problem 3.27.** What partial-derivative relation can you derive from the thermo-dynamic identity by considering a process that takes place at constant entropy? Does the resulting equation agree with what you already knew? Explain.

Entropy and Heat Revisited

The thermodynamic identity looks an awful lot like the first law of thermodynamics,

$$dU = Q + W. \tag{3.47}$$

It is therefore tempting to associate Q with $T\,dS$ and W with $-P\,dV$. However, these associations are not always valid. They *are* valid if any change in volume takes place quasistatically (so the pressure is always uniform throughout the system), if no other forms of work are done, and if no other relevant variables (such as particle numbers) are changing. Then we *know* that $W = -P\,dV$, so equations 3.46 and 3.47 imply

$$Q = T\,dS \qquad \text{(quasistatic).} \tag{3.48}$$

Thus, under these restricted circumstances, the change in a system's entropy is Q/T, even if work is being done on it during the process. (In the special case of an adiabatic process ($Q = 0$) that is also quasistatic, the entropy is unchanged; such a process is called **isentropic**. In short, adiabatic + quasistatic = isentropic.)

This result (3.48) allows us to go back and repeat much of the discussion in Section 3.2, removing the restriction of constant volume. For example, when a liter of water is boiled at $100°\text{C}$ and atmospheric pressure, the heat added is 2260 kJ and so the increase in its entropy is

$$\Delta S = \frac{Q}{T} = \frac{2260 \text{ kJ}}{373 \text{ K}} = 6060 \text{ J/K}. \tag{3.49}$$

And for constant-pressure processes in which the temperature changes, we can write $Q = C_P\,dT$, then integrate to obtain

$$(\Delta S)_P = \int_{T_i}^{T_f} \frac{C_P}{T}\,dT. \tag{3.50}$$

Since most tabulated heat capacities are for constant pressure rather than constant volume, this formula is more practical than the analogous equation (3.19) for constant volume.

But even though many familiar processes are approximately quasistatic, it's important to remember that there are exceptions. As an example, suppose you have
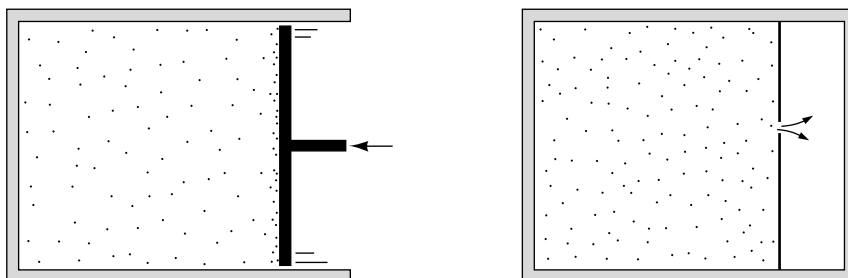
Figure 3.16. Two types of non-quasistatic volume changes: very fast compression that creates internal disequilibrium, and free expansion into a vacuum.

a gas in a cylinder with a piston, and you hit the piston *very* hard, so that it moves inward much faster than the gas molecules themselves are moving (see Figure 3.16). Molecules build up in front of the piston, exerting a very large backward force on it which you must overcome. Let's say that the piston stops after moving only a very small distance, so that after everything settles down, the pressure has increased only infinitesimally. The work you have done on the gas is now *greater* than $-P\,dV$, so any heat that was simultaneously added must be *less* than $T\,dS$. In this example, then,

$$dS > \frac{Q}{T} \qquad \text{(when } W > -P\,dV\text{).} \tag{3.51}$$

You've created "extra" entropy, because you added extra energy to the gas—more than was needed to accomplish the change in volume.

A related example is the free expansion of a gas into a vacuum, discussed in Section 2.6. Suppose that a membrane partitions a chamber into two parts, one filled with gas and the other containing a vacuum. The membrane is suddenly broken, allowing the gas to expand into the vacuum. Here no work is done on or by the gas, nor does any heat flow into it, so the first law tells us $\Delta U = 0$. Meanwhile, if the increase in the volume of the gas is very small, the thermodynamic identity (3.46) must still apply, so $T\,dS = P\,dV > 0$, that is, there is a positive change in the entropy of the gas. (If it's an ideal gas, you can also see this directly from the Sackur-Tetrode equation for S, as discussed in Section 2.6.)

In both of these examples, there is a mechanical process that creates new entropy, over and above any entropy that might "flow" into the system through heat. It's always possible to create *more* entropy. But the second law says that once we've created it, we can never make it disappear.

Problem 3.28. A liter of air, initially at room temperature and atmospheric pressure, is heated at constant pressure until it doubles in volume. Calculate the increase in its entropy during this process.

Problem 3.29. Sketch a qualitatively accurate graph of the entropy of a substance (perhaps H_2O) as a function of temperature, at fixed pressure. Indicate where the substance is solid, liquid, and gas. Explain each feature of the graph briefly.

Problem 3.30. As shown in Figure 1.14, the heat capacity of diamond near room temperature is approximately linear in T. Extrapolate this function up to 500 K, and estimate the change in entropy of a mole of diamond as its temperature is raised from 298 K to 500 K. Add on the tabulated value at 298 K (from the back of this book) to obtain $S(500 \text{ K})$.

Problem 3.31. Experimental measurements of heat capacities are often represented in reference works as empirical formulas. For graphite, a formula that works well over a fairly wide range of temperatures is (for one mole)

$$C_P = a + bT - \frac{c}{T^2},$$

where $a = 16.86$ J/K, $b = 4.77 \times 10^{-3}$ J/K^2, and $c = 8.54 \times 10^5$ J·K. Suppose, then, that a mole of graphite is heated at constant pressure from 298 K to 500 K. Calculate the increase in its entropy during this process. Add on the tabulated value of $S(298 \text{ K})$ (from the back of this book) to obtain $S(500 \text{ K})$.

Problem 3.32. A cylinder contains one liter of air at room temperature (300 K) and atmospheric pressure (10^5 N/m^2). At one end of the cylinder is a massless piston, whose surface area is 0.01 m^2. Suppose that you push the piston in *very* suddenly, exerting a force of 2000 N. The piston moves only one millimeter, before it is stopped by an immovable barrier of some sort.

    (a) How much work have you done on this system?

    (b) How much heat has been added to the gas?

    (c) Assuming that all the energy added goes into the gas (not the piston or cylinder walls), by how much does the energy of the gas increase?

    (d) Use the thermodynamic identity to calculate the change in the entropy of the gas (once it has again reached equilibrium).

Problem 3.33. Use the thermodynamic identity to derive the heat capacity formula

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

which is occasionally more convenient than the more familiar expression in terms of U. Then derive a similar formula for C_P, by first writing dH in terms of dS and dP.

Problem 3.34. Polymers, like rubber, are made of very long molecules, usually tangled up in a configuration that has lots of entropy. As a very crude model of a rubber band, consider a chain of N links, each of length ℓ (see Figure 3.17). Imagine that each link has only two possible states, pointing either left or right. The total length L of the rubber band is the net displacement from the beginning of the first link to the end of the last link.
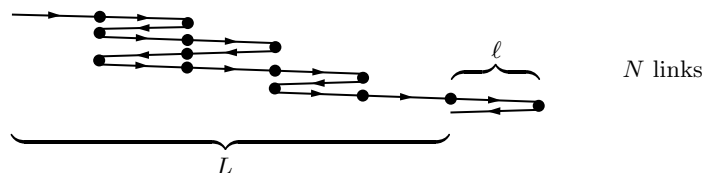

Figure 3.17. A crude model of a rubber band as a chain in which each link can only point left or right.

(a) Find an expression for the entropy of this system in terms of N and N_R, the number of links pointing to the right.

(b) Write down a formula for L in terms of N and N_R.

(c) For a one-dimensional system such as this, the length L is analogous to the volume V of a three-dimensional system. Similarly, the pressure P is replaced by the tension force F. Taking F to be positive when the rubber band is pulling inward, write down and explain the appropriate thermodynamic identity for this system.

(d) Using the thermodynamic identity, you can now express the tension force F in terms of a partial derivative of the entropy. From this expression, compute the tension in terms of L, T, N, and ℓ.

(e) Show that when $L \ll N\ell$, the tension force is directly proportional to L (Hooke's law).

(f) Discuss the dependence of the tension force on temperature. If you increase the temperature of a rubber band, does it tend to expand or contract? Does this behavior make sense?

(g) Suppose that you hold a relaxed rubber band in both hands and suddenly stretch it. Would you expect its temperature to increase or decrease? Explain. Test your prediction with a real rubber band (preferably a fairly heavy one with lots of stretch), using your lips or forehead as a thermometer. (Hint: The entropy you computed in part (a) is not the total entropy of the rubber band. There is additional entropy associated with the vibrational energy of the molecules; this entropy depends on U but is approximately independent of L.)

3.5 Diffusive Equilibrium and Chemical Potential

When two systems are in *thermal* equilibrium, their temperatures are the same. When they're in *mechanical* equilibrium, their pressures are the same. What quantity is the same when they're in *diffusive* equilibrium?

We can find out by applying the same logic as in the previous section. Consider two systems, A and B, that are free to exchange both energy and particles, as shown in Figure 3.18. (The volumes of the systems could also vary, but I'll take these to be fixed for simplicity.) I've drawn a system of two interacting gases, but it could just as well be a gas interacting with a liquid or solid, or even two solids in which atoms gradually migrate around. I'm assuming, though, that both systems are made of the same *species* of particles, for instance, H_2O molecules.
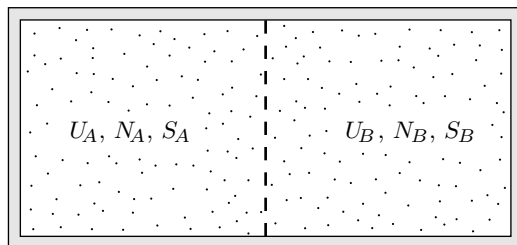

Figure 3.18. Two systems that can exchange both energy and particles.

Assuming that the total energy and total number of particles are fixed, the total entropy of this system is a function of U_A and N_A. At equilibrium, the total entropy is a maximum, so

$$\left(\frac{\partial S_{\text{total}}}{\partial U_A}\right)_{N_A, V_A} = 0 \qquad \text{and} \qquad \left(\frac{\partial S_{\text{total}}}{\partial N_A}\right)_{U_A, V_A} = 0. \tag{3.52}$$

(If the volumes of the systems are allowed to vary, then $\partial S_{\text{total}}/\partial V_A = 0$ as well.) Again, the first condition says that the two systems must be at the same temperature. The second condition is new, but is entirely analogous to the condition on volume from the previous section. Following the same reasoning as there, we can conclude

$$\frac{\partial S_A}{\partial N_A} = \frac{\partial S_B}{\partial N_B} \qquad \text{at equilibrium,} \tag{3.53}$$

where the partial derivatives are taken at fixed energy and volume. We're free to multiply this equation through by a factor of T, the temperature, since the systems are also in thermal equilibrium. By convention, we also multiply by -1:

$$-T \frac{\partial S_A}{\partial N_A} = -T \frac{\partial S_B}{\partial N_B} \qquad \text{at equilibrium.} \tag{3.54}$$

The quantity $-T(\partial S/\partial N)$ is much less familiar to most of us than temperature or pressure, but it's still extremely important. It is called the **chemical potential**, denoted μ:

$$\mu \equiv -T\left(\frac{\partial S}{\partial N}\right)_{U, V}. \tag{3.55}$$

This is the quantity that's the same for both systems when they're in diffusive equilibrium:

$$\mu_A = \mu_B \qquad \text{at equilibrium.} \tag{3.56}$$

If the two systems are *not* in equilibrium, then the one with the larger value of $\partial S/\partial N$ will tend to gain particles, since it will thereby gain more entropy than the other loses. However, because of the minus sign in definition 3.55, this system has the *smaller* value of μ. Conclusion: Particles tend to flow from the system with higher μ into the system with lower μ (see Figure 3.19).
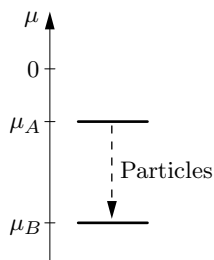

Figure 3.19. Particles tend to flow toward lower values of the chemical potential, even if both values are negative.

It's not hard to generalize the thermodynamic identity to include processes in which N changes. If we imagine changing U by dU, V by dV, and N by dN, then, by the same logic as in the previous section, the total change in the entropy is

$$dS = \left(\frac{\partial S}{\partial U}\right)_{N,V} dU + \left(\frac{\partial S}{\partial V}\right)_{N,U} dV + \left(\frac{\partial S}{\partial N}\right)_{U,V} dN$$
$$= \frac{1}{T} dU + \frac{P}{T} dV - \frac{\mu}{T} dN. \tag{3.57}$$

Solving for dU as before, we obtain

$$dU = T\, dS - P\, dV + \mu\, dN. \tag{3.58}$$

Just as the $-P\, dV$ term is usually associated with mechanical work, the $\mu\, dN$ term is sometimes referred to as "chemical work."

This generalized thermodynamic identity is a great way to remember the various partial-derivative formulas for T, P, and μ, and to generate other similar formulas. Notice that four quantities are changing in this equation: U, S, V, and N. Now just imagine a process in which any two of these are fixed. For instance, in a process with fixed U and V,

$$0 = T\, dS + \mu\, dN, \qquad \text{that is,} \qquad \mu = -T\left(\frac{\partial S}{\partial N}\right)_{U,V}. \tag{3.59}$$

Similarly, in a process with fixed S and V,

$$dU = \mu\, dN, \qquad \text{that is,} \qquad \mu = \left(\frac{\partial U}{\partial N}\right)_{S,V}. \tag{3.60}$$

This last result is another useful formula for the chemical potential. It tells us directly that μ has units of energy; specifically, μ is the amount by which a system's energy changes, when you add one particle and keep the entropy and volume fixed. Normally, to hold the entropy (or multiplicity) fixed, you must *remove* some energy as you add a particle, so μ is negative. However, if you have to give the particle some potential energy (gravitational, if the system lives on a mountain top, or chemical, if the system is a solid crystal) to get it into the system, this energy also contributes to μ. In Chapter 7 we'll see an example where you have to give a particle *kinetic* energy just to get it into a system.

Now let's look at some examples. First consider a very small Einstein solid, with three oscillators and three units of energy. The multiplicity is 10, so the entropy is $k \ln 10$. Now suppose we add one more oscillator (thinking of each oscillator as a "particle"). If we leave all three units of energy in the system, the multiplicity increases to 20 and the entropy increases to $k \ln 20$. To hold the entropy fixed, we need to remove one unit of energy, as shown in Figure 3.20. Thus the chemical potential of this system is

$$\mu = \left(\frac{\Delta U}{\Delta N}\right)_S = \frac{-\epsilon}{1} = -\epsilon, \tag{3.61}$$

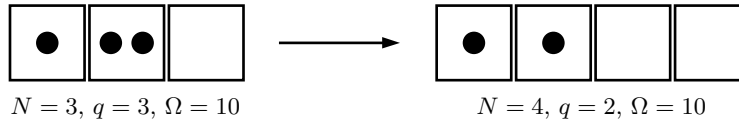$$N = 3,\ q = 3,\ \Omega = 10 \qquad\qquad N = 4,\ q = 2,\ \Omega = 10$$

Figure 3.20. In order to add an oscillator (represented by a box) to this very small Einstein solid while holding the entropy (or multiplicity) fixed, we must remove one unit of energy (represented by a dot).

if ϵ is the size of a unit of energy. (Because the addition of one particle is not an infinitesimal change for such a small system, this example should be taken with a grain of salt. Strictly speaking, the derivative $\partial U/\partial N$ is not well defined. Besides, in a real solid crystal, adding an atom would entail adding three oscillators, not just one, and we would also have to add some negative potential energy to create the chemical bonds around the added atom.)

As a more realistic example, let's compute μ for a monatomic ideal gas. Here we need the full Sackur-Tetrode equation (2.49) for the entropy,

$$S = Nk\left[\ln\left(V\left(\frac{4\pi mU}{3h^2}\right)^{3/2}\right) - \ln N^{5/2} + \frac{5}{2}\right]. \tag{3.62}$$

Differentiating with respect to N gives

$$
\begin{aligned}
\mu &= -T\left\{k\left[\ln\left(V\left(\frac{4\pi mU}{3h^2}\right)^{3/2}\right) - \ln N^{5/2} + \frac{5}{2}\right] - Nk\cdot\frac{5}{2}\frac{1}{N}\right\} \\
&= -kT\ln\left[\frac{V}{N}\left(\frac{4\pi mU}{3Nh^2}\right)^{3/2}\right] \\
&= -kT\ln\left[\frac{V}{N}\left(\frac{2\pi mkT}{h^2}\right)^{3/2}\right].
\end{aligned}
\tag{3.63}
$$

(In the last line I used the relation $U = \frac{3}{2}NkT$.) At room temperature and atmospheric pressure, the volume per molecule, V/N, is 4.2×10^{-26} m^3, while the quantity $(h^2/2\pi mkT)^{3/2}$ is much smaller. For helium, this quantity is 1.3×10^{-31} m^3, so the argument of the logarithm is 3.3×10^5, the logarithm itself is 12.7, and the chemical potential is

$$\mu = -0.32\text{ eV} \qquad \text{for helium at 300 K, } 10^5\text{ N/m}^2. \tag{3.64}$$

If the concentration is increased while holding the temperature fixed, μ becomes less negative, indicating that the gas becomes more willing to give up particles to other nearby systems. More generally, increasing the density of particles in a system always increases its chemical potential.

Throughout this section, I've implicitly assumed that each system contains only one type of particle. If a system contains several types of particles (such as air, a mixture of nitrogen and oxygen molecules), then each species has its own chemical potential:

$$\mu_1 \equiv -T\left(\frac{\partial S}{\partial N_1}\right)_{U,V,N_2}, \qquad \mu_2 \equiv -T\left(\frac{\partial S}{\partial N_2}\right)_{U,V,N_1}, \tag{3.65}$$

and so on for each species $1, 2, \ldots$. The generalized thermodynamic identity is then

$$dU = T\, dS - P\, dV + \sum_i \mu_i\, dN_i, \tag{3.66}$$

where the sum runs over all species, $i = 1, 2, \ldots$. If two systems are in diffusive equilibrium, the chemical potentials must be separately equal for each species: $\mu_{1A} = \mu_{1B}$, $\mu_{2A} = \mu_{2B}$, and so on, where A and B are the two systems.

The chemical potential is a central concept in the study of equilibrium in chemical reactions and phase transformations. It also plays a central role in "quantum statistics," the study of exotic, dense gases and other related systems. We'll make use of it many times in Chapters 5 and 7.

One more comment: I should mention that chemists usually define the chemical potential in terms of *moles*, not individual particles:

$$\mu_{\text{chemistry}} \equiv -T\left(\frac{\partial S}{\partial n}\right)_{U,V}, \tag{3.67}$$

where $n = N/N_A$ is the number of moles of whatever type of particle is being considered. This means that their chemical potentials are always larger than ours by a factor of Avogadro's number, N_A. To translate this section into chemistry conventions, just change every N to an n, except in the examples in equations 3.61 through 3.64, where every formula for μ should be multiplied by N_A.

Problem 3.35. In the text I showed that for an Einstein solid with three oscillators and three units of energy, the chemical potential is $\mu = -\epsilon$ (where ϵ is the size of an energy unit and we treat each oscillator as a "particle"). Suppose instead that the solid has three oscillators and *four* units of energy. How does the chemical potential then compare to $-\epsilon$? (Don't try to get an actual *value* for the chemical potential; just explain whether it is more or less than $-\epsilon$.)

Problem 3.36. Consider an Einstein solid for which both N and q are much greater than 1. Think of each oscillator as a separate "particle."

(a) Show that the chemical potential is

$$\mu = -kT \ln\left(\frac{N+q}{N}\right).$$

(b) Discuss this result in the limits $N \gg q$ and $N \ll q$, concentrating on the question of how much S increases when another particle carrying no energy is added to the system. Does the formula make intuitive sense?

Problem 3.37. Consider a monatomic ideal gas that lives at a height z above sea level, so each molecule has potential energy mgz in addition to its kinetic energy.

(a) Show that the chemical potential is the same as if the gas were at sea level, plus an additional term mgz:

$$\mu(z) = -kT \ln\left[\frac{V}{N}\left(\frac{2\pi mkT}{h^2}\right)^{3/2}\right] + mgz.$$

(You can derive this result from either the definition $\mu = -T(\partial S/\partial N)_{U,V}$ or the formula $\mu = (\partial U/\partial N)_{S,V}$.)

(b) Suppose you have two chunks of helium gas, one at sea level and one at height z, each having the same temperature and volume. Assuming that they are in diffusive equilibrium, show that the number of molecules in the higher chunk is

$$N(z) = N(0)e^{-mgz/kT},$$

in agreement with the result of Problem 1.16.

Problem 3.38. Suppose you have a *mixture* of gases (such as air, a mixture of nitrogen and oxygen). The **mole fraction** x_i of any species i is defined as the fraction of all the molecules that belong to that species: $x_i = N_i/N_{\text{total}}$. The **partial pressure** P_i of species i is then defined as the corresponding fraction of the total pressure: $P_i = x_i P$. Assuming that the mixture of gases is ideal, argue that the chemical potential μ_i of species i in this system is the same as if the other gases were not present, at a fixed partial pressure P_i.

3.6 Summary and a Look Ahead

This chapter completes our treatment of the basic principles of thermal physics. The most central principle is the second law: Entropy tends to increase. Because this law governs the tendency of systems to exchange energy, volume, and particles, the derivatives of the entropy with respect to these three variables are of great interest and are relatively easy to measure. Table 3.3 summarizes the three types of interactions and the associated derivatives of the entropy. The three partial-derivative formulas are conveniently summarized in the thermodynamic identity,

$$dU = T\,dS - P\,dV + \mu\,dN. \tag{3.68}$$

These concepts and principles form the foundation of what is called **classical thermodynamics**: the study of systems comprised of large numbers of particles, based on general laws that do not depend on the detailed microscopic behavior of those particles. The formulas that appear here apply to *any* large system whose macrostate is determined by the variables U, V, and N, and these formulas can be generalized with little difficulty to other large systems.

Type of interaction	Exchanged quantity	Governing variable	Formula
thermal	energy	temperature	$\dfrac{1}{T} = \left(\dfrac{\partial S}{\partial U}\right)_{V,N}$
mechanical	volume	pressure	$\dfrac{P}{T} = \left(\dfrac{\partial S}{\partial V}\right)_{U,N}$
diffusive	particles	chemical potential	$\dfrac{\mu}{T} = -\left(\dfrac{\partial S}{\partial N}\right)_{U,V}$

Table 3.3. Summary of the three types of interactions considered in this chapter, and the associated variables and partial-derivative relations.

In addition to these very general concepts, we have also worked with three *specific* model systems: the two-state paramagnet, the Einstein solid, and the monatomic ideal gas. For each of these systems we used the laws of microscopic physics to find explicit formulas for the multiplicity and entropy, and hence computed heat capacities and a variety of other measurable quantities. The business of using microscopic models to derive these kinds of predictions is called **statistical mechanics**.

The remainder of this book explores further applications of thermal physics. Chapters 4 and 5 apply the general laws of classical thermodynamics to a variety of systems of practical interest in engineering, chemistry, and related disciplines. Chapters 6, 7, and 8 then return to statistical mechanics, introducing more sophisticated microscopic models and the mathematical tools needed to derive predictions from them.

Problem 3.39. In Problem 2.32 you computed the entropy of an ideal monatomic gas that lives in a two-dimensional universe. Take partial derivatives with respect to U, A, and N to determine the temperature, pressure, and chemical potential of this gas. (In two dimensions, pressure is defined as force per unit *length*.) Simplify your results as much as possible, and explain whether they make sense.

A good many times I have been present at gatherings of people who, by the standards of the traditional culture, are thought highly educated and who have with considerable gusto been expressing their incredulity at the illiteracy of scientists. Once or twice I have been provoked and have asked the company how many of them could describe the Second Law of Thermodynamics. The response was cold: it was also negative. Yet I was asking something which is about the scientific equivalent of: Have you read a work of Shakespeare's?

—C. P. Snow, *The Two Cultures* (Cambridge University Press, Cambridge, 1959). Reprinted with the permission of Cambridge University Press.