(d) Calculate the entropy of this system for each value of q from 0 to 6, and draw a graph of entropy vs. energy. Make a rough estimate of the slope of this graph near $q = 6$, to obtain another estimate of the temperature of this system at that point. Check that it is in rough agreement with your answer to part (c).

Problem 7.17. In analogy with the previous problem, consider a system of identical spin-0 *bosons* trapped in a region where the energy levels are evenly spaced. Assume that N is a large number, and again let q be the number of energy units.

(a) Draw diagrams representing all allowed system states from $q = 0$ up to $q = 6$. Instead of using dots as in the previous problem, use numbers to indicate the number of bosons occupying each level.

(b) Compute the occupancy of each energy level, for $q = 6$. Draw a graph of the occupancy as a function of the energy of the level.

(c) Estimate the values of μ and T that you would have to plug into the Bose-Einstein distribution to best fit the graph of part (b).

(d) As in part (d) of the previous problem, draw a graph of entropy vs. energy and estimate the temperature at $q = 6$ from this graph.

Problem 7.18. Imagine that there exists a third type of particle, which can share a single-particle state with one other particle of the same type but no more. Thus the number of these particles in any state can be 0, 1, or 2. Derive the distribution function for the average occupancy of a state by particles of this type, and plot the occupancy as a function of the state's energy, for several different temperatures.

7.3 Degenerate Fermi Gases

As a first application of quantum statistics and the Fermi-Dirac distribution, I'd like to consider a "gas" of fermions at very low temperature. The fermions could be helium-3 atoms, or protons and neutrons in an atomic nucleus, or electrons in a white dwarf star, or neutrons in a neutron star. The most familiar example, though, is the conduction electrons inside a chunk of metal. In this section I'll say "electrons" to be specific, even though the results apply to other types of fermions as well.

By "very low temperature," I do *not* necessarily mean low compared to room temperature. What I mean is that the condition for Boltzmann statistics to apply to an ideal gas, $V/N \gg v_Q$, is badly violated, so that in fact $V/N \ll v_Q$. For an electron at room temperature, the quantum volume is

$$v_Q = \left(\frac{h}{\sqrt{2\pi mkT}}\right)^3 = (4.3 \text{ nm})^3. \tag{7.32}$$

But in a typical metal there is about one conduction electron per atom, so the volume per conduction electron is roughly the volume of an atom, $(0.2 \text{ nm})^3$. Thus, the temperature is *much* too low for Boltzmann statistics to apply. Instead, we are in the opposite limit, where for many purposes we can pretend that $T = 0$. Let us therefore first consider the properties of an electron gas *at* $T = 0$, and later ask what happens at small nonzero temperatures.

Zero Temperature

At $T = 0$ the Fermi-Dirac distribution becomes a step function (see Figure 7.9). All single-particle states with energy less than μ are occupied, while all states with energy greater than μ are unoccupied. In this context μ is also called the **Fermi energy**, denoted ϵ_F:

$$\epsilon_F \equiv \mu(T = 0). \tag{7.33}$$

When a gas of fermions is so cold that nearly all states below ϵ_F are occupied while nearly all states above ϵ_F are unoccupied, it is said to be **degenerate**. (This use of the word is completely unrelated to its other use to describe a set of quantum states that have the same energy.)

The *value* of ϵ_F is determined by the total number of electrons present. Imagine an empty box, to which you add electrons one at a time, with no excess energy. Each electron goes into the lowest available state, until the last electron goes into a state with energy just below ϵ_F. To add one more electron you would have to give it an energy essentially equal to $\epsilon_F = \mu$; in this context, the equation $\mu = (\partial U/\partial N)_{S,V}$ makes perfect physical sense, since $dU = \mu$ when $dN = 1$ (and S is fixed at zero when all the electrons are packed into the lowest-energy states).

In order to calculate ϵ_F, as well as other interesting quantities such as the total energy and the pressure of the electron gas, I'll make the approximation that the electrons are *free* particles, subject to no forces whatsoever except that they are confined inside a box of volume $V = L^3$. For the conduction electrons in a metal, this approximation is not especially accurate. Although it is reasonable to neglect long-range electrostatic forces in any electrically neutral material, each conduction electron still feels attractive forces from nearby ions in the crystal lattice, and I'm neglecting these forces.*

The definite-energy wavefunctions of a free electron inside a box are just sine waves, exactly as for the gas molecules treated in Section 6.7. For a one-dimensional

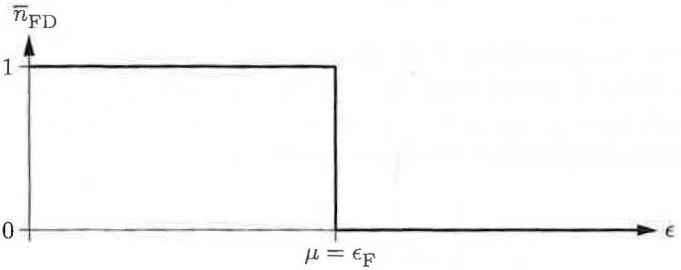

Figure 7.9. At $T = 0$, the Fermi-Dirac distribution equals 1 for all states with $\epsilon < \mu$ and equals 0 for all states with $\epsilon > \mu$.

*Problems 7.33 and 7.34 treat some of the effects of the crystal lattice on the conduction electrons. For much more detail, see a solid state physics textbook such as Kittel (1996) or Ashcroft and Mermin (1976).

box the allowed wavelengths and momenta are (as before)

$$\lambda_n = \frac{2L}{n}, \qquad p_n = \frac{h}{\lambda_n} = \frac{hn}{2L}, \tag{7.34}$$

where n is any positive integer. In a three-dimensional box these equations apply separately to the x, y, and z directions, so

$$p_x = \frac{hn_x}{2L}, \qquad p_y = \frac{hn_y}{2L}, \qquad p_z = \frac{hn_z}{2L}, \tag{7.35}$$

where (n_x, n_y, n_z) is a triplet of positive integers. The allowed energies are therefore

$$\epsilon = \frac{|\vec{p}|^2}{2m} = \frac{h^2}{8mL^2}(n_x^2 + n_y^2 + n_z^2). \tag{7.36}$$

To visualize the set of allowed states, I like to draw a picture of "n-space," the three-dimensional space whose axes are n_x, n_y, and n_z (see Figure 7.10). Each allowed $\vec{n}$ vector corresponds to a point in this space with positive integer coordinates; the set of all allowed states forms a huge lattice filling the first octant of n-space. Each lattice point actually represents *two* states, since for each spatial wavefunction there are two independent spin orientations.

In n-space, the energy of any state is proportional to the square of the *distance* from the origin, $n_x^2 + n_y^2 + n_z^2$. So as we add electrons to the box, they settle into states starting at the origin and gradually working outward. By the time we're done, the total number of occupied states is so huge that the occupied region of n-space is essentially an eighth of a sphere. (The roughness of the edges is insignificant, compared to the enormous size of the entire sphere.) I'll call the radius of this sphere $n_{\max}$.

It's now quite easy to relate the total number of electrons, N, to the chemical potential or Fermi energy, $\mu = \epsilon_F$. On one hand, ϵ_F is the energy of a state that sits just on the surface of the sphere in n-space, so

$$\epsilon_F = \frac{h^2 n_{\max}^2}{8mL^2}. \tag{7.37}$$

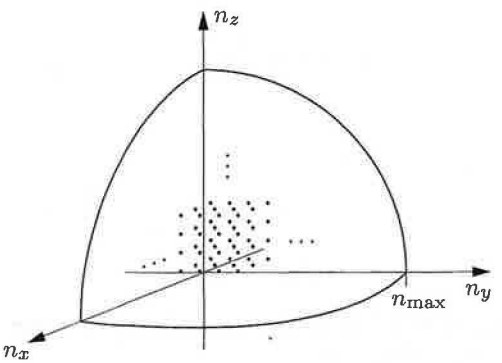

Figure 7.10. Each triplet of integers (n_x, n_y, n_z) represents a pair of definite-energy electron states (one with each spin orientation). The set of all independent states fills the positive octant of n-space.

On the other hand, the total volume of the eighth-sphere in n-space equals the number of lattice points enclosed, since the separation between lattice points is 1 in all three directions. Therefore the total number of occupied states is twice this volume (because of the two spin orientations):

$$N = 2 \times (\text{volume of eighth-sphere}) = 2 \cdot \frac{1}{8} \cdot \frac{4}{3} \pi n_{\max}^3 = \frac{\pi n_{\max}^3}{3}. \tag{7.38}$$

Combining these two equations gives the Fermi energy as a function of N and the volume $V = L^3$ of the box:

$$\epsilon_F = \frac{h^2}{8m} \left(\frac{3N}{\pi V} \right)^{2/3}. \tag{7.39}$$

Notice that this quantity is intensive, since it depends only on the number density of electrons, N/V. For a larger container with correspondingly more electrons, ϵ_F comes out the same. Although I have derived this result only for electrons in a cube-shaped box, it actually applies to macroscopic containers (or chunks of metal) of any shape.

The Fermi energy is the *highest* energy of all the electrons. On average, they'll have somewhat less energy, a little more than half ϵ_F. To be more precise, we have to do an integral, to find the *total* energy of all the electrons; the average is just the total divided by N.

To calculate the total energy of all the electrons, I'll add up the energies of the electrons in all occupied states. This entails a triple sum over n_x, n_y, and n_z:

$$U = 2 \sum_{n_x} \sum_{n_y} \sum_{n_z} \epsilon(\vec{n}) = 2 \int\int\int \epsilon(\vec{n}) \, dn_x \, dn_y \, dn_z. \tag{7.40}$$

The factor of 2 is for the two spin orientations for each $\vec{n}$. I'm allowed to change the sum into an integral because the number of terms is so huge, it might as well be a continuous function. To evaluate the triple integral I'll use spherical coordinates, as illustrated in Figure 7.11. Note that the volume element $dn_x \, dn_y \, dn_z$ becomes

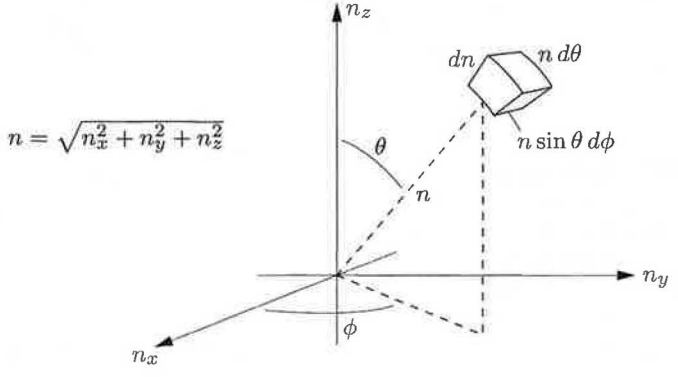

Figure 7.11. In spherical coordinates (n, θ, ϕ), the infinitesimal volume element is $(dn)(n\,d\theta)(n \sin\theta\, d\phi)$.

$n^2 \sin\theta \, dn \, d\theta \, d\phi$. The total energy of all the electrons is therefore

$$U = 2 \int_0^{n_{\max}} dn \int_0^{\pi/2} d\theta \int_0^{\pi/2} d\phi \, n^2 \sin\theta \, \epsilon(n). \tag{7.41}$$

The angular integrals give $\pi/2$, one-eighth the surface area of a unit sphere. This leaves us with

$$U = \pi \int_0^{n_{\max}} \epsilon(n) \, n^2 \, dn = \frac{\pi h^2}{8mL^2} \int_0^{n_{\max}} n^4 \, dn = \frac{\pi h^2 n_{\max}^5}{40mL^2} = \frac{3}{5} N \epsilon_{\mathrm{F}}. \tag{7.42}$$

The *average* energy of the electrons is therefore 3/5 the Fermi energy.

If you plug in some numbers, you'll find that the Fermi energy for conduction electrons in a typical metal is a few electron-volts. This is *huge* compared to the average *thermal* energy of a particle at room temperature, roughly $kT \approx 1/40$ eV. In fact, comparing the Fermi energy to the average thermal energy is essentially the same as comparing the quantum volume to the average volume per particle, as I did at the beginning of this section:

$$\frac{V}{N} \ll v_Q \qquad \text{is the same as} \qquad kT \ll \epsilon_{\mathrm{F}}. \tag{7.43}$$

When this condition is met, the approximation $T \approx 0$ is fairly accurate for many purposes, and the gas is said to be degenerate. The temperature that a Fermi gas would have to have in order for kT to equal ϵ_{F} is called the **Fermi temperature**: $T_{\mathrm{F}} \equiv \epsilon_{\mathrm{F}}/k$. This temperature is purely hypothetical for electrons in a metal, since metals liquefy and evaporate long before it is reached.

Using the formula $P = -(\partial U/\partial V)_{S,N}$, which you can derive from the thermodynamic identity or straight from classical mechanics, we can calculate the pressure of a degenerate electron gas:

$$P = -\frac{\partial}{\partial V}\left[\frac{3}{5} N \frac{h^2}{8m}\left(\frac{3N}{\pi}\right)^{2/3} V^{-2/3}\right] = \frac{2N\epsilon_{\mathrm{F}}}{5V} = \frac{2}{3}\frac{U}{V}. \tag{7.44}$$

This quantity is called the **degeneracy pressure**. It is positive because when you compress a degenerate electron gas, the wavelengths of all the wavefunctions are reduced, hence the energies of all the wavefunctions increase. Degeneracy pressure is what keeps matter from collapsing under the huge electrostatic forces that try to pull electrons and protons together. Please note that degeneracy pressure has absolutely nothing to do with electrostatic repulsion between the electrons (which we've completely ignored); it arises purely by virtue of the exclusion principle.

Numerically, the degeneracy pressure comes out to a few *billion* $\mathrm{N/m^2}$ for a typical metal. But this number is not directly measurable—it is canceled by the electrostatic forces that hold the electrons inside the metal in the first place. A more measurable quantity is the **bulk modulus**, that is, the change in pressure when the material is compressed, divided by the fractional change in volume:

$$B = -V\left(\frac{\partial P}{\partial V}\right)_T = \frac{10}{9}\frac{U}{V}. \tag{7.45}$$

This quantity is also quite large in SI units, but it is *not* completely canceled by the electrostatic forces; the formula actually agrees with experiment, within a factor of 3 or so, for most metals.

Problem 7.19. Each atom in a chunk of copper contributes one conduction electron. Look up the density and atomic mass of copper, and calculate the Fermi energy, the Fermi temperature, the degeneracy pressure, and the contribution of the degeneracy pressure to the bulk modulus. Is room temperature sufficiently low to treat this system as a degenerate electron gas?

Problem 7.20. At the center of the sun, the temperature is approximately 10^7 K and the concentration of electrons is approximately 10^{32} per cubic meter. Would it be (approximately) valid to treat these electrons as a "classical" ideal gas (using Boltzmann statistics), or as a degenerate Fermi gas (with $T \approx 0$), or neither?

Problem 7.21. An atomic nucleus can be crudely modeled as a gas of nucleons with a number density of 0.18 fm^{-3} (where 1 fm = 10^{-15} m). Because nucleons come in two different types (protons and neutrons), each with spin 1/2, each spatial wavefunction can hold *four* nucleons. Calculate the Fermi energy of this system, in MeV. Also calculate the Fermi temperature, and comment on the result.

Problem 7.22. Consider a degenerate electron gas in which essentially all of the electrons are highly relativistic ($\epsilon \gg mc^2$), so that their energies are $\epsilon = pc$ (where p is the magnitude of the momentum vector).

(a) Modify the derivation given above to show that for a relativistic electron gas at zero temperature, the chemical potential (or Fermi energy) is given by $\mu = hc(3N/8\pi V)^{1/3}$.

(b) Find a formula for the total energy of this system in terms of N and μ.

Problem 7.23. A **white dwarf** star (see Figure 7.12) is essentially a degenerate electron gas, with a bunch of nuclei mixed in to balance the charge and to provide the gravitational attraction that holds the star together. In this problem you will derive a relation between the mass and the radius of a white dwarf star, modeling the star as a uniform-density sphere. White dwarf stars tend to be extremely hot by our standards; nevertheless, it is an excellent approximation in this problem to set $T = 0$.

(a) Use dimensional analysis to argue that the gravitational potential energy of a uniform-density sphere (mass M, radius R) must equal

$$U_{\text{grav}} = -(\text{constant})\frac{GM^2}{R},$$

where (constant) is some numerical constant. Be sure to explain the minus sign. The constant turns out to equal 3/5; you can derive it by calculating the (negative) work needed to assemble the sphere, shell by shell, from the inside out.

(b) Assuming that the star contains one proton and one neutron for each electron, and that the electrons are nonrelativistic, show that the total (kinetic) energy of the degenerate electrons equals

$$U_{\text{kinetic}} = (0.0088)\frac{h^2 M^{5/3}}{m_e m_p^{5/3} R^2}.$$

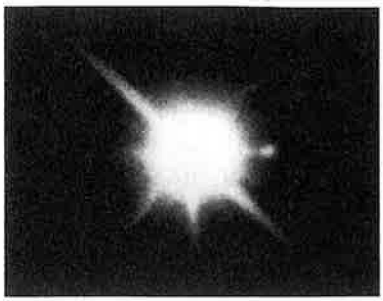

Figure 7.12. The double star system Sirius A and B. Sirius A (greatly overexposed in the photo) is the brightest star in our night sky. Its companion, Sirius B, is hotter but very faint, indicating that it must be extremely small—a white dwarf. From the orbital motion of the pair we know that Sirius B has about the same mass as our sun. (UCO/Lick Observatory photo.)

The numerical factor can be expressed exactly in terms of π and cube roots and such, but it's not worth it.

(c) The equilibrium radius of the white dwarf is that which minimizes the total energy $U_{\text{grav}} + U_{\text{kinetic}}$. Sketch the total energy as a function of R, and find a formula for the equilibrium radius in terms of the mass. As the mass increases, does the radius increase or decrease? Does this make sense?

(d) Evaluate the equilibrium radius for $M = 2 \times 10^{30}$ kg, the mass of the sun. Also evaluate the density. How does the density compare to that of water?

(e) Calculate the Fermi energy and the Fermi temperature, for the case considered in part (d). Discuss whether the approximation $T = 0$ is valid.

(f) Suppose instead that the electrons in the white dwarf star are highly relativistic. Using the result of the previous problem, show that the total kinetic energy of the electrons is now proportional to $1/R$ instead of $1/R^2$. Argue that there is no stable equilibrium radius for such a star.

(g) The transition from the nonrelativistic regime to the ultrarelativistic regime occurs approximately where the average kinetic energy of an electron is equal to its rest energy, mc^2. Is the nonrelativistic approximation valid for a one-solar-mass white dwarf? Above what mass would you expect a white dwarf to become relativistic and hence unstable?

Problem 7.24. A star that is too heavy to stabilize as a white dwarf can collapse further to form a **neutron star**: a star made entirely of neutrons, supported against gravitational collapse by degenerate neutron pressure. Repeat the steps of the previous problem for a neutron star, to determine the following: the mass-radius relation; the radius, density, Fermi energy, and Fermi temperature of a one-solar-mass neutron star; and the critical mass above which a neutron star becomes relativistic and hence unstable to further collapse.

Small Nonzero Temperatures

One property of a Fermi gas that we *cannot* calculate using the approximation $T = 0$ is the heat capacity, since this is a measure of how the energy of the system depends on T. Let us therefore consider what happens when the temperature is very small but nonzero. Before doing any careful calculations, I'll explain what happens qualitatively and try to give some plausibility arguments.

At temperature T, all particles typically acquire a thermal energy of roughly kT. However, in a degenerate electron gas, most of the electrons *cannot* acquire such a small amount of energy, because all the states that they might jump into are already occupied (recall the shape of the Fermi-Dirac distribution, Figure 7.6).

The only electrons that *can* acquire some thermal energy are those that are already within about kT of the Fermi energy—these can jump up into unoccupied states above ϵ_F. (The spaces they leave behind allow *some*, but not many, of the lower-lying electrons to also gain energy.) Notice that the number of electrons that can be affected by the increase in T is proportional to T. This number must also be proportional to N, because it is an extensive quantity.

Thus, the additional energy that a degenerate electron gas acquires when its temperature is raised from zero to T is *doubly* proportional to T:

$$\begin{aligned}\text{additional energy} &\propto (\text{number of affected electrons}) \times (\text{energy acquired by each}) \\ &\propto (NkT) \times (kT) \\ &\propto N(kT)^2. \end{aligned} \tag{7.46}$$

We can guess the constant of proportionality using dimensional analysis. The quantity $N(kT)^2$ has units of (energy)^2, so to get something with units of (energy)^1, we need to divide by some constant with units of energy. The only such constant available is ϵ_F, so the additional energy must be $N(kT)^2/\epsilon_F$, times some constant of order 1. In a few pages we'll see that this constant is $\pi^2/4$, so the total energy of a degenerate Fermi gas for $T \ll \epsilon_F/k$ is

$$U = \frac{3}{5}N\epsilon_F + \frac{\pi^2}{4}N\frac{(kT)^2}{\epsilon_F}. \tag{7.47}$$

From this result we can easily calculate the heat capacity:

$$C_V = \left(\frac{\partial U}{\partial T}\right)_V = \frac{\pi^2 N k^2 T}{2\epsilon_F}. \tag{7.48}$$

Notice that the heat capacity goes to zero at $T = 0$, as required by the third law of thermodynamics. The approach to zero is *linear* in T, and this prediction agrees well with experiments on metals at low temperatures. (Above a few kelvins, lattice vibrations also contribute significantly to the heat capacity of a metal.) The numerical coefficient of $\pi^2/2$ usually agrees with experiment to within 50% or better, but there are exceptions.

Problem 7.25. Use the results of this section to estimate the contribution of conduction electrons to the heat capacity of one mole of copper at room temperature. How does this contribution compare to that of lattice vibrations, assuming that these are not frozen out? (The electronic contribution has been measured at low temperatures, and turns out to be about 40% more than predicted by the free electron model used here.)

Problem 7.26. In this problem you will model helium-3 as a noninteracting Fermi gas. Although ^{3}He liquefies at low temperatures, the liquid has an unusually low density and behaves in many ways like a gas because the forces between the atoms are so weak. Helium-3 atoms are spin-1/2 fermions, because of the unpaired neutron in the nucleus.

(a) Pretending that liquid ^{3}He is a noninteracting Fermi gas, calculate the Fermi energy and the Fermi temperature. The molar volume (at low pressures) is 37 cm^3.

(b) Calculate the heat capacity for $T \ll T_F$, and compare to the experimental result $C_V = (2.8\ \mathrm{K}^{-1})NkT$ (in the low-temperature limit). (Don't expect perfect agreement.)

(c) The entropy of *solid* ^{3}He below 1 K is almost entirely due to its multiplicity of nuclear spin alignments. Sketch a graph S vs. T for liquid and solid ^{3}He at low temperature, and estimate the temperature at which the liquid and solid have the same entropy. Discuss the shape of the solid-liquid phase boundary shown in Figure 5.13.

Problem 7.27. The argument given above for why $C_V \propto T$ does not depend on the details of the energy levels available to the fermions, so it should also apply to the model considered in Problem 7.16: a gas of fermions trapped in such a way that the energy levels are evenly spaced and nondegenerate.

(a) Show that, in this model, the number of possible system states for a given value of q is equal to the number of distinct ways of writing q as a sum of positive integers. (For example, there are three system states for $q = 3$, corresponding to the sums 3, $2 + 1$, and $1 + 1 + 1$. Note that $2 + 1$ and $1 + 2$ are not counted separately.) This combinatorial function is called the number of **unrestricted partitions** of q, denoted $p(q)$. For example, $p(3) = 3$.

(b) By enumerating the partitions explicitly, compute $p(7)$ and $p(8)$.

(c) Make a table of $p(q)$ for values of q up to 100, by either looking up the values in a mathematical reference book, or using a software package that can compute them, or writing your own program to compute them. From this table, compute the entropy, temperature, and heat capacity of this system, using the same methods as in Section 3.3. Plot the heat capacity as a function of temperature, and note that it is approximately linear.

(d) Ramanujan and Hardy (two famous mathematicians) have shown that when q is large, the number of unrestricted partitions of q is given approximately by

$$p(q) \approx \frac{e^{\pi\sqrt{2q/3}}}{4\sqrt{3}\,q}.$$

Check the accuracy of this formula for $q = 10$ and for $q = 100$. Working in this approximation, calculate the entropy, temperature, and heat capacity of this system. Express the heat capacity as a series in decreasing powers of kT/η, assuming that this ratio is large and keeping the two largest terms. Compare to the numerical results you obtained in part (c). Why is the heat capacity of this system independent of N, unlike that of the three-dimensional box of fermions discussed in the text?

The Density of States

To better visualize—and quantify—the behavior of a Fermi gas at small nonzero temperatures, I need to introduce a new concept. Let's go back to the energy integral (7.42), and change variables from n to the electron energy ϵ:

$$\epsilon = \frac{h^2}{8mL^2}n^2, \qquad n = \sqrt{\frac{8mL^2}{h^2}}\sqrt{\epsilon}, \qquad dn = \sqrt{\frac{8mL^2}{h^2}}\frac{1}{2\sqrt{\epsilon}}\,d\epsilon. \tag{7.49}$$

With this substitution, you can show that the energy integral for a Fermi gas at zero temperature becomes

$$U = \int_0^{\epsilon_F} \epsilon \left[\frac{\pi}{2} \left(\frac{8mL^2}{h^2} \right)^{3/2} \sqrt{\epsilon} \right] d\epsilon \qquad (T = 0). \tag{7.50}$$

The quantity in square brackets has a nice interpretation: It is the number of single-particle states per unit energy. To compute the total energy of the system we carry out a sum over all energies of the energy in question times the number of states with that energy.

The number of single-particle states per unit energy is called the **density of states**. The symbol for it is $g(\epsilon)$, and it can be written in various ways:

$$g(\epsilon) = \frac{\pi(8m)^{3/2}}{2h^3} V\sqrt{\epsilon} = \frac{3N}{2\epsilon_F^{3/2}} \sqrt{\epsilon}. \tag{7.51}$$

The second expression is compact and handy, but perhaps rather confusing since it seems to imply that $g(\epsilon)$ depends on N, when in fact the N dependence is canceled by ϵ_F. I like the first expression better, since it shows explicitly that $g(\epsilon)$ is proportional to V and independent of N. But either way, the most important point is that $g(\epsilon)$, for a three-dimensional box of free particles, is proportional to $\sqrt{\epsilon}$. A graph of the function is a parabola opening to the right, as shown in Figure 7.13. If you want to know how many states there are between two energies ϵ_1 and ϵ_2, you just integrate this function over the desired range. The density of states is a function whose purpose in life is to be integrated.

The density-of-states idea can be applied to lots of other systems besides this one. Equation 7.51 and Figure 7.13 are for the specific case of a gas of "free" electrons, confined inside a fixed volume but not subject to any other forces. In more realistic models of metals we would want to take into account the attraction of the electrons toward the positive ions of the crystal lattice. Then the wavefunctions and their energies would be quite different, and therefore $g(\epsilon)$ would be a much more complicated function. The nice thing is that determining g is purely a problem of quantum mechanics, having nothing to do with thermal effects or temperature. And

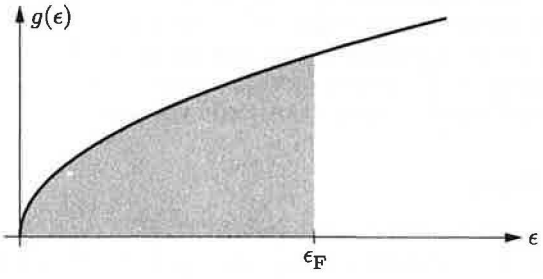

Figure 7.13. Density of states for a system of noninteracting, nonrelativistic particles in a three-dimensional box. The number of states within any energy interval is the area under the graph. For a Fermi gas at $T = 0$, all states with $\epsilon < \epsilon_F$ are occupied while all states with $\epsilon > \epsilon_F$ are unoccupied.

once you know g for some system, you can then forget about quantum mechanics and concentrate on the thermal physics.

For an electron gas at *zero* temperature, we can get the total number of electrons by just integrating the density of states up to the Fermi energy:

$$N = \int_0^{\epsilon_F} g(\epsilon)\, d\epsilon \qquad (T = 0). \tag{7.52}$$

(For a free electron gas this is the same as equation 7.50 for the energy, but without the extra factor of ϵ.) But what if T is nonzero? Then we need to multiply $g(\epsilon)$ by the *probability* of a state with that energy being occupied, that is, by the Fermi-Dirac distribution function. Also we need to integrate all the way up to infinity, since any state could conceivably be occupied:

$$N = \int_0^\infty g(\epsilon)\, \overline{n}_{\text{FD}}(\epsilon)\, d\epsilon = \int_0^\infty g(\epsilon)\, \frac{1}{e^{(\epsilon-\mu)/kT}+1}\, d\epsilon \qquad (\text{any } T). \tag{7.53}$$

And to get the total energy of all the electrons, just slip in an ϵ:

$$U = \int_0^\infty \epsilon\, g(\epsilon)\, \overline{n}_{\text{FD}}(\epsilon)\, d\epsilon = \int_0^\infty \epsilon\, g(\epsilon)\, \frac{1}{e^{(\epsilon-\mu)/kT}+1}\, d\epsilon \qquad (\text{any } T). \tag{7.54}$$

Figure 7.14 shows a graph of the integrand of the N-integral (7.53), for a free electron gas at nonzero T. Instead of falling immediately to zero at $\epsilon = \epsilon_F$, the number of electrons per unit energy now drops more gradually, over a width of a few times kT. The chemical potential, μ, is the point where the probability of a state being occupied is exactly $1/2$, and it's important to note that this point is no longer the same as it was at zero temperature:

$$\mu(T) \neq \epsilon_F \qquad \text{except when } T = 0. \tag{7.55}$$

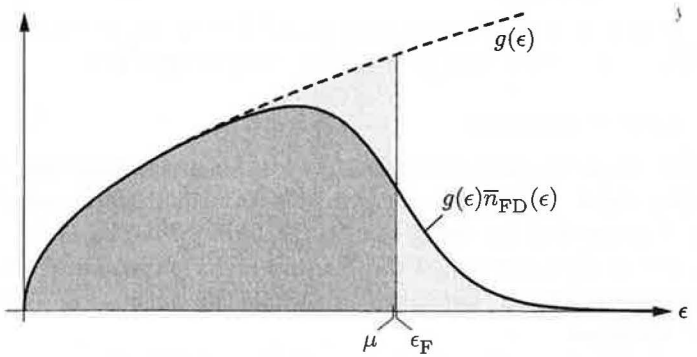

Figure 7.14. At nonzero T, the number of fermions per unit energy is given by the density of states times the Fermi-Dirac distribution. Because increasing the temperature does not change the total number of fermions, the two lightly shaded areas must be equal. Since $g(\epsilon)$ is greater above ϵ_F than below, this means that the chemical potential decreases as T increases. This graph is drawn for $T/T_F = 0.1$; at this temperature μ is about 1% less than ϵ_F.

Why not? Recall from Problem 7.12 that the Fermi-Dirac distribution function is symmetrical about $\epsilon = \mu$: The probability of a state above μ being occupied is the same as the probability of a state the same amount below μ being *un*occupied. Now suppose that μ were to remain constant as T increases from zero. Then since the density of states is greater to the right of μ than to the left, the number of electrons we would be adding at $\epsilon > \mu$ would be greater than the number we are losing from $\epsilon < \mu$. In other words, we could increase the total number of electrons just by raising the temperature! To prevent such nonsense, the chemical potential has to decrease slightly, thus lowering all of the probabilities by a small amount.

The precise formula for $\mu(T)$ is determined implicitly by the integral for N, equation 7.53. *If* we could carry out this integral, we could take the resulting formula and solve it for $\mu(T)$ (since N is a fixed constant). Then we could plug our value of $\mu(T)$ into the energy integral (7.54), and try to carry out *that* integral to find $U(T)$ (and hence the heat capacity). The bad news is that these integrals cannot be evaluated exactly, even for the simple case of a free electron gas. The good news is that they *can* be evaluated approximately, in the limit $kT \ll \epsilon_F$. In this limit the answer for the energy integral is what I wrote in equation 7.47.

Problem 7.28. Consider a free Fermi gas in two dimensions, confined to a square area $A = L^2$.

(a) Find the Fermi energy (in terms of N and A), and show that the average energy of the particles is $\epsilon_F/2$.

(b) Derive a formula for the density of states. You should find that it is a constant, independent of ϵ.

(c) Explain how the chemical potential of this system should behave as a function of temperature, both when $kT \ll \epsilon_F$ and when T is much higher.

(d) Because $g(\epsilon)$ is a constant for this system, it is possible to carry out the integral 7.53 for the number of particles analytically. Do so, and solve for μ as a function of N. Show that the resulting formula has the expected qualitative behavior.

(e) Show that in the high-temperature limit, $kT \gg \epsilon_F$, the chemical potential of this system is the same as that of an ordinary ideal gas.

The Sommerfeld Expansion

After talking about the integrals 7.53 and 7.54 for so long, it's about time I explained how to evaluate them, to find the chemical potential and total energy of a free electron gas. The method for doing this in the limit $kT \ll \epsilon_F$ is due to Arnold Sommerfeld, and is therefore called the **Sommerfeld expansion**. None of the steps are particularly difficult, but taken as a whole the calculation is rather tricky and intricate. Hang on.

I'll start with the integral for N:

$$N = \int_0^\infty g(\epsilon)\,\overline{n}_{FD}(\epsilon)\,d\epsilon = g_0 \int_0^\infty \epsilon^{1/2}\,\overline{n}_{FD}(\epsilon)\,d\epsilon. \tag{7.56}$$

(In the second expression I've introduced the abbreviation g_0 for the constant that multiplies $\sqrt{\epsilon}$ in equation 7.51 for the density of states.) Although this integral

runs over all positive ϵ, the most interesting region is near $\epsilon = \mu$, where $\overline{n}_{\rm FD}(\epsilon)$ falls off steeply (for $T \ll \epsilon_{\rm F}$). So the first trick is to isolate this region, by integrating by parts:

$$N = \frac{2}{3} g_0 \epsilon^{3/2} \overline{n}_{\rm FD}(\epsilon)\Big|_0^\infty + \frac{2}{3} g_0 \int_0^\infty \epsilon^{3/2} \left(-\frac{d\overline{n}_{\rm FD}}{d\epsilon} \right) d\epsilon. \tag{7.57}$$

The boundary term vanishes at both limits, leaving us with an integral that is much nicer, because $d\overline{n}_{\rm FD}/d\epsilon$ is negligible everywhere except in a narrow region around $\epsilon = \mu$ (see Figure 7.15). Explicitly, we can compute

$$-\frac{d\overline{n}_{\rm FD}}{d\epsilon} = -\frac{d}{d\epsilon}\left(e^{(\epsilon-\mu)/kT} + 1\right)^{-1} = \frac{1}{kT}\frac{e^x}{(e^x+1)^2}, \tag{7.58}$$

where $x = (\epsilon - \mu)/kT$. Thus the integral that we need to evaluate is

$$N = \frac{2}{3} g_0 \int_0^\infty \frac{1}{kT}\frac{e^x}{(e^x+1)^2}\,\epsilon^{3/2}\,d\epsilon = \frac{2}{3} g_0 \int_{-\mu/kT}^\infty \frac{e^x}{(e^x+1)^2}\,\epsilon^{3/2}\,dx, \tag{7.59}$$

where in the last expression I've changed the integration variable to x.

Because the integrand in this expression dies out exponentially when $|\epsilon - \mu| \gg kT$, we can now make two approximations. First, we can extend the lower limit on the integral down to $-\infty$; this makes things look more symmetrical, and it's harmless because the integrand is utterly negligible at negative ϵ values anyway. Second, we can expand the function $\epsilon^{3/2}$ in a Taylor series about the point $\epsilon = \mu$, and keep only the first few terms:

$$\begin{aligned} \epsilon^{3/2} &= \mu^{3/2} + (\epsilon-\mu)\frac{d}{d\epsilon}\epsilon^{3/2}\Big|_{\epsilon=\mu} + \frac{1}{2}(\epsilon-\mu)^2\frac{d^2}{d\epsilon^2}\epsilon^{3/2}\Big|_{\epsilon=\mu} + \cdots \\ &= \mu^{3/2} + \frac{3}{2}(\epsilon-\mu)\mu^{1/2} + \frac{3}{8}(\epsilon-\mu)^2\mu^{-1/2} + \cdots. \end{aligned} \tag{7.60}$$

With these approximations our integral becomes

$$N = \frac{2}{3} g_0 \int_{-\infty}^\infty \frac{e^x}{(e^x+1)^2}\left[\mu^{3/2} + \frac{3}{2}xkT\mu^{1/2} + \frac{3}{8}(xkT)^2\mu^{-1/2} + \cdots\right] dx. \tag{7.61}$$

Now, with only integer powers of x appearing, the integrals can actually be performed, term by term.

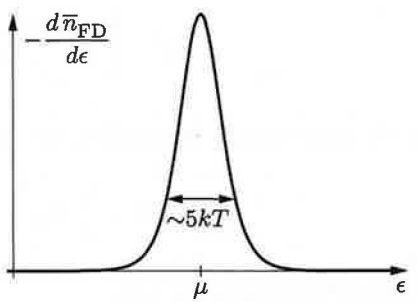

Figure 7.15. The derivative of the Fermi-Dirac distribution is negligible everywhere except within a few kT of μ.

The first term is easy:

$$\int_{-\infty}^{\infty} \frac{e^x}{(e^x+1)^2}\,dx = \int_{-\infty}^{\infty} -\frac{d\,\overline{n}_{\rm FD}}{d\epsilon}\,d\epsilon = \overline{n}_{\rm FD}(-\infty) - \overline{n}_{\rm FD}(\infty) = 1 - 0 = 1. \quad (7.62)$$

The second term is also easy, since the integrand is an odd function of x:

$$\int_{-\infty}^{\infty} \frac{x\,e^x}{(e^x+1)^2}\,dx = \int_{-\infty}^{\infty} \frac{x}{(e^x+1)(1+e^{-x})}\,dx = 0. \quad (7.63)$$

The third integral is the hard one. It *can* be evaluated analytically, as shown in Appendix B:

$$\int_{-\infty}^{\infty} \frac{x^2\,e^x}{(e^x+1)^2}\,dx = \frac{\pi^2}{3}. \quad (7.64)$$

You can also look it up in tables, or evaluate it numerically.

Assembling the pieces of equation 7.61, we obtain for the number of electrons

$$\begin{aligned} N &= \frac{2}{3}g_0\mu^{3/2} + \frac{1}{4}g_0(kT)^2\mu^{-1/2}\cdot\frac{\pi^2}{3} + \cdots \\ &= N\Big(\frac{\mu}{\epsilon_{\rm F}}\Big)^{3/2} + N\frac{\pi^2}{8}\frac{(kT)^2}{\epsilon_{\rm F}^{3/2}\mu^{1/2}} + \cdots. \end{aligned} \quad (7.65)$$

(In the second line I've plugged in $g_0 = 3N/2\epsilon_{\rm F}^{3/2}$, from equation 7.51.) Canceling the N's, we now see that $\mu/\epsilon_{\rm F}$ is approximately equal to 1, with a correction proportional to $(kT/\epsilon_{\rm F})^2$ (which we assume to be very small). Since the correction term is already quite small, we can approximate $\mu \approx \epsilon_{\rm F}$ in that term, then solve for $\mu/\epsilon_{\rm F}$ to obtain

$$\begin{aligned} \frac{\mu}{\epsilon_{\rm F}} &= \left[1 - \frac{\pi^2}{8}\Big(\frac{kT}{\epsilon_{\rm F}}\Big)^2 + \cdots\right]^{2/3} \\ &= 1 - \frac{\pi^2}{12}\Big(\frac{kT}{\epsilon_{\rm F}}\Big)^2 + \cdots. \end{aligned} \quad (7.66)$$

As predicted, the chemical potential gradually decreases as T is raised. The behavior of μ over a wide range of temperatures is shown in Figure 7.16.

The integral (7.54) for the total energy can be evaluated using exactly the same sequence of tricks. I'll leave it for you to do in Problem 7.29; the result is

$$U = \frac{3}{5}N\frac{\mu^{5/2}}{\epsilon_{\rm F}^{3/2}} + \frac{3\pi^2}{8}N\frac{(kT)^2}{\epsilon_{\rm F}} + \cdots. \quad (7.67)$$

Finally you can plug in formula 7.66 for μ and do just a bit more algebra to obtain

$$U = \frac{3}{5}N\epsilon_{\rm F} + \frac{\pi^2}{4}N\frac{(kT)^2}{\epsilon_{\rm F}} + \cdots, \quad (7.68)$$

as I claimed in equation 7.47.

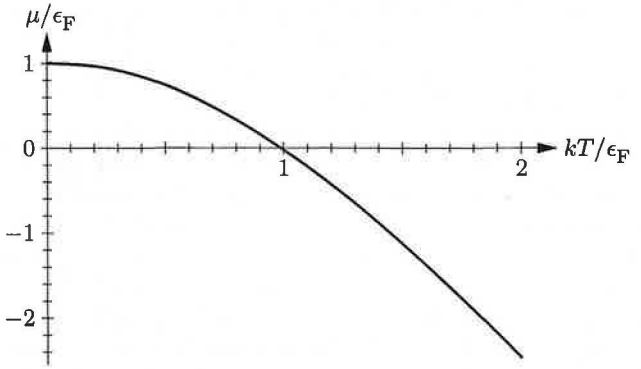

Figure 7.16. Chemical potential of a noninteracting, nonrelativistic Fermi gas in a three-dimensional box, calculated numerically as described in Problem 7.32. At low temperatures μ is given approximately by equation 7.66, while at high temperatures μ becomes negative and approaches the form for an ordinary gas obeying Boltzmann statistics.

Now admittedly, that was a lot of work just to get a factor of $\pi^2/4$ (since we had already guessed the rest by dimensional analysis). But I've presented this calculation in detail not so much because the *answer* is important, as because the *methods* are so typical of what professional physicists (and many other scientists and engineers) often do. Very few real-world problems can be solved exactly, so it's crucial for a scientist to learn when and how to make approximations. And more often than not, it's only *after* doing the hard calculation that one develops enough intuition to see how to guess most of the answer.

Problem 7.29. Carry out the Sommerfeld expansion for the energy integral (7.54), to obtain equation 7.67. Then plug in the expansion for μ to obtain the final answer, equation 7.68.

Problem 7.30. The Sommerfeld expansion is an expansion in powers of kT/ϵ_F, which is assumed to be small. In this section I kept all terms through order $(kT/\epsilon_F)^2$, omitting higher-order terms. Show at each relevant step that the term proportional to T^3 is zero, so that the next nonvanishing terms in the expansions for μ and U are proportional to T^4. (If you enjoy such things, you might try evaluating the T^4 terms, possibly with the aid of a computer algebra program.)

Problem 7.31. In Problem 7.28 you found the density of states and the chemical potential for a two-dimensional Fermi gas. Calculate the heat capacity of this gas in the limit $kT \ll \epsilon_F$. Also show that the heat capacity has the expected behavior when $kT \gg \epsilon_F$. Sketch the heat capacity as a function of temperature.

Problem 7.32. Although the integrals (7.53 and 7.54) for N and U cannot be carried out analytically for all T, it's not difficult to evaluate them numerically using a computer. This calculation has little relevance for electrons in metals (for which the limit $kT \ll \epsilon_F$ is always sufficient), but it is needed for liquid ^{3}He and for astrophysical systems like the electrons at the center of the sun.

(a) As a warm-up exercise, evaluate the N integral (7.53) for the case $kT = \epsilon_F$ and $\mu = 0$, and check that your answer is consistent with the graph shown

above. (Hint: As always when solving a problem on a computer, it's best to first put everything in terms of dimensionless variables. So let $t = kT/\epsilon_F$, $c = \mu/\epsilon_F$, and $x = \epsilon/\epsilon_F$. Rewrite everything in terms of these variables, and *then* put it on the computer.)

(b) The next step is to vary μ, holding T fixed, until the integral works out to the desired value, N. Do this for values of kT/ϵ_F ranging from 0.1 up to 2, and plot the results to reproduce Figure 7.16. (It's probably not a good idea to try to use numerical methods when kT/ϵ_F is much smaller than 0.1, since you can start getting overflow errors from exponentiating large numbers. But this is the region where we've already solved the problem analytically.)

(c) Plug your calculated values of μ into the energy integral (7.54), and evaluate that integral numerically to obtain the energy as a function of temperature for kT up to $2\epsilon_F$. Plot the results, and evaluate the slope to obtain the heat capacity. Check that the heat capacity has the expected behavior at both low and high temperatures.

Problem 7.33. When the attractive forces of the ions in a crystal are taken into account, the allowed electron energies are no longer given by the simple formula 7.36; instead, the allowed energies are grouped into **bands**, separated by **gaps** where there are no allowed energies. In a **conductor** the Fermi energy lies within one of the bands; in this section we have treated the electrons in this band as "free" particles confined to a fixed volume. In an **insulator**, on the other hand, the Fermi energy lies within a gap, so that at $T = 0$ the band below the gap is completely occupied while the band above the gap is unoccupied. Because there are no empty states close in energy to those that are occupied, the electrons are "stuck in place" and the material does not conduct electricity. A **semiconductor** is an insulator in which the gap is narrow enough for a few electrons to jump across it at room temperature. Figure 7.17 shows the density of states in the vicinity of the Fermi energy for an idealized semiconductor, and defines some terminology and notation to be used in this problem.

(a) As a first approximation, let us model the density of states near the bottom of the conduction band using the same function as for a free Fermi gas, with an appropriate zero-point: $g(\epsilon) = g_0\sqrt{\epsilon - \epsilon_c}$, where g_0 is the same constant as in equation 7.51. Let us also model the density of states near the top

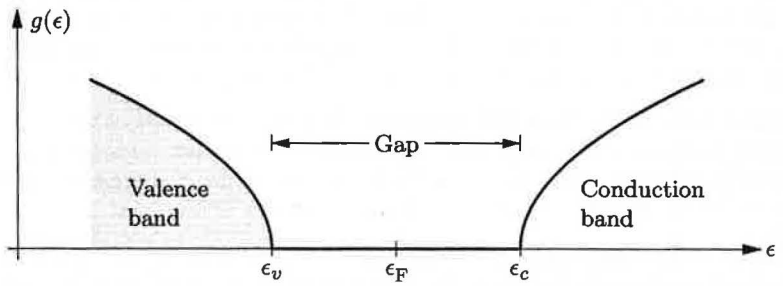

Figure 7.17. The periodic potential of a crystal lattice results in a density-of-states function consisting of "bands" (with many states) and "gaps" (with no states). For an insulator or a semiconductor, the Fermi energy lies in the middle of a gap so that at $T = 0$, the "valence band" is completely full while the "conduction band" is completely empty.

of the valence band as a mirror image of this function. Explain why, in this approximation, the chemical potential must always lie precisely in the middle of the gap, regardless of temperature.

(b) Normally the width of the gap is much greater than kT. Working in this limit, derive an expression for the number of conduction electrons per unit volume, in terms of the temperature and the width of the gap.

(c) For silicon near room temperature, the gap between the valence and conduction bands is approximately 1.11 eV. Roughly how many conduction electrons are there in a cubic centimeter of silicon at room temperature? How does this compare to the number of conduction electrons in a similar amount of copper?

(d) Explain why a semiconductor conducts electricity much better at higher temperatures. Back up your explanation with some numbers. (Ordinary conductors like copper, on the other hand, conduct better at *low* temperatures.)

(e) Very roughly, how wide would the gap between the valence and conduction bands have to be in order to consider a material an insulator rather than a semiconductor?

Problem 7.34. In a real semiconductor, the density of states at the bottom of the conduction band will differ from the model used in the previous problem by a numerical factor, which can be small or large depending on the material. Let us therefore write for the conduction band $g(\epsilon) = g_{0c}\sqrt{\epsilon - \epsilon_c}$, where g_{0c} is a new normalization constant that differs from g_0 by some fudge factor. Similarly, write $g(\epsilon)$ at the top of the valence band in terms of a new normalization constant g_{0v}.

(a) Explain why, if $g_{0v} \neq g_{0c}$, the chemical potential will now vary with temperature. When will it increase, and when will it decrease?

(b) Write down an expression for the number of conduction electrons, in terms of T, μ, ϵ_c, and g_{0c}. Simplify this expression as much as possible, assuming $\epsilon_c - \mu \gg kT$.

(c) An empty state in the valence band is called a **hole**. In analogy to part (b), write down an expression for the number of holes, and simplify it in the limit $\mu - \epsilon_v \gg kT$.

(d) Combine the results of parts (b) and (c) to find an expression for the chemical potential as a function of temperature.

(e) For silicon, $g_{0c}/g_0 = 1.09$ and $g_{0v}/g_0 = 0.44$.* Calculate the shift in μ for silicon at room temperature.

Problem 7.35. The previous two problems dealt with pure semiconductors, also called **intrinsic** semiconductors. Useful semiconductor devices are instead made from **doped** semiconductors, which contain substantial numbers of impurity atoms. One example of a doped semiconductor was treated in Problem 7.5. Let us now consider that system again. (Note that in Problem 7.5 we measured all energies relative to the bottom of the conduction band, ϵ_c. We also neglected the distinction between g_0 and g_{0c}; this simplification happens to be ok for conduction electrons in silicon.)

*These values can be calculated from the "effective masses" of electrons and holes. See, for example, S. M. Sze, *Physics of Semiconductor Devices*, second edition (Wiley, New York, 1981).

(a) Calculate and plot the chemical potential as a function of temperature, for silicon doped with 10^{17} phosphorus atoms per cm^3 (as in Problem 7.5). Continue to assume that the conduction electrons can be treated as an ordinary ideal gas.

(b) Discuss whether it is legitimate to assume for this system that the conduction electrons can be treated as an ordinary ideal gas, as opposed to a Fermi gas. Give some numerical examples.

(c) Estimate the temperature at which the number of valence electrons excited to the conduction band would become comparable to the number of conduction electrons from donor impurities. Which source of conduction electrons is more important at room temperature?

Problem 7.36. Most spin-1/2 fermions, including electrons and helium-3 atoms, have nonzero magnetic moments. A gas of such particles is therefore paramagnetic. Consider, for example, a gas of free electrons, confined inside a three-dimensional box. The z component of the magnetic moment of each electron is $\pm\mu_B$. In the presence of a magnetic field B pointing in the z direction, each "up" state acquires an additional energy of $-\mu_B B$, while each "down" state acquires an additional energy of $+\mu_B B$.

(a) Explain why you would expect the magnetization of a degenerate electron gas to be substantially less than that of the electronic paramagnets studied in Chapters 3 and 6, for a given number of particles at a given field strength.

(b) Write down a formula for the density of states of this system in the presence of a magnetic field B, and interpret your formula graphically.

(c) The magnetization of this system is $\mu_B(N_\uparrow - N_\downarrow)$, where $N_\uparrow$ and $N_\downarrow$ are the numbers of electrons with up and down magnetic moments, respectively. Find a formula for the magnetization of this system at $T = 0$, in terms of N, μ_B, B, and the Fermi energy.

(d) Find the first temperature-dependent correction to your answer to part (c), in the limit $T \ll T_F$. You may assume that $\mu_B B \ll kT$; this implies that the presence of the magnetic field has negligible effect on the chemical potential μ. (To avoid confusing μ_B with μ, I suggest using an abbreviation such as δ for the quantity $\mu_B B$.)

7.4 Blackbody Radiation

As a next application of quantum statistics, I'd like to consider the electromagnetic radiation inside some "box" (like an oven or kiln) at a given temperature. First let me discuss what we would expect of such a system in classical (i.e., non-quantum) physics.

The Ultraviolet Catastrophe

In classical physics, we treat electromagnetic radiation as a continuous "field" that permeates all space. Inside a box, we can think of this field as a combination of various standing-wave patterns, as shown in Figure 7.18. Each standing-wave pattern behaves as a harmonic oscillator with frequency $f = c/\lambda$. Like a mechanical oscillator, each electromagnetic standing wave has two degrees of freedom,