- **(c)** The spectrum of the star Betelgeuse, plotted as a function of energy, peaks at a photon energy of 0.8 eV, while Betelgeuse is approximately 10,000 times as luminous as the sun. How does the radius of Betelgeuse compare to the sun's radius? Why is Betelgeuse called a "red supergiant"?

Problem 7.55. Suppose that the concentration of infrared-absorbing gases in earth's atmosphere were to double, effectively creating a second "blanket" to warm the surface. Estimate the equilibrium surface temperature of the earth that would result from this catastrophe. (Hint: First show that the lower atmospheric blanket is warmer than the upper one by a factor of $2^{1/4}$. The surface is warmer than the lower blanket by a smaller factor.)

Problem 7.56. The planet Venus is different from the earth in several respects. First, it is only 70% as far from the sun. Second, its thick clouds reflect 77% of all incident sunlight. Finally, its atmosphere is much more opaque to infrared light.

- **(a)** Calculate the solar constant at the location of Venus, and estimate what the average surface temperature of Venus would be if it had no atmosphere and did not reflect any sunlight.
- **(b)** Estimate the surface temperature again, taking the reflectivity of the clouds into account.
- **(c)** The opaqueness of Venus's atmosphere at infrared wavelengths is roughly 70 times that of earth's atmosphere. You can therefore model the atmosphere of Venus as 70 successive "blankets" of the type considered in the text, with each blanket at a different equilibrium temperature. Use this model to estimate the surface temperature of Venus. (Hint: The temperature of the top layer is what you found in part (b). The next layer down is warmer by a factor of $2^{1/4}$. The *next* layer down is warmer by a smaller factor. Keep working your way down until you see the pattern.)

7.5 Debye Theory of Solids

In Section 2.2 I introduced the **Einstein model** of a solid crystal, in which each atom is treated as an independent three-dimensional harmonic oscillator. In Problem 3.25, you used this model to derive a prediction for the heat capacity,

$$C_V = 3Nk\,\frac{(\epsilon/kT)^2 e^{\epsilon/kT}}{(e^{\epsilon/kT}-1)^2} \qquad \text{(Einstein model)}, \qquad (7.103)$$

where N is the number of *atoms* and $\epsilon = hf$ is the universal size of the units of energy for the identical oscillators. When $kT \gg \epsilon$, the heat capacity approaches a constant value, $3Nk$, in agreement with the equipartition theorem. Below $kT \approx \epsilon$, the heat capacity falls off, approaching zero as the temperature goes to zero. This prediction agrees with experiment to a first approximation, but not in detail. In particular, equation 7.103 predicts that the heat capacity goes to zero *exponentially* in the limit $T \to 0$, whereas experiments show that the true low-temperature behavior is cubic: $C_V \propto T^3$.

The problem with the Einstein model is that the atoms in a crystal do *not* vibrate independently of each other. If you wiggle one atom, its neighbors will also start to wiggle, in a complicated way that depends on the frequency of oscillation.

There are low-frequency modes of oscillation in which large groups of atoms are all moving together, and also high-frequency modes in which atoms are moving opposite to their neighbors. The units of energy come in different sizes, proportional to the frequencies of the modes of vibration. Even at very low temperatures, when the high-frequency modes are frozen out, a few low-frequency modes are still active. This is the reason why the heat capacity goes to zero less dramatically than the Einstein model predicts.

In many ways, the modes of oscillation of a solid crystal are similar to the modes of oscillation of the electromagnetic field in vacuum. This similarity suggests that we try to adapt our recent treatment of electromagnetic radiation to the mechanical oscillations of the crystal. Mechanical oscillations are also called sound waves, and behave very much like light waves. There are a few differences, however:

- Sound waves travel much slower than light waves, at a speed that depends on the stiffness and density of the material. I'll call this speed c_s, and treat it as a constant, neglecting the fact that it can depend on wavelength and direction.
- Whereas light waves must be transversely polarized, sound waves can also be longitudinally polarized. (In seismology, transversely polarized waves are called shear waves, or S-waves, while longitudinally polarized waves are called pressure waves, or P-waves.) So instead of two polarizations we have three. For simplicity, I'll pretend that all three polarizations have the same speed.
- Whereas light waves can have arbitrarily short wavelengths, sound waves in solids cannot have wavelengths shorter than twice the atomic spacing.

The first two differences are easy to take into account. The third will require some thought.

Aside from these three differences, sound waves behave almost identically to light waves. Each mode of oscillation has a set of equally spaced energy levels, with the unit of energy equal to

$$\epsilon = hf = \frac{hc_s}{\lambda} = \frac{hc_s n}{2L}. \tag{7.104}$$

In the last expression, L is the length of the crystal and $n = |\vec{n}|$ is the magnitude of the vector in n-space specifying the shape of the wave. When this mode is in equilibrium at temperature T, the number of units of energy it contains, on average, is given by the Planck distribution:

$$\overline{n}_{\text{Pl}} = \frac{1}{e^{\epsilon/kT} - 1}. \tag{7.105}$$

(This $\overline{n}$ is not to be confused with the n in the previous equation.) As with electromagnetic waves, we can think of these units of energy as particles obeying Bose-Einstein statistics with $\mu = 0$. This time the "particles" are called **phonons**.

To calculate the total thermal energy of the crystal, we add up the energies of all allowed modes:

$$U = 3\sum_{n_x}\sum_{n_y}\sum_{n_z} \epsilon\, \overline{n}_{\text{Pl}}(\epsilon). \tag{7.106}$$

The factor of 3 counts the three polarization states for each $\vec{n}$. The next step will be to convert the sum to an integral. But first we'd better worry about what values of $\vec{n}$ are being summed over.

If these were electromagnetic oscillations, there would be an infinite number of allowed modes and each sum would go to infinity. But in a crystal, the atomic spacing puts a strict lower limit on the wavelength. Consider a lattice of atoms in just one dimension (see Figure 7.26). Each mode of oscillation has its own distinct shape, with the number of "bumps" equal to n. Because each bump must contain at least one atom, n cannot exceed the number of atoms in a row. If the three-dimensional crystal is a perfect cube, then the number of atoms along any direction is $\sqrt[3]{N}$, so each sum in equation 7.106 should go from 1 to $\sqrt[3]{N}$. In other words, we're summing over a *cube* in n-space. If the crystal itself is not a perfect cube, then neither is the corresponding volume of n-space. Still, however, the sum will run over a region in n-space whose total volume is N.

Now comes the tricky approximation. Summing (or integrating) over a cube or some other complicated region of n-space is no fun, because the function we're summing depends on n_x, n_y, and n_z in a very complicated way (an exponential of a square root). On the other hand, the function depends on the *magnitude* of $\vec{n}$ in a simpler way, and it doesn't depend on the *angle* in n-space at all. So Peter Debye got the clever idea to pretend that the relevant region of n-space is a sphere, or rather, an eighth of a sphere. To preserve the total number of degrees of freedom, he chose a sphere whose total volume is N. You can easily show that the radius of the sphere has to be

$$n_{\max} = \left(\frac{6N}{\pi}\right)^{1/3}. \tag{7.107}$$

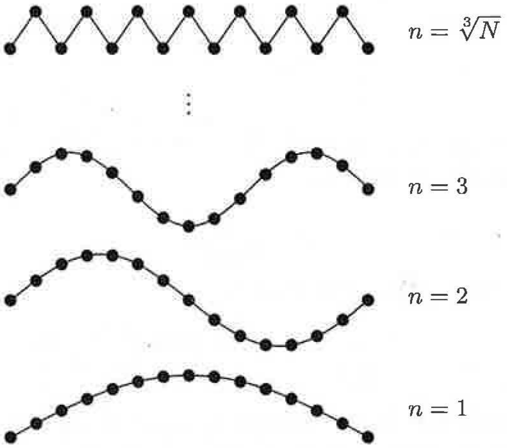

Figure 7.26. Modes of oscillation of a row of atoms in a crystal. If the crystal is a cube, then the number of atoms along any row is $\sqrt[3]{N}$. This is also the total number of modes along this direction, because each "bump" in the wave form must contain at least one atom.

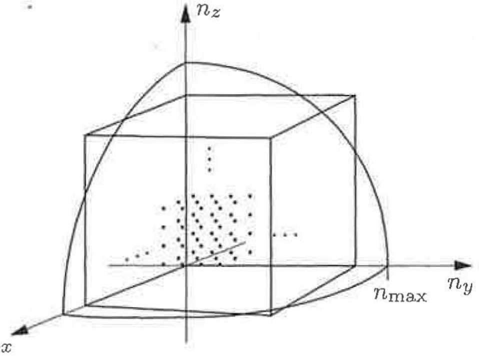

Figure 7.27. The sum in equation 7.106 is technically over a cube in n-space whose width is $\sqrt[3]{N}$. As an approximation, we instead sum over an eighth-sphere with the same total volume.

Figure 7.27 shows the cube in n-space, and the sphere that approximates it.

Remarkably, Debye's approximation is exact in *both* the high-temperature and low-temperature limits. At high temperature, all that matters is the total number of modes, that is, the total number of degrees of freedom; this number is preserved by choosing the sphere to have the correct volume. At low temperature, modes with large $\vec{n}$ are frozen out anyway, so we can count them however we like. At intermediate temperatures, we'll get results that are not exact, but they'll still be surprisingly good.

When we make Debye's approximation, and convert the sums to integrals in spherical coordinates, equation 7.106 becomes

$$U = 3\int_0^{n_{\text{max}}} dn \int_0^{\pi/2} d\theta \int_0^{\pi/2} d\phi\, n^2 \sin\theta\, \frac{\epsilon}{e^{\epsilon/kT}-1}. \tag{7.108}$$

The angular integrals give $\pi/2$ (yet again), leaving us with

$$U = \frac{3\pi}{2}\int_0^{n_{\text{max}}} \frac{hc_s}{2L}\frac{n^3}{e^{hc_s n/2LkT}-1}\,dn. \tag{7.109}$$

This integral cannot be done analytically, but it's at least a little cleaner if we change to the dimensionless variable

$$x = \frac{hc_s n}{2LkT}. \tag{7.110}$$

The upper limit on the integral will then be

$$x_{\text{max}} = \frac{hc_s n_{\text{max}}}{2LkT} = \frac{hc_s}{2kT}\left(\frac{6N}{\pi V}\right)^{1/3} \equiv \frac{T_{\text{D}}}{T}, \tag{7.111}$$

where the last equality defines the **Debye temperature**, T_{D}—essentially an abbreviation for all the constants. Making the variable change and collecting all the constants is now straightforward. When the smoke clears, we obtain

$$U = \frac{9NkT^4}{T_{\text{D}}^3}\int_0^{T_{\text{D}}/T} \frac{x^3}{e^x-1}\,dx. \tag{7.112}$$

At this point you can do the integral on a computer if you like, for any desired temperature. Without a computer, though, we can still check the low-temperature and high-temperature limits.

When $T \gg T_\mathrm{D}$, the upper limit of the integral is much less than 1, so x is always very small and we can approximate $e^x \approx 1 + x$ in the denominator. The 1 cancels, leaving the x to cancel one power of x in the numerator. The integral then gives simply $\frac{1}{3}(T_\mathrm{D}/T)^3$, leading to the final result

$$U = 3NkT \qquad \text{when } T \gg T_\mathrm{D}, \tag{7.113}$$

in agreement with the equipartition theorem (and the Einstein model). The heat capacity in this limit is just $C_V = 3Nk$.

When $T \ll T_\mathrm{D}$, the upper limit on the integral is so large that by the time we get to it, the integrand is dead (due to the e^x in the denominator). So we might as well replace the upper limit by infinity—the extra modes we're adding don't contribute anyway. In this approximation, the integral is the same as the one we did for the photon gas (equation 7.85), and evaluates to $\pi^4/15$. So the total energy is

$$\cancel{U} = \frac{3\pi^4}{5}\frac{NkT^4}{T_\mathrm{D}^3} \qquad \text{when } T \ll T_\mathrm{D}. \tag{7.114}$$

To get the heat capacity, differentiate with respect to T:

$$C_V = \frac{12\pi^4}{5}\left(\frac{T}{T_\mathrm{D}}\right)^3 Nk \qquad \text{when } T \ll T_\mathrm{D}. \tag{7.115}$$

The prediction $C_V \propto T^3$ agrees beautifully with low-temperature experiments on almost any solid material. For metals, though, there is also a linear contribution to the heat capacity from the conduction electrons, as described in Section 7.3. The total heat capacity at low temperature is therefore

$$C = \gamma T + \frac{12\pi^4 Nk}{5T_\mathrm{D}^3}T^3 \qquad (\text{metal, } T \ll T_\mathrm{D}), \tag{7.116}$$

where $\gamma = \pi^2 Nk^2/2\epsilon_\mathrm{F}$ in the free electron model. Figure 7.28 shows plots of C/T

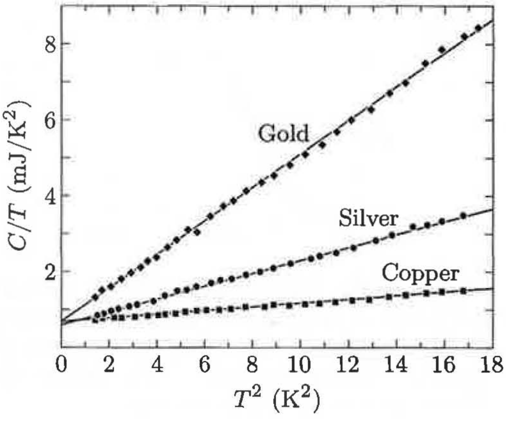

Figure 7.28. Low-temperature measurements of the heat capacities (per mole) of copper, silver, and gold. Adapted with permission from William S. Corak et al., *Physical Review* **98**, 1699 (1955).

vs. T^2 for three familiar metals. The linearity of the data confirms the Debye theory of lattice vibrations, while the intercepts give us the experimental values of γ.

At intermediate temperatures, you have to do a numerical integral to get the total thermal energy in the crystal. If what you really want is the heat capacity, it's best to differentiate equation 7.109 analytically, then change variables to x. The result is

$$C_V = 9Nk\left(\frac{T}{T_\mathrm{D}}\right)^3 \int_0^{T_\mathrm{D}/T} \frac{x^4\,e^x}{(e^x-1)^2}\,dx. \tag{7.117}$$

A computer-generated plot of this function is shown in Figure 7.29. For comparison, the Einstein model prediction, equation 7.103, is also plotted, with the constant ϵ chosen to make the curves agree at relatively high temperatures. As you can see, the two curves still differ significantly at low temperatures. Figure 1.14 shows further comparisons of experimental data to the prediction of the Debye model.

The Debye temperature of any particular substance can be predicted from the speed of sound in that substance, using equation 7.111. Usually, however, one obtains a better fit to the data by choosing T_D so that the measured heat capacity best fits the theoretical prediction. Typical values of T_D range from 88 K for lead (which is soft and dense) to 1860 K for diamond (which is stiff and light). Since the heat capacity reaches 95% of its maximum value at $T = T_\mathrm{D}$, the Debye temperature gives you a rough idea of when you can get away with just using the equipartition theorem. When you can't, Debye's formula usually gives a good, but not great, estimate of the heat capacity over the full range of temperatures. To do better, we'd have to do a lot more work, taking into account the fact that the speed of a phonon depends on its wavelength, polarization, and direction of travel with respect to the crystal axes. That kind of analysis belongs in a book on solid state physics.

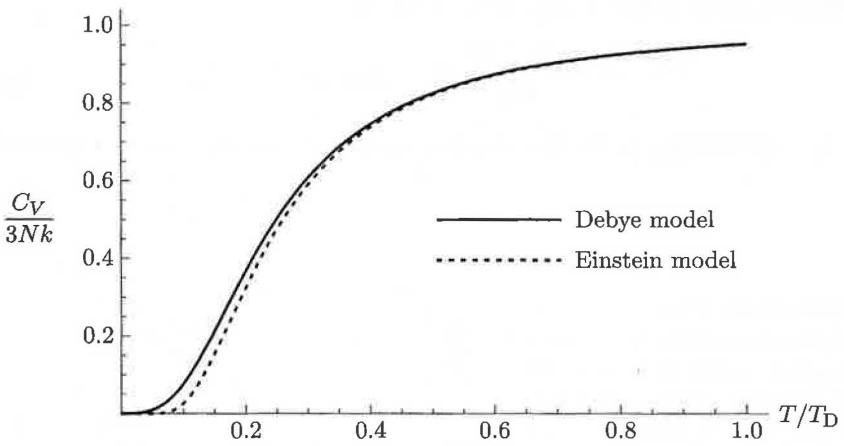

Figure 7.29. The Debye prediction for the heat capacity of a solid, with the prediction of the Einstein model plotted for comparison. The constant ϵ in the Einstein model has been chosen to obtain the best agreement with the Debye model at high temperatures. Note that the Einstein curve is much flatter than the Debye curve at low temperatures.

Problem 7.57. Fill in the steps to derive equations 7.112 and 7.117.

Problem 7.58. The speed of sound in copper is 3560 m/s. Use this value to calculate its theoretical Debye temperature. Then determine the experimental Debye temperature from Figure 7.28, and compare.

Problem 7.59. Explain in some detail why the three graphs in Figure 7.28 all intercept the vertical axis in about the same place, whereas their slopes differ considerably.

Problem 7.60. Sketch the heat capacity of copper as a function of temperature from 0 to 5 K, showing the contributions of lattice vibrations and conduction electrons separately. At what temperature are these two contributions equal?

Problem 7.61. The heat capacity of liquid ^{4}He below 0.6 K is proportional to T^3, with the measured value $C_V/Nk = (T/4.67\text{ K})^3$. This behavior suggests that the dominant excitations at low temperature are long-wavelength phonons. The only important difference between phonons in a liquid and phonons in a solid is that a liquid cannot transmit transversely polarized waves—sound waves must be longitudinal. The speed of sound in liquid ^{4}He is 238 m/s, and the density is 0.145 g/cm^3. From these numbers, calculate the phonon contribution to the heat capacity of ^{4}He in the low-temperature limit, and compare to the measured value.

Problem 7.62. Evaluate the integrand in equation 7.112 as a power series in x, keeping terms through x^4. Then carry out the integral to find a more accurate expression for the energy in the high-temperature limit. Differentiate this expression to obtain the heat capacity, and use the result to estimate the percent deviation of C_V from $3Nk$ at $T = T_{\text{D}}$ and $T = 2T_{\text{D}}$.

Problem 7.63. Consider a two-dimensional solid, such as a stretched drumhead or a layer of mica or graphite. Find an expression (in terms of an integral) for the thermal energy of a square chunk of this material of area $A = L^2$, and evaluate the result approximately for very low and very high temperatures. Also find an expression for the heat capacity, and use a computer or a calculator to plot the heat capacity as a function of temperature. Assume that the material can only vibrate perpendicular to its own plane, i.e., that there is only one "polarization."

Problem 7.64. A **ferromagnet** is a material (like iron) that magnetizes spontaneously, even in the absence of an externally applied magnetic field. This happens because each elementary dipole has a strong tendency to align parallel to its neighbors. At $T = 0$ the magnetization of a ferromagnet has the maximum possible value, with all dipoles perfectly lined up; if there are N atoms, the total magnetization is typically $\sim 2\mu_{\text{B}}N$, where μ_{B} is the Bohr magneton. At somewhat higher temperatures, the excitations take the form of **spin waves**, which can be visualized classically as shown in Figure 7.30. Like sound waves, spin waves are quantized: Each wave mode can have only integer multiples of a basic energy unit. In analogy with phonons, we think of the energy units as particles, called **magnons.** Each magnon reduces the total spin of the system by one unit of $h/2\pi$, and therefore reduces the magnetization by $\sim 2\mu_{\text{B}}$. However, whereas the frequency of a sound wave is inversely proportional to its wavelength, the frequency of a spin wave is proportional to the *square* of $1/\lambda$ (in the limit of long wavelengths). Therefore, since $\epsilon = hf$ and $p = h/\lambda$ for any "particle," the energy of a magnon is proportional

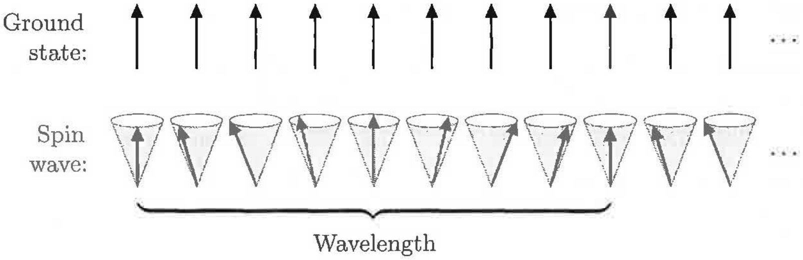

Figure 7.30. In the ground state of a ferromagnet, all the elementary dipoles point in the same direction. The lowest-energy excitations above the ground state are **spin waves**, in which the dipoles precess in a conical motion. A long-wavelength spin wave carries very little energy, because the difference in direction between neighboring dipoles is very small.

to the square of its momentum. In analogy with the energy-momentum relation for an ordinary nonrelativistic particle, we can write $\epsilon = p^2/2m^*$, where m^* is a constant related to the spin-spin interaction energy and the atomic spacing. For iron, m^* turns out to equal 1.24×10^{-29} kg, about 14 times the mass of an electron. Another difference between magnons and phonons is that each magnon (or spin wave mode) has only one possible polarization.

(a) Show that at low temperatures, the number of magnons per unit volume in a three-dimensional ferromagnet is given by.

$$\frac{N_m}{V} = 2\pi\left(\frac{2m^*kT}{h^2}\right)^{3/2} \int_0^\infty \frac{\sqrt{x}}{e^x - 1}\,dx.$$

Evaluate the integral numerically.

(b) Use the result of part (a) to find an expression for the fractional reduction in magnetization, $(M(0) - M(T))/M(0)$. Write your answer in the form $(T/T_0)^{3/2}$, and estimate the constant T_0 for iron.

(c) Calculate the heat capacity due to magnetic excitations in a ferromagnet at low temperature. You should find $C_V/Nk = (T/T_1)^{3/2}$, where T_1 differs from T_0 only by a numerical constant. Estimate T_1 for iron, and compare the magnon and phonon contributions to the heat capacity. (The Debye temperature of iron is 470 K.)

(d) Consider a *two*-dimensional array of magnetic dipoles at low temperature. Assume that each elementary dipole can still point in any (three-dimensional) direction, so spin waves are still possible. Show that the integral for the total number of magnons diverges in this case. (This result is an indication that there can be no spontaneous magnetization in such a two-dimensional system. However, in Section 8.2 we will consider a different two-dimensional model in which magnetization *does* occur.)