From Ch 3
of Schroeder

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 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).

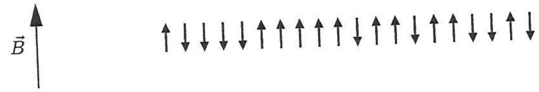

Figure 3.6. A two-state paramagnet, consisting of N microscopic magnetic dipoles, each of which is either "up" or "down" at any moment. The dipoles respond only to the influence of the external magnetic field B; they do not interact with their neighbors (except to exchange energy).

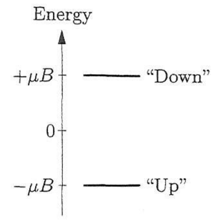

Figure 3.7. The energy levels of a single dipole in an ideal two-state paramagnet are $-\mu B$ (for the "up" state) and $+\mu B$ (for the "down" state).

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
⋮	⋮	⋮	⋮	⋮	⋮	⋮
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
⋮	⋮	⋮	⋮	⋮	⋮	⋮
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 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.

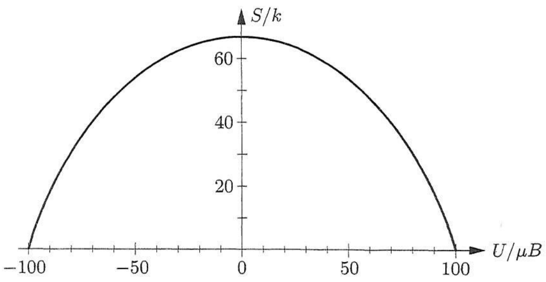

Figure 3.8. Entropy as a function of energy for a two-state paramagnet consisting of 100 elementary dipoles.

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

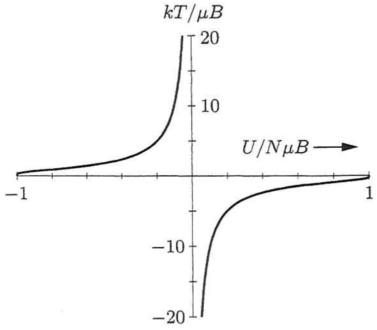

Figure 3.9. Temperature as a function of energy for a two-state paramagnet. (This graph was plotted from the analytic formulas derived later in the text; a plot of the data in Table 3.2 would look similar but less smooth.)

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 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.

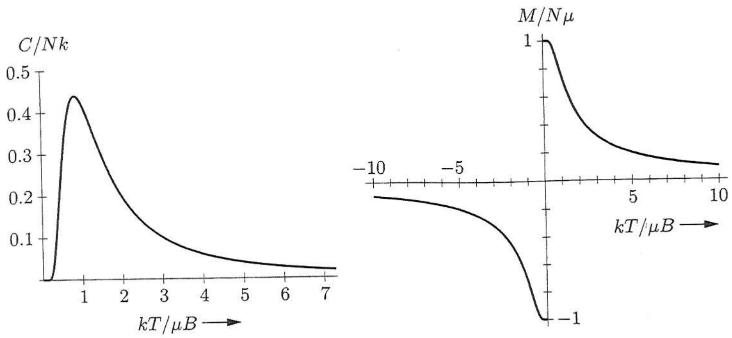

Figure 3.10. Heat capacity and magnetization of a two-state paramagnet (computed from the analytic formulas derived later in the text).

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).

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*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).

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.

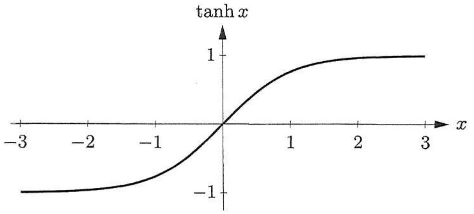

Figure 3.11. The hyperbolic tangent function. In the formulas for the energy and magnetization of a two-state paramagnet, the argument x of the hyperbolic tangent is $\mu B/kT$.

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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**,

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

(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

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

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.

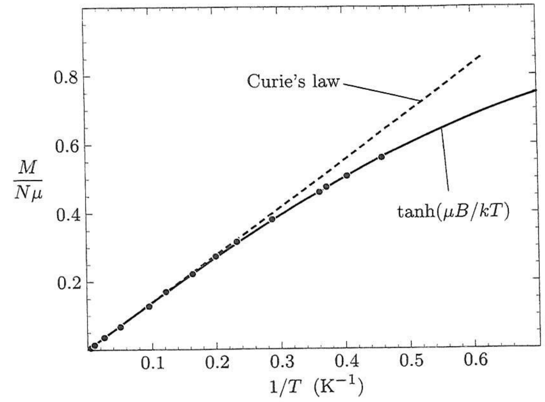

Figure 3.12. Experimental measurements of the magnetization of the organic free radical "DPPH" (in a 1:1 complex with benzene), taken at $B = 2.06$ T and temperatures ranging from 300 K down to 2.2 K. The solid curve is the prediction of equation 3.32 (with $\mu = \mu_B$), while the dashed line is the 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 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.

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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.

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 $T \to \infty$.

* * *

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