Problem 7.7. In Section 6.5 I derived the useful relation $F = -kT \ln Z$ between the Helmholtz free energy and the ordinary partition function. Use an analogous argument to prove that

$$\Phi = -kT \ln \mathcal{Z},$$

where $\mathcal{Z}$ is the grand partition function and Φ is the grand free energy introduced in Problem 5.23.

7.2 Bosons and Fermions

The most important application of Gibbs factors is to **quantum statistics**, the study of dense systems in which two or more identical particles have a reasonable chance of wanting to occupy the same single-particle state. In this situation, my derivation (in Section 6.6) of the partition function for a system of N indistinguishable, noninteracting particles,

$$Z = \frac{1}{N!} Z_1^N, \tag{7.16}$$

breaks down. The problem is that the counting factor of $N!$, the number of ways of interchanging the particles among their various states, is correct only if the particles are always in *different* states. (In this section I'll use the word "state" to mean a single-particle state. For the state of the system as a whole I'll always say "system state.")

To better understand this issue, let's consider a very simple example: a system containing two noninteracting particles, either of which can occupy any of five states (see Figure 7.3). Imagine that all five of these states have energy zero, so every Boltzmann factor equals 1 (and therefore Z is the same as Ω).

If the two particles are *distinguishable*, then each has five available states and the total number of *system* states is $Z = 5 \times 5 = 25$. If the two particles are *indistinguishable*, equation 7.16 would predict $Z = 5^2/2 = 12.5$, and this can't be right, since Z must (for this system) be an integer.

So let's count the system states more carefully. Since the particles are indistinguishable, all that matters is the number of particles in any given state. I can therefore represent any system state by a sequence of five integers, each representing the number of particles in a particular state. For instance, 01100 would represent the system state in which the second and third states each contain one particle,

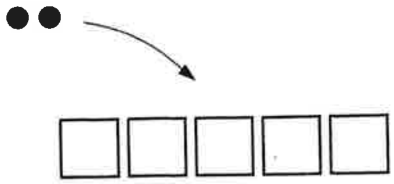

Figure 7.3. A simple model of five single-particle states, with two particles that can occupy these states.

while the rest contain none. Here, then, are all the allowed system states:

11000	01010	20000
10100	01001	02000
10010	00110	00200
10001	00101	00020
01100	00011	00002

(If you pretend that the states are harmonic oscillators and the particles are energy units, you can count the system states in the same way as for an Einstein solid.) There are 15 system states in all, of which 10 have the two particles in different states while 5 have the two particles in the same state. Each of the first 10 system states would actually be *two* different system states if the particles were distinguishable, since then they could be placed in either order. These 20 system states, plus the last 5 listed above, make the 25 counted in the previous paragraph. The factor of $1/N!$ in equation 7.16 correctly cuts the 20 down to 10, but also incorrectly cuts out half of the last five states.

Here I'm implicitly assuming that two identical particles *can* occupy the same state. It turns out that some types of particles can do this while others can't. Particles that *can* share a state with another of the same species are called **bosons**,[*] and include photons, pions, helium-4 atoms, and a variety of others. The number of identical bosons in a given state is unlimited. Experiments show, however, that many types of particles *cannot* share a state with another particle of the same type—not because they physically repel each other, but due to a quirk of quantum mechanics that I won't try to explain here (see Appendix A for some further discussion of this point). These particles are called **fermions**,[†] and include electrons, protons, neutrons, neutrinos, helium-3 atoms, and others. If the particles in the preceding example are identical fermions, then the five system states in the final column of the table are not allowed, so Z is only 10, not 15. (In formula 7.16, a system state with two particles in the same state is counted as half a system state, so this formula interpolates between the correct result for fermions and the correct result for bosons.) The rule that two identical fermions cannot occupy the same state is called the **Pauli exclusion principle**.

You can tell which particles are bosons and which are fermions by looking at their *spins*. Particles with integer spin (0, 1, 2, etc., in units of $h/2\pi$) are bosons, while particles with half-integer spin (1/2, 3/2, etc.) are fermions. This rule is *not* the *definition* of a boson or fermion, however; it is a nontrivial fact of nature, a deep consequence of the theories of relativity and quantum mechanics (as first derived by Wolfgang Pauli).

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[*] After Satyendra Nath Bose, who in 1924 introduced the method of treating a photon gas presented in Section 7.4. The generalization to other bosons was provided by Einstein shortly thereafter.

[†] After Enrico Fermi, who in 1926 worked out the basic implications of the exclusion principle for statistical mechanics. Paul A. M. Dirac independently did the same thing, in the same year.

In many situations, however, it just doesn't matter whether the particles in a fluid are bosons or fermions. When the number of available single-particle states is much greater than the number of particles,

$$Z_1 \gg N, \tag{7.17}$$

the chance of any two particles wanting to occupy the same state is negligible. More precisely, only a tiny fraction of all system states have a significant number of states doubly occupied. For an ideal gas, the single-particle partition function is $Z_1 = VZ_{\text{int}}/v_Q$, where Z_{int} is some reasonably small number and v_Q is the quantum volume,

$$v_Q = \ell_Q^3 = \left(\frac{h}{\sqrt{2\pi mkT}}\right)^3, \tag{7.18}$$

roughly the cube of the average de Broglie wavelength. The condition (7.17) for the formula $Z = Z_1^N/N!$ to apply then translates to

$$\frac{V}{N} \gg v_Q, \tag{7.19}$$

which says that the average distance between particles must be much greater than the average de Broglie wavelength. For the air we breathe, the average distance between molecules is about 3 nm while the average de Broglie wavelength is less than 0.02 nm, so this condition is definitely satisfied. Notice, by the way, that this condition depends not only on the density of the system, but also on the temperature and the mass of the particles, both through v_Q.

It's hard to visualize what actually happens in a gas when condition 7.17 breaks down and multiple particles start trying to get into the same state. Figure 7.4, though imperfect, is about the best I can do. Picture each particle as being smeared out in a quantum wavefunction filling a volume equal to v_Q. (This is equivalent to putting the particles into wavefunctions that are as localized in space as possible. To squeeze them into narrower wavefunctions we would have to introduce uncer-

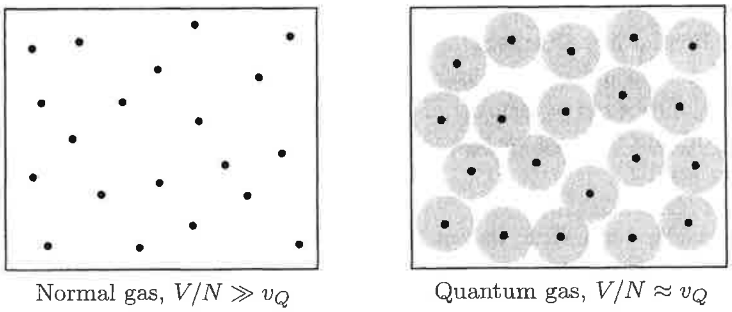
Normal gas, $V/N \gg v_Q$ Quantum gas, $V/N \approx v_Q$

Figure 7.4. In a normal gas, the space between particles is much greater than the typical size of a particle's wavefunction. When the wavefunctions begin to "touch" and overlap, we call it a **quantum gas**.

tainties in momentum that are large compared to the average momentum h/ℓ_Q, thus increasing the energy and temperature of the system.) In a normal gas, the effective volume thus occupied by all the particles will be much less than the volume of the container. (Often the quantum volume is less than the physical volume of a molecule.) But if the gas is sufficiently dense or v_Q is sufficiently large, then the wavefunctions will start trying to touch and overlap. At this point it starts to matter whether the particles are fermions or bosons; either way, the behavior will be much different from that of a normal gas.

There are plenty of systems that violate condition 7.17, either because they are very dense (like a neutron star), or very cold (like liquid helium), or composed of very light particles (like the electrons in a metal or the photons in a hot oven). The rest of this chapter is devoted to the study of these fascinating systems.

Problem 7.8. Suppose you have a "box" in which each particle may occupy any of 10 single-particle states. For simplicity, assume that each of these states has energy zero.

- (a) What is the partition function of this system if the box contains only one particle?
- (b) What is the partition function of this system if the box contains two distinguishable particles?
- (c) What is the partition function if the box contains two identical bosons?
- (d) What is the partition function if the box contains two identical fermions?
- (e) What would be the partition function of this system according to equation 7.16?
- (f) What is the probability of finding both particles in the same single-particle state, for the three cases of distinguishable particles, identical bosons, and identical fermions?

Problem 7.9. Compute the quantum volume for an N_2 molecule at room temperature, and argue that a gas of such molecules at atmospheric pressure can be treated using Boltzmann statistics. At about what temperature would quantum statistics become relevant for this system (keeping the density constant and pretending that the gas does not liquefy)?

Problem 7.10. Consider a system of five particles, inside a container where the allowed energy levels are nondegenerate and evenly spaced. For instance, the particles could be trapped in a one-dimensional harmonic oscillator potential. In this problem you will consider the allowed states for this system, depending on whether the particles are identical fermions, identical bosons, or distinguishable particles.

- (a) Describe the ground state of this system, for each of these three cases.
- (b) Suppose that the system has one unit of energy (above the ground state). Describe the allowed states of the system, for each of the three cases. How many possible system states are there in each case?
- (c) Repeat part (b) for two units of energy and for three units of energy.
- (d) Suppose that the temperature of this system is low, so that the total energy is low (though not necessarily zero). In what way will the behavior of the bosonic system differ from that of the system of distinguishable particles? Discuss.

The Distribution Functions

When a system violates the condition $Z_1 \gg N$, so that we cannot treat it using the methods of Chapter 6, we can use Gibbs factors instead. The idea is to first consider a "system" consisting of *one single-particle state*, rather than a particle itself. Thus the system will consist of a particular spatial wavefunction (and, for particles with spin, a particular spin orientation). This idea seems strange at first, because we normally work with wavefunctions of definite energy, and each of these wavefunctions shares its space with all the other wavefunctions. The "system" and the "reservoir" therefore occupy the same physical space, as in Figure 7.5. Fortunately, the mathematics that went into the derivation of the Gibbs factor couldn't care less whether the system is spatially distinct from the reservoir, so all those formulas still apply to a single-particle-state system.

So let's concentrate on just one single-particle state of a system (say, a particle in a box), whose energy when occupied by a single particle is ϵ. When the state is unoccupied, its energy is 0; if it can be occupied by n particles, then the energy will be $n\epsilon$. The probability of the state being occupied by n particles is

$$\mathcal{P}(n) = \frac{1}{\mathcal{Z}} e^{-(n\epsilon - \mu n)/kT} = \frac{1}{\mathcal{Z}} e^{-n(\epsilon-\mu)/kT}, \tag{7.20}$$

where $\mathcal{Z}$ is the grand partition function, that is, the sum of the Gibbs factors for all possible n.

If the particles in question are fermions, then n can only be 0 or 1, so the grand partition function is

$$\mathcal{Z} = 1 + e^{-(\epsilon-\mu)/kT} \qquad \text{(fermions)}. \tag{7.21}$$

From this we can compute the probability of the state being occupied or unoccupied, as a function of ϵ, μ, and T. We can also compute the *average* number of particles in the state, also called the **occupancy** of the state:

$$\begin{aligned} \overline{n} = \sum_n n\mathcal{P}(n) &= 0 \cdot \mathcal{P}(0) + 1 \cdot \mathcal{P}(1) = \frac{e^{-(\epsilon-\mu)/kT}}{1 + e^{-(\epsilon-\mu)/kT}} \\ &= \frac{1}{e^{(\epsilon-\mu)/kT} + 1} \qquad \text{(fermions)}. \end{aligned} \tag{7.22}$$

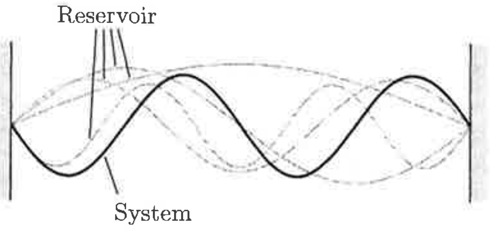

Figure 7.5. To treat a quantum gas using Gibbs factors, we consider a "system" consisting of one single-particle state (or wavefunction). The "reservoir" consists of all the other possible single-particle states.

This important formula is called the **Fermi-Dirac distribution**; I'll call it $\overline{n}_{\text{FD}}$:

$$\overline{n}_{\text{FD}} = \frac{1}{e^{(\epsilon-\mu)/kT}+1}. \tag{7.23}$$

The Fermi-Dirac distribution goes to zero when $\epsilon \gg \mu$, and goes to 1 when $\epsilon \ll \mu$. Thus, states with energy much less than μ tend to be occupied, while states with energy much greater than μ tend to be unoccupied. A state with energy exactly equal to μ has a 50% chance of being occupied, while the width of the fall-off from 1 to 0 is a few times kT. A graph of the Fermi-Dirac distribution vs. ϵ for three different temperatures is shown in Figure 7.6.

If instead the particles in question are bosons, then n can be any nonnegative integer, so the grand partition function is

$$\begin{aligned}\mathcal{Z} &= 1 + e^{-(\epsilon-\mu)/kT} + e^{-2(\epsilon-\mu)/kT} + \cdots \\ &= 1 + e^{-(\epsilon-\mu)/kT} + (e^{-(\epsilon-\mu)/kT})^2 + \cdots \\ &= \frac{1}{1-e^{-(\epsilon-\mu)/kT}} \qquad \text{(bosons)}.\end{aligned} \tag{7.24}$$

(Since the Gibbs factors cannot keep growing without limit, μ must be less than ϵ and therefore the series must converge.) Meanwhile, the average number of particles in the state is

$$\overline{n} = \sum_n n\mathcal{P}(n) = 0\cdot\mathcal{P}(0) + 1\cdot\mathcal{P}(1) + 2\cdot\mathcal{P}(2) + \cdots. \tag{7.25}$$

To evaluate this sum let's abbreviate $x \equiv (\epsilon-\mu)/kT$. Then

$$\overline{n} = \sum_n n\,\frac{e^{-nx}}{\mathcal{Z}} = -\frac{1}{\mathcal{Z}}\sum_n \frac{\partial}{\partial x}e^{-nx} = -\frac{1}{\mathcal{Z}}\frac{\partial \mathcal{Z}}{\partial x}. \tag{7.26}$$

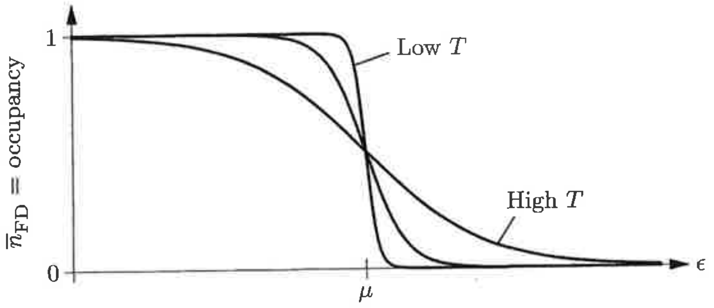

Figure 7.6. The Fermi-Dirac distribution goes to 1 for very low-energy states and to zero for very high-energy states. It equals 1/2 for a state with energy μ, falling off suddenly for low T and gradually for high T. (Although μ is fixed on this graph, in the next section we'll see that μ normally varies with temperature.)

You can easily check that this formula works for fermions. For bosons, we have

$$\begin{aligned}\overline{n} &= -(1-e^{-x})\frac{\partial}{\partial x}(1-e^{-x})^{-1} = (1-e^{-x})(1-e^{-x})^{-2}(e^{-x}) \\ &= \frac{1}{e^{(\epsilon-\mu)/kT}-1} \qquad \text{(bosons)}.\end{aligned} \tag{7.27}$$

This important formula is called the **Bose-Einstein distribution**; I'll call it $\overline{n}_{\text{BE}}$:

$$\overline{n}_{\text{BE}} = \frac{1}{e^{(\epsilon-\mu)/kT}-1}. \tag{7.28}$$

Like the Fermi-Dirac distribution, the Bose-Einstein distribution goes to zero when $\epsilon \gg \mu$. Unlike the Fermi-Dirac distribution, however, it goes to infinity as ϵ approaches μ from above (see Figure 7.7). It would be negative if ϵ could be less than μ, but we've already seen that this cannot happen. for Bosons

To better understand the Fermi-Dirac and Bose-Einstein distributions, it's useful to ask what $\overline{n}$ would be for particles obeying *Boltzmann* statistics. In this case, the probability of any single particle being in a certain state of energy ϵ is

$$\mathcal{P}(s) = \frac{1}{Z_1}e^{-\epsilon/kT} \qquad \text{(Boltzmann)}, \tag{7.29}$$

so if there are N independent particles in total, the average number in this state is

$$\overline{n}_{\text{Boltzmann}} = N\mathcal{P}(s) = \frac{N}{Z_1}e^{-\epsilon/kT}. \tag{7.30}$$

But according to the result of Problem 6.44, the chemical potential for such a system is $\mu = -kT\ln(Z_1/N)$. Therefore the average occupancy can be written

$$\overline{n}_{\text{Boltzmann}} = e^{\mu/kT}e^{-\epsilon/kT} = e^{-(\epsilon-\mu)/kT}. \tag{7.31}$$

When ϵ is sufficiently greater than μ, so that this exponential is very small, we can neglect the 1 in the denominator of either the Fermi-Dirac distribution (7.23) or the Bose-Einstein distribution (7.28), and both reduce to the Boltzmann distribution (7.31). The equality of the three distribution functions in this limit is shown in Figure 7.7. The precise condition for the three distributions to agree is that the exponent $(\epsilon-\mu)/kT$ be much greater than 1. If we take the lowest-energy state to have $\epsilon \approx 0$, then this condition will be met for all states whenever $\mu \ll -kT$, that is, when $Z_1 \gg N$. This is the same condition that we arrived at through different reasoning at the beginning of this section.

We now know how to compute the average number of particles occupying a single-particle state, whether the particles are fermions or bosons, in terms of the energy of the state, the temperature, and the chemical potential. To apply these ideas to any particular system, we still need to know what the energies of all the states are. This is a problem in quantum mechanics, and can be extremely difficult in many cases. In this book we'll deal mostly with particles in a "box," where the quantum-mechanical wavefunctions are simple sine waves and the corresponding energies can

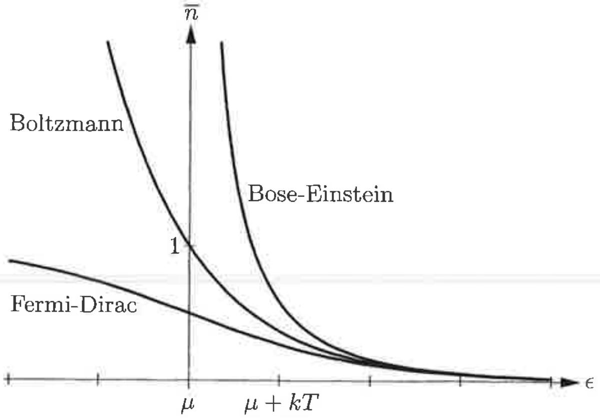

Figure 7.7. Comparison of the Fermi-Dirac, Bose-Einstein, and Boltzmann distributions, all for the same value of μ. When $(\epsilon - \mu)/kT \gg 1$, the three distributions become equal.

be determined straightforwardly. The particles could be electrons in a metal, neutrons in a neutron star, atoms in a fluid at very low temperature, photons inside a hot oven, or even "phonons," the quantized units of vibrational energy in a solid.

For any of these applications, before we can apply the Fermi-Dirac or Bose-Einstein distribution, we'll also have to figure out what the chemical potential is. In a few cases this is quite easy, but in other applications it will require considerable work. As we'll see, μ is usually determined indirectly by the total number of particles in the system.

Problem 7.11. For a system of fermions at room temperature, compute the probability of a single-particle state being occupied if its energy is

(a) 1 eV less than μ

(b) 0.01 eV less than μ

(c) equal to μ

(d) 0.01 eV greater than μ

(e) 1 eV greater than μ

Problem 7.12. Consider two single-particle states, A and B, in a system of fermions, where $\epsilon_A = \mu - x$ and $\epsilon_B = \mu + x$; that is, level A lies below μ by the same amount that level B lies above μ. Prove that the probability of level B being occupied is the same as the probability of level A being *un*occupied. In other words, the Fermi-Dirac distribution is "symmetrical" about the point where $\epsilon = \mu$.

Problem 7.13. For a system of bosons at room temperature, compute the average occupancy of a single-particle state and the probability of the state containing 0, 1, 2, or 3 bosons, if the energy of the state is

(a) 0.001 eV greater than μ

(b) 0.01 eV greater than μ

(c) 0.1 eV greater than μ

(d) 1 eV greater than μ

Problem 7.14. For a system of particles at room temperature, how large must $\epsilon - \mu$ be before the Fermi-Dirac, Bose-Einstein, and Boltzmann distributions agree within 1%? Is this condition ever violated for the gases in our atmosphere? Explain.

Problem 7.15. For a system obeying Boltzmann statistics, we know what μ is from Chapter 6. Suppose, though, that you knew the distribution function (equation 7.31) but didn't know μ. You could still determine μ by requiring that the total number of particles, summed over all single-particle states, equal N. Carry out this calculation, to rederive the formula $\mu = -kT \ln(Z_1/N)$. (This is normally how μ is determined in quantum statistics, although the math is usually more difficult.)

Problem 7.16. Consider an isolated system of N identical fermions, inside a container where the allowed energy levels are nondegenerate and evenly spaced.* For instance, the fermions could be trapped in a one-dimensional harmonic oscillator potential. For simplicity, neglect the fact that fermions can have multiple spin orientations (or assume that they are all forced to have the same spin orientation). Then each energy level is either occupied or unoccupied, and any allowed system state can be represented by a column of dots, with a filled dot representing an occupied level and a hollow dot representing an unoccupied level. The lowest-energy system state has all levels below a certain point occupied, and all levels above that point unoccupied. Let η be the spacing between energy levels, and let q be the number of energy units (each of size η) in excess of the ground-state energy. Assume that $q < N$. Figure 7.8 shows all system states up to $q = 3$.

(a) Draw dot diagrams, as in the figure, for all allowed system states with $q = 4$, $q = 5$, and $q = 6$.

(b) According to the fundamental assumption, all allowed system states with a given value of q are equally probable. Compute the probability of each energy level being occupied, for $q = 6$. Draw a graph of this probability as a function of the energy of the level.

(c) In the thermodynamic limit where q is large, the probability of a level being occupied should be given by the Fermi-Dirac distribution. Even though 6 is not a large number, estimate the values of μ and T that you would have to plug into the Fermi-Dirac distribution to best fit the graph you drew in part (b).

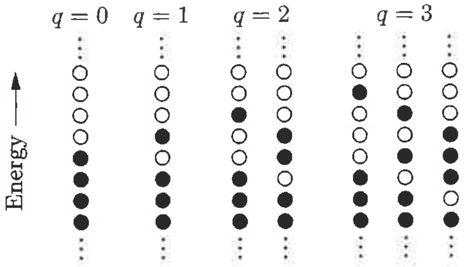

Figure 7.8. A representation of the system states of a fermionic system with evenly spaced, nondegenerate energy levels. A filled dot represents an occupied single-particle state, while a hollow dot represents an unoccupied single-particle state.

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*This problem and Problem 7.27 are based on an article by J. Arnaud et al., *American Journal of Physics* **67**, 215 (1999).

(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.