

7 Quantum Statistics

7.1 The Gibbs Factor

In deriving the Boltzmann factor in Section 6.1, I allowed the small system and the reservoir to exchange energy, but not particles. Often, however, it is useful to consider a system that *can* exchange particles with its environment (see Figure 7.1). Let me now modify the previous derivation to allow for this possibility.

As in Section 6.1, we can write the ratio of probabilities for two different microstates as

$$\frac{\mathcal{P}(s_2)}{\mathcal{P}(s_1)} = \frac{\Omega_R(s_2)}{\Omega_R(s_1)} = \frac{e^{S_R(s_2)/k}}{e^{S_R(s_1)/k}} = e^{[S_R(s_2) - S_R(s_1)]/k}. \quad (7.1)$$

The exponent now contains the change in the entropy of the reservoir as the system goes from state 1 to state 2. This is an infinitesimal change from the reservoir's viewpoint, so we can invoke the thermodynamic identity:

$$dS_R = \frac{1}{T}(dU_R + P dV_R - \mu dN_R). \quad (7.2)$$

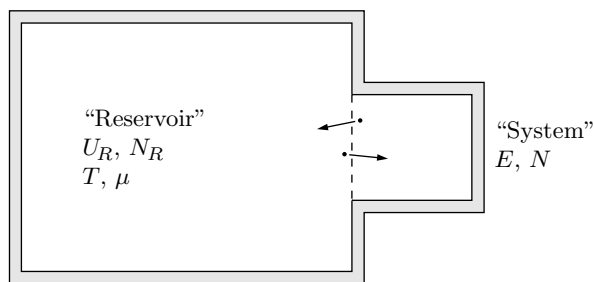


Figure 7.1. A system in thermal and diffusive contact with a much larger reservoir, whose temperature and chemical potential are effectively constant.

Since any energy, volume, or particles gained by the reservoir must be lost by the system, each of the changes on the right-hand side can be written as minus the same change for the system.

As in Section 6.1, I'll throw away the PdV term; this term is often zero, or at least very small compared to the others. This time, however, I'll keep the μdN term. Then the change in entropy can be written

$$S_R(s_2) - S_R(s_1) = -\frac{1}{T} [E(s_2) - E(s_1) - \mu N(s_2) + \mu N(s_1)]. \quad (7.3)$$

On the right-hand side both E and N refer to the small system, hence the overall minus sign. Plugging this expression into equation 7.1 gives

$$\frac{\mathcal{P}(s_2)}{\mathcal{P}(s_1)} = \frac{e^{-[E(s_2) - \mu N(s_2)]/kT}}{e^{-[E(s_1) - \mu N(s_1)]/kT}}. \quad (7.4)$$

As before, the ratio of probabilities is a ratio of simple exponential factors, each of which is a function of the temperature of the reservoir and the energy of the corresponding microstate. Now, however, the factor depends also on the number of particles in the system for state s . This new exponential factor is called a **Gibbs factor**:

$$\text{Gibbs factor} = e^{-[E(s) - \mu N(s)]/kT}. \quad (7.5)$$

If we want an absolute probability instead of a ratio of probabilities, again we have to slip a constant of proportionality in front of the exponential:

$$\mathcal{P}(s) = \frac{1}{\mathcal{Z}} e^{-[E(s) - \mu N(s)]/kT}. \quad (7.6)$$

The quantity \mathcal{Z} is called the **grand partition function*** or the **Gibbs sum**. By requiring that the sum of the probabilities of all states equal 1, you can easily show that

$$\mathcal{Z} = \sum_s e^{-[E(s) - \mu N(s)]/kT}, \quad (7.7)$$

where the sum runs over all possible states (including all possible values of N).

If more than one type of particle can be present in the system, then the μdN term in equation 7.2 becomes a sum over species of $\mu_i dN_i$, and each subsequent equation is modified in a similar way. For instance, if there are two types of particles, the Gibbs factor becomes

$$\text{Gibbs factor} = e^{-[E(s) - \mu_A N_A(s) - \mu_B N_B(s)]/kT} \quad (\text{two species}). \quad (7.8)$$

*In analogy with the terms “microcanonical” and “canonical” used to describe the methods of Chapters 2–3 and 6, the approach used here is called **grand canonical**. A hypothetical set of systems with probabilities assigned according to equation 7.6 is called a **grand canonical ensemble**.

An Example: Carbon Monoxide Poisoning

A good example of a system to illustrate the use of Gibbs factors is an adsorption site on a hemoglobin molecule, which carries oxygen in the blood. A single hemoglobin molecule has four adsorption sites, each consisting of an Fe^{2+} ion surrounded by various other atoms. Each site can carry one O_2 molecule. For simplicity I'll take the system to be just one of the four sites, and pretend that it is completely independent of the other three.* Then if oxygen is the only molecule that can occupy the site, the system has just two possible states: unoccupied and occupied (see Figure 7.2). I'll take the energies of these two states to be 0 and ϵ , with $\epsilon = -0.7 \text{ eV}$.†

The grand partition function for this single-site system has just two terms:

$$\mathcal{Z} = 1 + e^{-(\epsilon - \mu)/kT}. \quad (7.9)$$

The chemical potential μ is relatively high in the lungs, where oxygen is abundant, but is much lower in the cells where the oxygen is used. Let's consider the situation near the lungs. There the blood is in approximate diffusive equilibrium with the atmosphere, an ideal gas in which the partial pressure of oxygen is about 0.2 atm. The chemical potential can therefore be calculated from equation 6.93:

$$\mu = -kT \ln \left(\frac{V Z_{\text{int}}}{N v_Q} \right) \approx -0.6 \text{ eV} \quad (7.10)$$

at body temperature, 310 K. Plugging in these numbers gives for the second Gibbs factor

$$e^{-(\epsilon - \mu)/kT} \approx e^{(0.1 \text{ eV})/kT} \approx 40. \quad (7.11)$$

The probability of any given site being occupied is therefore

$$\mathcal{P}(\text{occupied by } \text{O}_2) = \frac{40}{1 + 40} = 98\%. \quad (7.12)$$

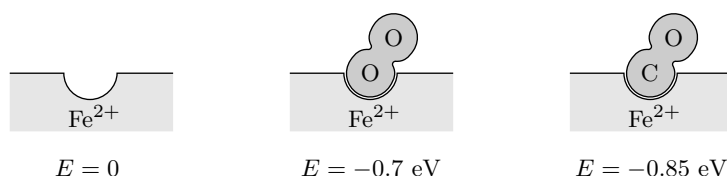


Figure 7.2. A single heme site can be unoccupied, occupied by oxygen, or occupied by carbon monoxide. (The energy values are only approximate.)

*The assumption of independent sites is quite accurate for myoglobin, a related protein that binds oxygen in muscles, which has only one adsorption site per molecule. A more accurate model of hemoglobin is presented in Problem 7.2.

†Biochemists *never* express energies in electron-volts. In fact, they rarely talk about individual bond energies at all (perhaps because these energies can vary so much under different conditions). I've chosen the ϵ values in this section to yield results that are in rough agreement with experimental measurements.

Suppose, however, that there is also some carbon monoxide present, which can also be adsorbed into the heme site. Now there are three states available to the site: unoccupied, occupied by O_2 , and occupied by CO. The grand partition function is

$$\mathcal{Z} = 1 + e^{-(\epsilon - \mu)/kT} + e^{-(\epsilon' - \mu')/kT}, \quad (7.13)$$

where ϵ' is the negative energy of a bound CO molecule and μ' is the chemical potential of CO in the environment. On the one hand, CO will never be as abundant as oxygen. If it is 100 times less abundant, then its chemical potential is lower by *roughly* $kT \ln 100 = 0.12$ eV, so μ' is roughly -0.72 eV. On the other hand, CO is more tightly bound to the site than oxygen, with $\epsilon' \approx -0.85$ eV. Plugging in these numbers gives for the third Gibbs factor

$$e^{-(\epsilon' - \mu')/kT} \approx e^{(0.13 \text{ eV})/kT} \approx 120. \quad (7.14)$$

The probability of the site being occupied by an *oxygen* molecule therefore drops to

$$\mathcal{P}(\text{occupied by } O_2) = \frac{40}{1 + 40 + 120} = 25\%. \quad (7.15)$$

Problem 7.1. Near the cells where oxygen is used, its chemical potential is significantly lower than near the lungs. Even though there is no gaseous oxygen near these cells, it is customary to express the abundance of oxygen in terms of the partial pressure of gaseous oxygen that *would* be in equilibrium with the blood. Using the independent-site model just presented, with only oxygen present, calculate and plot the fraction of occupied heme sites as a function of the partial pressure of oxygen. This curve is called the **Langmuir adsorption isotherm** (“isotherm” because it’s for a fixed temperature). Experiments show that adsorption by *myoglobin* follows the shape of this curve quite accurately.

Problem 7.2. In a real hemoglobin molecule, the tendency of oxygen to bind to a heme site increases as the other three heme sites become occupied. To model this effect in a simple way, imagine that a hemoglobin molecule has just two sites, either or both of which can be occupied. This system has four possible states (with only oxygen present). Take the energy of the unoccupied state to be zero, the energies of the two singly occupied states to be -0.55 eV, and the energy of the doubly occupied state to be -1.3 eV (so the change in energy upon binding the *second* oxygen is -0.75 eV). As in the previous problem, calculate and plot the fraction of occupied sites as a function of the effective partial pressure of oxygen. Compare to the graph from the previous problem (for independent sites). Can you think of why this behavior is preferable for the function of hemoglobin?

Problem 7.3. Consider a system consisting of a single hydrogen atom/ion, which has two possible states: unoccupied (i.e., no electron present) and occupied (i.e., one electron present, in the ground state). Calculate the ratio of the probabilities of these two states, to obtain the Saha equation, already derived in Section 5.6. Treat the electrons as a monatomic ideal gas, for the purpose of determining μ . Neglect the fact that an electron has two independent spin states.

Problem 7.4. Repeat the previous problem, taking into account the two independent spin states of the electron. Now the system has two “occupied” states, one with the electron in each spin configuration. However, the chemical potential of the electron gas is also slightly different. Show that the ratio of probabilities is the same as before: The spin degeneracy cancels out of the Saha equation.

Problem 7.5. Consider a system consisting of a single impurity atom/ion in a semiconductor. Suppose that the impurity atom has one “extra” electron compared to the neighboring atoms, as would a phosphorus atom occupying a lattice site in a silicon crystal. The extra electron is then easily removed, leaving behind a positively charged ion. The ionized electron is called a **conduction electron**, because it is free to move through the material; the impurity atom is called a **donor**, because it can “donate” a conduction electron. This system is analogous to the hydrogen atom considered in the previous two problems except that the ionization energy is much less, mainly due to the screening of the ionic charge by the dielectric behavior of the medium.

- (a) Write down a formula for the probability of a single donor atom being ionized. Do not neglect the fact that the electron, if present, can have two independent spin states. Express your formula in terms of the temperature, the ionization energy I , and the chemical potential of the “gas” of ionized electrons.
- (b) Assuming that the conduction electrons behave like an ordinary ideal gas (with two spin states per particle), write their chemical potential in terms of the number of conduction electrons per unit volume, N_c/V .
- (c) Now assume that every conduction electron comes from an ionized donor atom. In this case the number of conduction electrons is equal to the number of donors that are ionized. Use this condition to derive a quadratic equation for N_c in terms of the number of donor atoms (N_d), eliminating μ . Solve for N_c using the quadratic formula. (Hint: It’s helpful to introduce some abbreviations for dimensionless quantities. Try $x = N_c/N_d$, $t = kT/I$, and so on.)
- (d) For phosphorus in silicon, the ionization energy is 0.044 eV. Suppose that there are 10^{17} P atoms per cubic centimeter. Using these numbers, calculate and plot the fraction of ionized donors as a function of temperature. Discuss the results.

Problem 7.6. Show that when a system is in thermal and diffusive equilibrium with a reservoir, the average number of particles in the system is

$$\bar{N} = \frac{kT}{\mathcal{Z}} \frac{\partial \mathcal{Z}}{\partial \mu},$$

where the partial derivative is taken at fixed temperature and volume. Show also that the mean *square* number of particles is

$$\overline{N^2} = \frac{(kT)^2}{\mathcal{Z}} \frac{\partial^2 \mathcal{Z}}{\partial \mu^2}.$$

Use these results to show that the standard deviation of N is

$$\sigma_N = \sqrt{kT(\partial \bar{N} / \partial \mu)},$$

in analogy with Problem 6.18. Finally, apply this formula to an ideal gas, to obtain a simple expression for σ_N in terms of \bar{N} . Discuss your result briefly.

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,

$$Z = \frac{1}{N!} Z_1^N, \quad (7.16)$$

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,

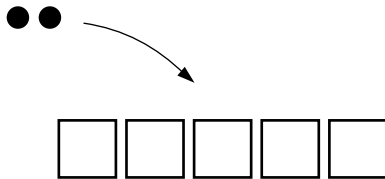


Figure 7.3. A simple model of five single-particle states, with two particles that can occupy these states.

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 $\hbar/2\pi$) 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).

*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,

$$Z_1 \gg N, \quad (7.17)$$

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 a nonrelativistic 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,

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

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

$$\frac{V}{N} \gg v_Q, \quad (7.19)$$

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-

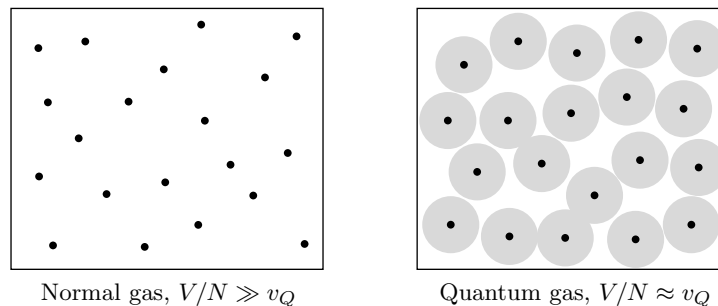


Figure 7.4. In a normal gas, the space between particles is much greater than the typical size of a particle's wavefunction. When the wavefunctions begin to "touch" and overlap, we call it a **quantum gas**.

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

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

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

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

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:

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

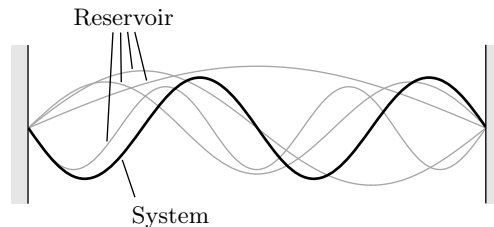


Figure 7.5. To treat a quantum gas using Gibbs factors, we consider a “system” consisting of one single-particle state (or wavefunction). The “reservoir” consists of all the other possible single-particle states.

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

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

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

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

(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

$$\bar{n} = \sum_n n \mathcal{P}(n) = 0 \cdot \mathcal{P}(0) + 1 \cdot \mathcal{P}(1) + 2 \cdot \mathcal{P}(2) + \dots \quad (7.25)$$

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

$$\bar{n} = \sum_n n \frac{e^{-nx}}{\mathcal{Z}} = -\frac{1}{\mathcal{Z}} \sum_n \frac{\partial}{\partial x} e^{-nx} = -\frac{1}{\mathcal{Z}} \frac{\partial \mathcal{Z}}{\partial x}. \quad (7.26)$$

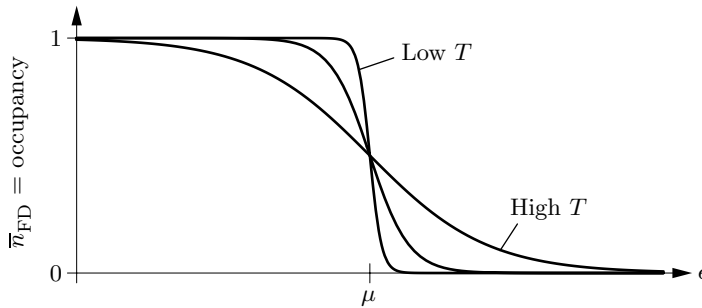


Figure 7.6. The Fermi-Dirac distribution goes to 1 for very low-energy states and to zero for very high-energy states. It equals 1/2 for a state with energy μ , falling off suddenly for low T and gradually for high T . (Although μ is fixed on this graph, in the next section we'll see that μ normally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

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

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

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

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

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.

To better understand the Fermi-Dirac and Bose-Einstein distributions, it's useful to ask what \bar{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

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

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

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

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

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

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

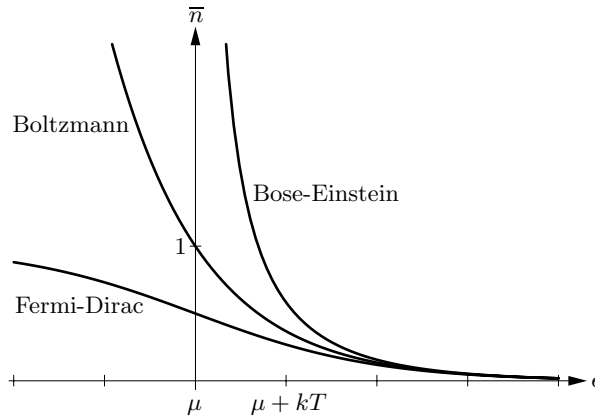


Figure 7.7. Comparison of the Fermi-Dirac, Bose-Einstein, and Boltzmann distributions, all for the same value of μ . When $(\epsilon - \mu)/kT \gg 1$, the three distributions become equal.

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 *unoccupied*. 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 $q = 3$.

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

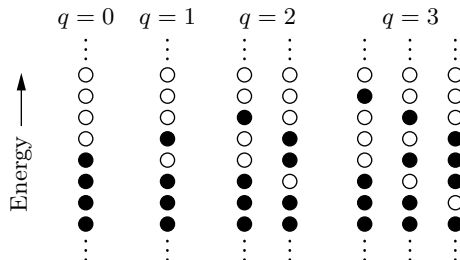


Figure 7.8. A representation of the system states of a fermionic system with evenly spaced, nondegenerate energy levels. A filled dot represents an occupied single-particle state, while a hollow dot represents an unoccupied single-particle state.

*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

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

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 :

$$\epsilon_F \equiv \mu(T = 0). \quad (7.33)$$

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

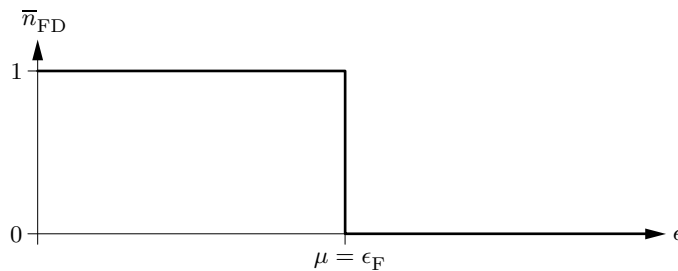


Figure 7.9. At $T = 0$, the Fermi-Dirac distribution equals 1 for all states with $\epsilon < \mu$ and equals 0 for all states with $\epsilon > \mu$.

*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)

$$\lambda_n = \frac{2L}{n}, \quad p_n = \frac{h}{\lambda_n} = \frac{hn}{2L}, \quad (7.34)$$

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

$$p_x = \frac{hn_x}{2L}, \quad p_y = \frac{hn_y}{2L}, \quad p_z = \frac{hn_z}{2L}, \quad (7.35)$$

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

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

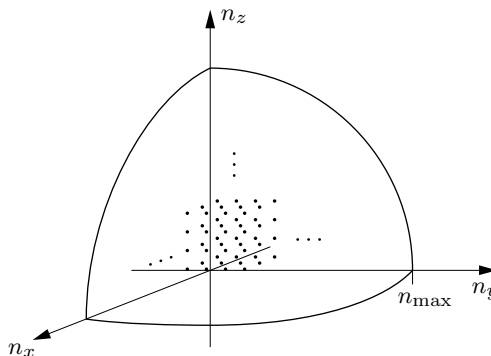
To visualize the set of allowed states, I like to draw a picture of “ n -space,” the three-dimensional space whose axes are n_x , n_y , and n_z (see Figure 7.10). Each allowed \vec{n} vector corresponds to a point in this space with positive integer coordinates; the set of all allowed states forms a 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

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

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):

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

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

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

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 :

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

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

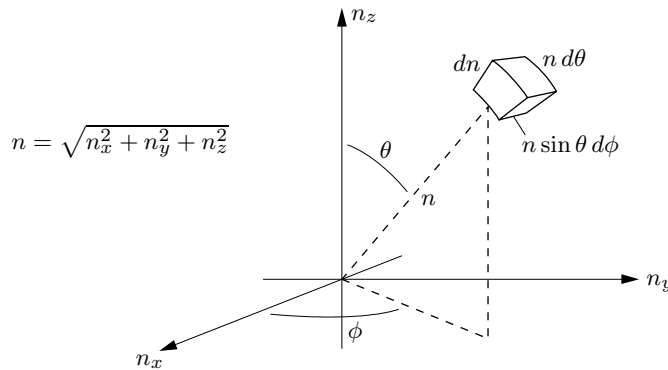


Figure 7.11. In spherical coordinates (n, θ, ϕ) , the infinitesimal volume element is $(dn)(n d\theta)(n \sin \theta d\phi)$.

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

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

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

$$U = \pi \int_0^{n_{\max}} \epsilon(n) \, n^2 \, dn = \frac{\pi \hbar^2}{8mL^2} \int_0^{n_{\max}} n^4 \, dn = \frac{\pi \hbar^2 n_{\max}^5}{40mL^2} = \frac{3}{5} N \epsilon_F. \quad (7.42)$$

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:

$$\frac{V}{N} \ll v_Q \quad \text{is the same as} \quad kT \ll \epsilon_F. \quad (7.43)$$

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**: $T_F \equiv \epsilon_F/k$. 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:

$$P = -\frac{\partial}{\partial V} \left[\frac{3}{5} N \frac{\hbar^2}{8m} \left(\frac{3N}{\pi} \right)^{2/3} V^{-2/3} \right] = \frac{2N\epsilon_F}{5V} = \frac{2}{3} \frac{U}{V}. \quad (7.44)$$

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* N/m² 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:

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

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 $1 \text{ fm} = 10^{-15} \text{ m}$). 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

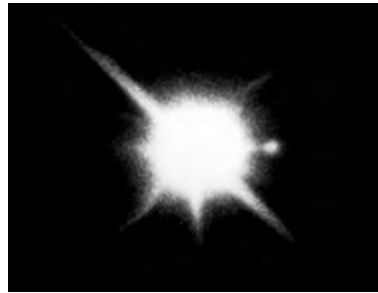
$$U_{\text{grav}} = -(\text{constant}) \frac{GM^2}{R},$$

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

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

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:

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

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 ^3He 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 ^3He 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 $C_V = (2.8 \text{ K}^{-1})NkT$ (in the low-temperature limit). (Don't expect perfect agreement.)
- (c) The entropy of *solid* ^3He below 1 K is almost entirely due to its multiplicity of nuclear spin alignments. Sketch a graph S vs. T for liquid and solid ^3He 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 :

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

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

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

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:

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

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

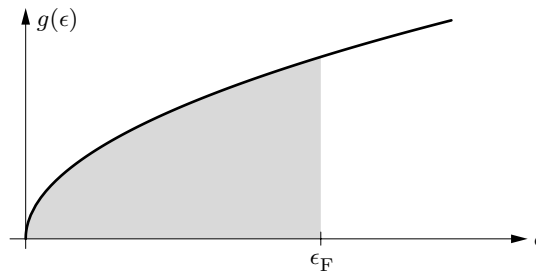


Figure 7.13. Density of states for a system of noninteracting, nonrelativistic particles in a three-dimensional box. The number of states within any energy interval is the area under the graph. For a Fermi gas at $T = 0$, all states with $\epsilon < \epsilon_F$ are occupied while all states with $\epsilon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

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

(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:

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

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

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

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:

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

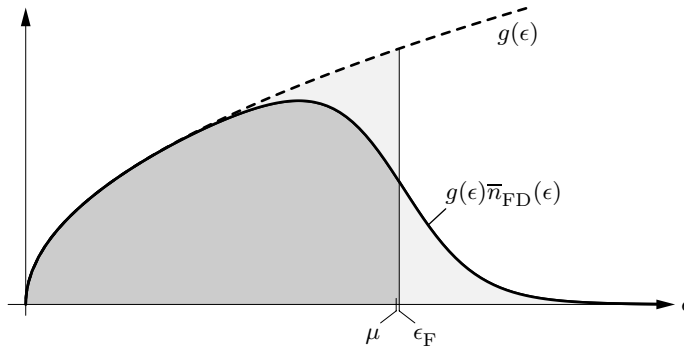


Figure 7.14. At nonzero T , the number of fermions per unit energy is given by the density of states times the Fermi-Dirac distribution. Because increasing the temperature does not change the total number of fermions, the two lightly shaded areas must be equal. Since $g(\epsilon)$ is greater above ϵ_F 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 *unoccupied*. 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 :

$$N = \int_0^\infty g(\epsilon) \bar{n}_{\text{FD}}(\epsilon) d\epsilon = g_0 \int_0^\infty \epsilon^{1/2} \bar{n}_{\text{FD}}(\epsilon) d\epsilon. \quad (7.56)$$

(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 $\bar{n}_{\text{FD}}(\epsilon)$ falls off steeply (for $T \ll \epsilon_{\text{F}}$). So the first trick is to isolate this region, by integrating by parts:

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

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

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

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

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

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:

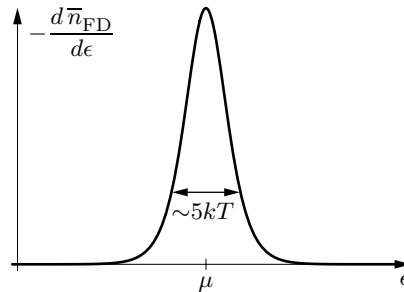
$$\begin{aligned} \epsilon^{3/2} &= \mu^{3/2} + (\epsilon - \mu)\frac{d}{d\epsilon}\epsilon^{3/2}\Big|_{\epsilon=\mu} + \frac{1}{2}(\epsilon - \mu)^2\frac{d^2}{d\epsilon^2}\epsilon^{3/2}\Big|_{\epsilon=\mu} + \dots \\ &= \mu^{3/2} + \frac{3}{2}(\epsilon - \mu)\mu^{1/2} + \frac{3}{8}(\epsilon - \mu)^2\mu^{-1/2}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

With these approximations our integral becomes

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

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:

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

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

$$\begin{aligned} N &= \frac{2}{3} g_0 \mu^{3/2} + \frac{1}{4} g_0 (kT)^2 \mu^{-1/2} \cdot \frac{\pi^2}{3} + \dots \\ &= N \left(\frac{\mu}{\epsilon_F} \right)^{3/2} + N \frac{\pi^2}{8} \frac{(kT)^2}{\epsilon_F^{3/2} \mu^{1/2}} + \dots \end{aligned} \quad (7.65)$$

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

$$\begin{aligned} \frac{\mu}{\epsilon_F} &= \left[1 - \frac{\pi^2}{8} \left(\frac{kT}{\epsilon_F} \right)^2 + \dots \right]^{2/3} \\ &= 1 - \frac{\pi^2}{12} \left(\frac{kT}{\epsilon_F} \right)^2 + \dots \end{aligned} \quad (7.66)$$

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

$$U = \frac{3}{5} N \frac{\mu^{5/2}}{\epsilon_F^{3/2}} + \frac{3\pi^2}{8} N \frac{(kT)^2}{\epsilon_F} + \dots \quad (7.67)$$

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

$$U = \frac{3}{5} N \epsilon_F + \frac{\pi^2}{4} N \frac{(kT)^2}{\epsilon_F} + \dots, \quad (7.68)$$

as I claimed in equation 7.47.

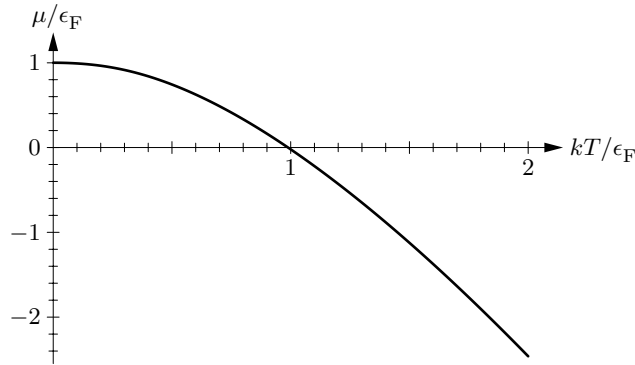


Figure 7.16. Chemical potential of a noninteracting, nonrelativistic Fermi gas in a three-dimensional box, calculated numerically as described in Problem 7.32. At low temperatures μ is given approximately by equation 7.66, while at high temperatures μ becomes negative and approaches the form for an ordinary 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 ${}^3\text{He}$ 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

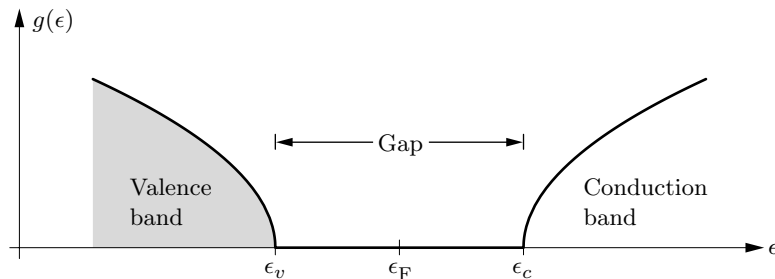


Figure 7.17. The periodic potential of a crystal lattice results in a density-of-states function consisting of “bands” (with many states) and “gaps” (with no states). For an insulator or a semiconductor, the Fermi energy lies in the middle of a gap so that at $T = 0$, the “valence band” is completely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

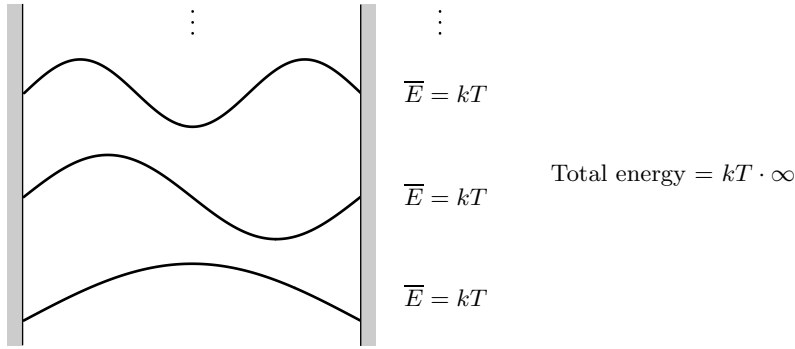


Figure 7.18. We can analyze the electromagnetic field in a box as a superposition of standing-wave modes of various wavelengths. Each mode is a harmonic oscillator with some well-defined frequency. Classically, each oscillator should have an average energy of kT . Since the total number of modes is infinite, so is the total energy in the box.

with an average thermal energy of $2 \cdot \frac{1}{2}kT$. Since the total number of oscillators in the electromagnetic field is infinite, the total thermal energy should also be infinite. Experimentally, though, you're not blasted with an infinite amount of electromagnetic radiation every time you open the oven door to check the cookies. This disagreement between classical theory and experiment is called the **ultraviolet catastrophe** (because the infinite energy would come mostly from very short wavelengths).

The Planck Distribution

The solution to the ultraviolet catastrophe comes from quantum mechanics. (Historically, the ultraviolet catastrophe led to the *birth* of quantum mechanics.) In quantum mechanics, a harmonic oscillator can't have just any amount of energy; its allowed energy levels are

$$E_n = 0, hf, 2hf, \dots \quad (7.69)$$

(As usual I'm measuring all energies relative to the ground-state energy. See Appendix A for more discussion of this point.) The partition function for a single oscillator is therefore

$$\begin{aligned} Z &= 1 + e^{-\beta hf} + e^{-2\beta hf} + \dots \\ &= \frac{1}{1 - e^{-\beta hf}}, \end{aligned} \quad (7.70)$$

and the average energy is

$$\overline{E} = -\frac{1}{Z} \frac{\partial Z}{\partial \beta} = \frac{hf}{e^{hf/kT} - 1}. \quad (7.71)$$

If we think of the energy as coming in “units” of hf , then the average *number* of units of energy in the oscillator is

$$\overline{n}_{\text{Pl}} = \frac{1}{e^{hf/kT} - 1}. \quad (7.72)$$

This formula is called the **Planck distribution** (after Max Planck).

According to the Planck distribution, short-wavelength modes of the electromagnetic field, with $hf \gg kT$, are *exponentially* suppressed: They are “frozen out,” and might as well not exist. Thus the total number of electromagnetic oscillators that effectively contribute to the energy inside the box is finite, and the ultraviolet catastrophe does not occur. Notice that this solution *requires* that the oscillator energies be quantized: It is the size of the energy units, compared to kT , that provides the exponential suppression factor.

Photons

“Units” of energy in the electromagnetic field can also be thought of as *particles*, called **photons**. They are bosons, so the number of them in any “mode” or wave pattern of the field ought to be given by the Bose-Einstein distribution:

$$\bar{n}_{\text{BE}} = \frac{1}{e^{(\epsilon - \mu)/kT} - 1}. \quad (7.73)$$

Here ϵ is the energy of each particle in the mode, that is, $\epsilon = hf$. Comparison with equation 7.72 therefore requires

$$\mu = 0 \quad \text{for photons.} \quad (7.74)$$

But why should this be true? I’ll give you two reasons, both based on the fact that photons can be created or destroyed in any quantity; their total number is not conserved.

First consider the Helmholtz free energy, which must attain the minimum possible value at equilibrium with T and V held fixed. In a system of photons, the number N of particles is not constrained, but rather takes whatever value will minimize F . If N then changes infinitesimally, F should be unchanged:

$$\left(\frac{\partial F}{\partial N} \right)_{T,V} = 0 \quad (\text{at equilibrium}). \quad (7.75)$$

But this partial derivative is precisely equal to the chemical potential.

A second argument makes use of the condition for chemical equilibrium derived in Section 5.6. Consider a typical reaction in which a photon (γ) is created or absorbed by an electron:



As we saw in Section 5.6, the equilibrium condition for such a reaction is the same as the reaction equation, with the name of each species replaced by its chemical potential. In this case,

$$\mu_e = \mu_e + \mu_\gamma \quad (\text{at equilibrium}). \quad (7.77)$$

In other words, the chemical potential for photons is zero.

By either argument, the chemical potential for a “gas” of photons inside a box at fixed temperature is zero, so the Bose-Einstein distribution reduces to the Planck distribution, as required.

Summing over Modes

The Planck distribution tells us how many photons are in any single “mode” (or “single-particle state”) of the electromagnetic field. Next we might want to know the *total* number of photons inside the box, and also the total *energy* of all the photons. To compute either one, we have to sum over all possible states, just as we did for electrons. I’ll compute the total energy, and let you compute the total number of photons in Problem 7.44.

Let’s start in one dimension, with a “box” of length L . The allowed wavelengths and momenta are the same for photons as for any other particles:

$$\lambda = \frac{2L}{n}; \quad p = \frac{hn}{2L}. \quad (7.78)$$

(Here n is a positive integer that labels which mode we’re talking about, not to be confused with \bar{n}_{Pl} , the average number of photons in a given mode.) Photons, however, are ultrarelativistic particles, so their energies are given by

$$\epsilon = pc = \frac{hcn}{2L} \quad (7.79)$$

instead of $\epsilon = p^2/2m$. (You can also derive this result straight from the Einstein relation $\epsilon = hf$ between a photon’s energy and its frequency. For light, $f = c/\lambda$, so $\epsilon = hc/\lambda = hcn/2L$.)

In three dimensions, momentum becomes a vector, with each component given by $h/2L$ times some integer. The energy is c times the *magnitude* of the momentum vector:

$$\epsilon = c\sqrt{p_x^2 + p_y^2 + p_z^2} = \frac{hc}{2L}\sqrt{n_x^2 + n_y^2 + n_z^2} = \frac{hcn}{2L}, \quad (7.80)$$

where in the last expression I’m using n for the magnitude of the \vec{n} vector, as in Section 7.3.

Now the average energy in any particular mode is equal to ϵ times the occupancy of that mode, and the occupancy is given by the Planck distribution. To get the total energy in all modes, we sum over n_x , n_y , and n_z . We also need to slip in a factor of 2, since each wave shape can hold photons with two independent polarizations. So the total energy is

$$U = 2 \sum_{n_x} \sum_{n_y} \sum_{n_z} \epsilon \bar{n}_{\text{Pl}}(\epsilon) = \sum_{n_x, n_y, n_z} \frac{hcn}{L} \frac{1}{e^{hcn/2LkT} - 1}. \quad (7.81)$$

As in Section 7.3, we can convert the sums to integrals and carry out the integration in spherical coordinates (see Figure 7.11). This time, however, the upper limit on the integration over n is infinity:

$$U = \int_0^\infty dn \int_0^{\pi/2} d\theta \int_0^{\pi/2} d\phi n^2 \sin\theta \frac{hcn}{L} \frac{1}{e^{hcn/2LkT} - 1}. \quad (7.82)$$

Again the angular integrals give $\pi/2$, the surface area of an eighth of a unit sphere.

The Planck Spectrum

The integral over n looks a little nicer if we change variables to the photon energy, $\epsilon = hc n/2L$. We then get an overall factor of $L^3 = V$, so the total energy per unit volume is

$$\frac{U}{V} = \int_0^\infty \frac{8\pi\epsilon^3/(hc)^3}{e^{\epsilon/kT} - 1} d\epsilon. \quad (7.83)$$

Here the integrand has a nice interpretation: It is the energy density per unit photon energy, or the **spectrum** of the photons:

$$u(\epsilon) = \frac{8\pi}{(hc)^3} \frac{\epsilon^3}{e^{\epsilon/kT} - 1}. \quad (7.84)$$

This function, first derived by Planck, gives the relative intensity of the radiation as a function of photon energy (or as a function of frequency, if you change variables again to $f = \epsilon/h$). If you integrate $u(\epsilon)$ from ϵ_1 to ϵ_2 , you get the energy per unit volume within that range of photon energies.

To actually evaluate the integral over ϵ , it's convenient to change variables again, to $x = \epsilon/kT$. Then equation 7.83 becomes

$$\frac{U}{V} = \frac{8\pi(kT)^4}{(hc)^3} \int_0^\infty \frac{x^3}{e^x - 1} dx. \quad (7.85)$$

The integrand is still proportional to the Planck spectrum; this function is plotted in Figure 7.19. The spectrum peaks at $x = 2.82$, or $\epsilon = 2.82kT$. Not surprisingly, higher temperatures tend to give higher photon energies. (This fact is called

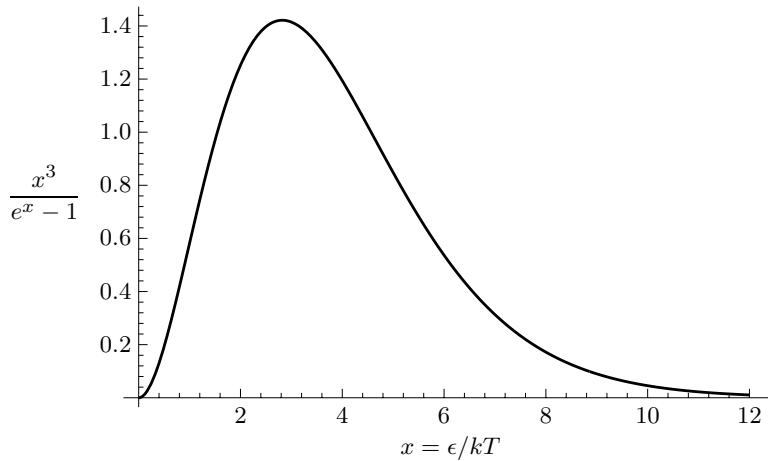


Figure 7.19. The Planck spectrum, plotted in terms of the dimensionless variable $x = \epsilon/kT = hf/kT$. The area under any portion of this graph, multiplied by $8\pi(kT)^4/(hc)^3$, equals the energy density of electromagnetic radiation within the corresponding frequency (or photon energy) range; see equation 7.85.

Wien's law.) You can measure the temperature inside an oven (or more likely, a kiln) by letting a bit of the radiation out and looking at its color. For instance, a typical clay-firing temperature of 1500 K gives a spectrum that peaks at $\epsilon = 0.36$ eV, in the near infrared. (Visible-light photons have higher energies, in the range of about 2–3 eV.)

Problem 7.37. Prove that the peak of the Planck spectrum is at $x = 2.82$.

Problem 7.38. It's not obvious from Figure 7.19 how the Planck spectrum changes as a function of temperature. To examine the temperature dependence, make a quantitative plot of the function $u(\epsilon)$ for $T = 3000$ K and $T = 6000$ K (both on the same graph). Label the horizontal axis in electron-volts.

Problem 7.39. Change variables in equation 7.83 to $\lambda = hc/\epsilon$, and thus derive a formula for the photon spectrum as a function of wavelength. Plot this spectrum, and find a numerical formula for the wavelength where the spectrum peaks, in terms of hc/kT . Explain why the peak does not occur at $hc/(2.82kT)$.

Problem 7.40. Starting from equation 7.83, derive a formula for the density of states of a photon gas (or any other gas of ultrarelativistic particles having two polarization states). Sketch this function.

Problem 7.41. Consider any two internal states, s_1 and s_2 , of an atom. Let s_2 be the higher-energy state, so that $E(s_2) - E(s_1) = \epsilon$ for some positive constant ϵ . If the atom is currently in state s_2 , then there is a certain probability per unit time for it to spontaneously decay down to state s_1 , emitting a photon with energy ϵ . This probability per unit time is called the **Einstein A coefficient**:

$A = \text{probability of spontaneous decay per unit time.}$

On the other hand, if the atom is currently in state s_1 and we shine light on it with frequency $f = \epsilon/h$, then there is a chance that it will absorb a photon, jumping into state s_2 . The probability for this to occur is proportional not only to the amount of time elapsed but also to the intensity of the light, or more precisely, the energy density of the light per unit frequency, $u(f)$. (This is the function which, when integrated over any frequency interval, gives the energy per unit volume within that frequency interval. For our atomic transition, all that matters is the value of $u(f)$ at $f = \epsilon/h$.) The probability of absorbing a photon, per unit time per unit intensity, is called the **Einstein B coefficient**:

$$B = \frac{\text{probability of absorption per unit time}}{u(f)}.$$

Finally, it is also possible for the atom to make a *stimulated* transition from s_2 down to s_1 , again with a probability that is proportional to the intensity of light at frequency f . (Stimulated emission is the fundamental mechanism of the laser: Light Amplification by Stimulated Emission of Radiation.) Thus we define a third coefficient, B' , that is analogous to B :

$$B' = \frac{\text{probability of stimulated emission per unit time}}{u(f)}.$$

As Einstein showed in 1917, knowing any one of these three coefficients is as good as knowing them all.

- (a) Imagine a collection of many of these atoms, such that N_1 of them are in state s_1 and N_2 are in state s_2 . Write down a formula for dN_1/dt in terms of A , B , B' , N_1 , N_2 , and $u(f)$.
- (b) Einstein's trick is to imagine that these atoms are bathed in *thermal* radiation, so that $u(f)$ is the Planck spectral function. At equilibrium, N_1 and N_2 should be constant in time, with their ratio given by a simple Boltzmann factor. Show, then, that the coefficients must be related by

$$B' = B \quad \text{and} \quad \frac{A}{B} = \frac{8\pi h f^3}{c^3}.$$

Total Energy

Enough about the spectrum—what about the total electromagnetic energy inside the box? Equation 7.85 is essentially the final answer, except for the integral over x , which is just some dimensionless number. From Figure 7.19 you can estimate that this number is about 6.5; a beautiful but very tricky calculation (see Appendix B) gives it exactly as $\pi^4/15$. Therefore the total energy density, summing over all frequencies, is

$$\frac{U}{V} = \frac{8\pi^5 (kT)^4}{15(hc)^3}. \quad (7.86)$$

The most important feature of this result is its dependence on the *fourth* power of the temperature. If you double the temperature of your oven, the amount of electromagnetic energy inside increases by a factor of $2^4 = 16$.

Numerically, the total electromagnetic energy inside a typical oven is quite small. At cookie-baking temperature, 375°F or about 460 K , the energy per unit volume comes out to $3.5 \times 10^{-5}\text{ J/m}^3$. This is *tiny* compared to the thermal energy of the air inside the oven.

Formula 7.86 may look complicated, but you could have guessed the answer, aside from the numerical coefficient, by dimensional analysis. The average energy per photon must be something of order kT , so the total energy must be proportional to NkT , where N is the total number of photons. Since N is extensive, it must be proportional to the volume V of the container; thus the total energy must be of the form

$$U = (\text{constant}) \cdot \frac{V kT}{\ell^3}, \quad (7.87)$$

where ℓ is something with units of length. (If you want, you can pretend that each photon occupies a volume of ℓ^3 .) But the only relevant length in the problem is the typical de Broglie wavelength of the photons, $\lambda = h/p = hc/E \propto hc/kT$. Plugging this in for ℓ yields equation 7.86, aside from the factor of $8\pi^5/15$.

Problem 7.42. Consider the electromagnetic radiation inside a kiln, with a volume of 1 m^3 and a temperature of 1500 K .

- (a) What is the total energy of this radiation?
- (b) Sketch the spectrum of the radiation as a function of photon energy.
- (c) What fraction of all the energy is in the *visible* portion of the spectrum, with wavelengths between 400 nm and 700 nm ?

Problem 7.43. At the surface of the sun, the temperature is approximately 5800 K.

- (a) How much energy is contained in the electromagnetic radiation filling a cubic meter of space at the sun's surface?
- (b) Sketch the spectrum of this radiation as a function of photon energy. Mark the region of the spectrum that corresponds to visible wavelengths, between 400 nm and 700 nm.
- (c) What fraction of the energy is in the visible portion of the spectrum? (Hint: Do the integral numerically.)

Entropy of a Photon Gas

Besides the total energy of a photon gas, we might want to know a number of other quantities, for instance, the total number of photons present or the total entropy. These two quantities turn out to be equal, up to a constant factor. Let me now compute the entropy.

The easiest way to compute the entropy is from the heat capacity. For a box of thermal photons with volume V ,

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V = 4aT^3, \quad (7.88)$$

where a is an abbreviation for $8\pi^5 k^4 V / 15(hc)^3$. This expression is good all the way down to absolute zero, so we can integrate it to find the absolute entropy. Introducing the symbol T' for the integration variable,

$$S(T) = \int_0^T \frac{C_V(T')}{T'} dT' = 4a \int_0^T (T')^2 dT' = \frac{4}{3}aT^3 = \frac{32\pi^5}{45} V \left(\frac{kT}{hc} \right)^3 k. \quad (7.89)$$

The total *number* of photons is given by the same formula, with a different numerical coefficient, and without the final k (see Problem 7.44).

The Cosmic Background Radiation

The grandest example of a photon gas is the radiation that fills the entire observable universe, with an almost perfect thermal spectrum at a temperature of 2.73 K. Interpreting this temperature is a bit tricky, however: There is no longer any mechanism to keep the photons in thermal equilibrium with each other or with anything else; the radiation is instead thought to be left over from a time when the universe was filled with ionized gas that interacted strongly with electromagnetic radiation. At that time, the temperature was more like 3000 K; since then the universe has expanded a thousandfold in all directions, and the photon wavelengths have been stretched out accordingly (Doppler-shifted, if you care to think of it this way), preserving the shape of the spectrum but shifting the effective temperature down to 2.73 K.

The photons making up the cosmic background radiation have rather low energies: The spectrum peaks at $\epsilon = 2.82kT = 6.6 \times 10^{-4}$ eV. This corresponds to

wavelengths of about a millimeter, in the far infrared. These wavelengths don't penetrate our atmosphere, but the long-wavelength tail of the spectrum, in the microwave region of a few centimeters, can be detected without much difficulty. It was discovered accidentally by radio astronomers in 1965. Figure 7.20 shows a more recent set of measurements over a wide range of wavelengths, made from above earth's atmosphere by the *Cosmic Background Explorer* satellite.

According to formula 7.86, the total energy in the cosmic background radiation is only 0.26 MeV/m^3 . This is to be contrasted with the average energy density of ordinary matter, which on cosmic scales is of the order of a proton per cubic meter or 1000 MeV/m^3 . (Ironically, the density of the exotic background radiation is known to three significant figures, while the average density of ordinary matter is uncertain by nearly a factor of 10.) On the other hand, the *entropy* of the background radiation is much greater than that of ordinary matter: According to equation 7.89, every cubic meter of space contains a photon entropy of $(1.5 \times 10^9)k$, a billion and a half “units” of entropy. The entropy of ordinary matter is not easy to calculate precisely, but if we pretend that this matter is an ordinary ideal gas we can estimate that its entropy is Nk times some small number, in other words, only a few k per cubic meter.

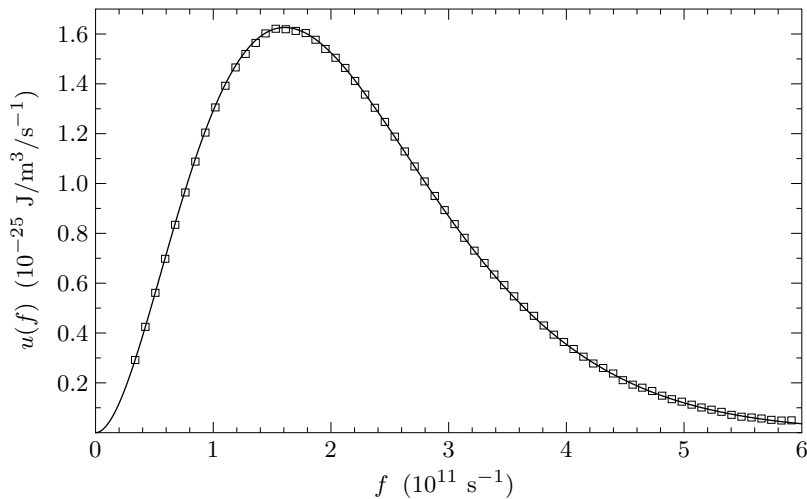


Figure 7.20. Spectrum of the cosmic background radiation, as measured by the *Cosmic Background Explorer* satellite. Plotted vertically is the energy density per unit frequency, in SI units. Note that a frequency of $3 \times 10^{11} \text{ s}^{-1}$ corresponds to a wavelength of $\lambda = c/f = 1.0 \text{ mm}$. Each square represents a measured data point. The point-by-point uncertainties are too small to show up on this scale; the size of the squares instead represents a liberal estimate of the uncertainty due to systematic effects. The solid curve is the theoretical Planck spectrum, with the temperature adjusted to 2.735 K to give the best fit. From J. C. Mather et al., *Astrophysical Journal Letters* **354**, L37 (1990); adapted courtesy of NASA/GSFC and the COBE Science Working Group. Subsequent measurements from this experiment and others now give a best-fit temperature of $2.728 \pm 0.002 \text{ K}$.

Problem 7.44. Number of photons in a photon gas.

- (a) Show that the number of photons in equilibrium in a box of volume V at temperature T is

$$N = 8\pi V \left(\frac{kT}{hc} \right)^3 \int_0^\infty \frac{x^2}{e^x - 1} dx.$$

The integral cannot be done analytically; either look it up in a table or evaluate it numerically.

- (b) How does this result compare to the formula derived in the text for the entropy of a photon gas? (What is the entropy per photon, in terms of k ?)
- (c) Calculate the number of photons per cubic meter at the following temperatures: 300 K; 1500 K (a typical kiln); 2.73 K (the cosmic background radiation).

Problem 7.45. Use the formula $P = -(\partial U / \partial V)_{S,N}$ to show that the pressure of a photon gas is $1/3$ times the energy density (U/V). Compute the pressure exerted by the radiation inside a kiln at 1500 K, and compare to the ordinary gas pressure exerted by the air. Then compute the pressure of the radiation at the center of the sun, where the temperature is 15 million K. Compare to the gas pressure of the ionized hydrogen, whose density is approximately 10^5 kg/m^3 .

Problem 7.46. Sometimes it is useful to know the free energy of a photon gas.

- (a) Calculate the (Helmholtz) free energy directly from the definition $F = U - TS$. (Express the answer in terms of T and V .)
- (b) Check the formula $S = -(\partial F / \partial T)_V$ for this system.
- (c) Differentiate F with respect to V to obtain the pressure of a photon gas. Check that your result agrees with that of the previous problem.
- (d) A more interesting way to calculate F is to apply the formula $F = -kT \ln Z$ separately to each mode (that is, each effective oscillator), then sum over all modes. Carry out this calculation, to obtain

$$F = 8\pi V \frac{(kT)^4}{(hc)^3} \int_0^\infty x^2 \ln(1 - e^{-x}) dx.$$

Integrate by parts, and check that your answer agrees with part (a).

Problem 7.47. In the text I claimed that the universe was filled with ionized gas until its temperature cooled to about 3000 K. To see why, assume that the universe contains only photons and hydrogen atoms, with a constant ratio of 10^9 photons per hydrogen atom. Calculate and plot the fraction of atoms that were ionized as a function of temperature, for temperatures between 0 and 6000 K. How does the result change if the ratio of photons to atoms is 10^8 , or 10^{10} ? (Hint: Write everything in terms of dimensionless variables such as $t = kT/I$, where I is the ionization energy of hydrogen.)

Problem 7.48. In addition to the cosmic background radiation of photons, the universe is thought to be permeated with a background radiation of neutrinos (ν) and antineutrinos ($\bar{\nu}$), currently at an effective temperature of 1.95 K. There are three species of neutrinos, each of which has an antiparticle, with only one allowed polarization state for each particle or antiparticle. For parts (a) through (c) below, assume that all three species are exactly massless.

- (a) It is reasonable to assume that for each species, the concentration of neutrinos equals the concentration of antineutrinos, so that their chemical potentials are equal: $\mu_\nu = \mu_{\bar{\nu}}$. Furthermore, neutrinos and antineutrinos can be produced and annihilated in pairs by the reaction

$$\nu + \bar{\nu} \leftrightarrow 2\gamma$$

(where γ is a photon). Assuming that this reaction is at equilibrium (as it would have been in the very early universe), prove that $\mu = 0$ for both the neutrinos and the antineutrinos.

- (b) If neutrinos are massless, they must be highly relativistic. They are also fermions: They obey the exclusion principle. Use these facts to derive a formula for the total energy density (energy per unit volume) of the neutrino-antineutrino background radiation. (Hint: There are very few differences between this “neutrino gas” and a photon gas. Antiparticles still have positive energy, so to include the antineutrinos all you need is a factor of 2. To account for the three species, just multiply by 3.) To evaluate the final integral, first change to a dimensionless variable and then use a computer or look it up in a table or consult Appendix B.
- (c) Derive a formula for the *number* of neutrinos per unit volume in the neutrino background radiation. Evaluate your result numerically for the present neutrino temperature of 1.95 K.
- (d) It is possible that neutrinos have very small, but nonzero, masses. This wouldn’t have affected the production of neutrinos in the early universe, when mc^2 would have been negligible compared to typical thermal energies. But today, the total mass of all the background neutrinos could be significant. Suppose, then, that just one of the three species of neutrinos (and the corresponding antineutrino) has a nonzero mass m . What would mc^2 have to be (in eV), in order for the total mass of neutrinos in the universe to be comparable to the total mass of ordinary matter?

Problem 7.49. For a brief time in the early universe, the temperature was hot enough to produce large numbers of electron-positron pairs. These pairs then constituted a third type of “background radiation,” in addition to the photons and neutrinos (see Figure 7.21). Like neutrinos, electrons and positrons are fermions. Unlike neutrinos, electrons and positrons are known to be massive (each with the same mass), and each has two independent polarization states. During the time period of interest the densities of electrons and positrons were approximately equal, so it is a good approximation to set the chemical potentials equal to zero as in

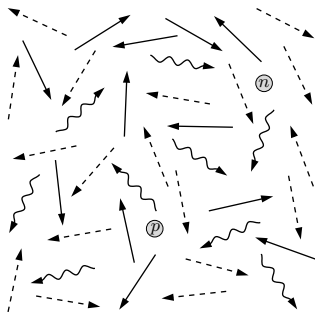


Figure 7.21. When the temperature was greater than the electron mass times c^2/k , the universe was filled with three types of radiation: electrons and positrons (solid arrows); neutrinos (dashed); and photons (wavy). Bathed in this radiation were a few protons and neutrons, roughly one for every billion radiation particles.

the previous problem. Recall from special relativity that the energy of a massive particle is $\epsilon = \sqrt{(pc)^2 + (mc^2)^2}$.

- (a) Show that the energy density of electrons and positrons at temperature T is given by

$$\frac{U}{V} = \frac{16\pi(kT)^4}{(hc)^3} u(T),$$

where

$$u(T) = \int_0^\infty \frac{x^2 \sqrt{x^2 + (mc^2/kT)^2}}{e^{\sqrt{x^2 + (mc^2/kT)^2}} + 1} dx.$$

- (b) Show that $u(T)$ goes to zero when $kT \ll mc^2$, and explain why this is a reasonable result.
 (c) Evaluate $u(T)$ in the limit $kT \gg mc^2$, and compare to the result of the previous problem for the neutrino radiation.
 (d) Use a computer to calculate and plot $u(T)$ at intermediate temperatures.
 (e) Use the method of Problem 7.46, part (d), to show that the free energy density of the electron-positron radiation is

$$\frac{F}{V} = -\frac{16\pi(kT)^4}{(hc)^3} f(T),$$

where

$$f(T) = \int_0^\infty x^2 \ln\left(1 + e^{-\sqrt{x^2 + (mc^2/kT)^2}}\right) dx.$$

Evaluate $f(T)$ in both limits, and use a computer to calculate and plot $f(T)$ at intermediate temperatures.

- (f) Write the entropy of the electron-positron radiation in terms of the functions $u(T)$ and $f(T)$. Evaluate the entropy explicitly in the high- T limit.

Problem 7.50. The results of the previous problem can be used to explain why the current temperature of the cosmic neutrino background (Problem 7.48) is 1.95 K rather than 2.73 K. Originally the temperatures of the photons and the neutrinos would have been equal, but as the universe expanded and cooled, the interactions of neutrinos with other particles soon became negligibly weak. Shortly thereafter, the temperature dropped to the point where kT/c^2 was no longer much greater than the electron mass. As the electrons and positrons disappeared during the next few minutes, they “heated” the photon radiation but not the neutrino radiation.

- (a) Imagine that the universe has some finite total volume V , but that V is increasing with time. Write down a formula for the total entropy of the electrons, positrons, and photons as a function of V and T , using the auxiliary functions $u(T)$ and $f(T)$ introduced in the previous problem. Argue that this total entropy would have been conserved in the early universe, assuming that no other species of particles interacted with these.
 (b) The entropy of the neutrino radiation would have been separately conserved during this time period, because the neutrinos were unable to interact with anything. Use this fact to show that the neutrino temperature T_ν and the photon temperature T are related by

$$\left(\frac{T}{T_\nu}\right)^3 \left[\frac{2\pi^4}{45} + u(T) + f(T) \right] = \text{constant}$$

as the universe expands and cools. Evaluate the constant by assuming that $T = T_\nu$ when the temperatures are very high.

- (c) Calculate the ratio T/T_ν in the limit of low temperature, to confirm that the present neutrino temperature should be 1.95 K.
- (d) Use a computer to plot the ratio T/T_ν as a function of T , for kT/mc^2 ranging from 0 to 3.*

Photons Escaping through a Hole

So far in this section I have analyzed the gas of photons *inside* an oven or any other box in thermal equilibrium. Eventually, though, we'd like to understand the photons *emitted* by a hot object. To begin, let's ask what happens if you start with a photon gas in a box, then poke a hole in the box to let some photons out (see Figure 7.22).

All photons travel at the same speed (in vacuum), regardless of their wavelengths. So low-energy photons will escape through the hole with the same probability as high-energy photons, and thus the spectrum of the photons coming out will look the same as the spectrum of the photons inside. What's harder to figure out is the total *amount* of radiation that escapes; the calculation doesn't involve much physics, but the geometry is rather tricky.

The photons that escape now, during a time interval dt , were once pointed at the hole from somewhere within a hemispherical shell, as shown in Figure 7.23. The radius R of the shell depends on how long ago we're looking, while the thickness of the shell is $c dt$. I'll use spherical coordinates to label various points on the shell, as shown. The angle θ ranges from 0, at the left end of the shell, to $\pi/2$, at the extreme edges on the right. There's also an azimuthal angle ϕ , not shown, which ranges from 0 to 2π as you go from the top edge of the shell into the page, down

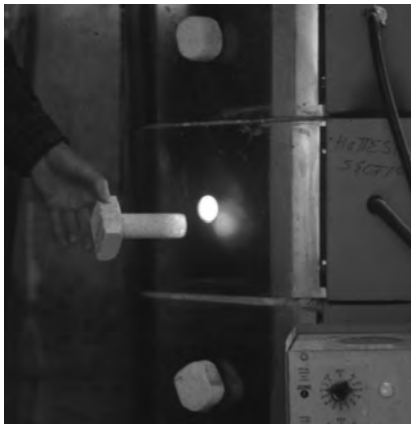


Figure 7.22. When you open a hole in a container filled with radiation (here a kiln), the spectrum of the light that escapes is the same as the spectrum of the light inside. The total amount of energy that escapes is proportional to the size of the hole and to the amount of time that passes.

*Now that you've finished this problem, you'll find it relatively easy to work out the dynamics of the early universe, to determine *when* all this happened. The basic idea is to assume that the universe is expanding at "escape velocity." Everything you need to know is in Weinberg (1977).

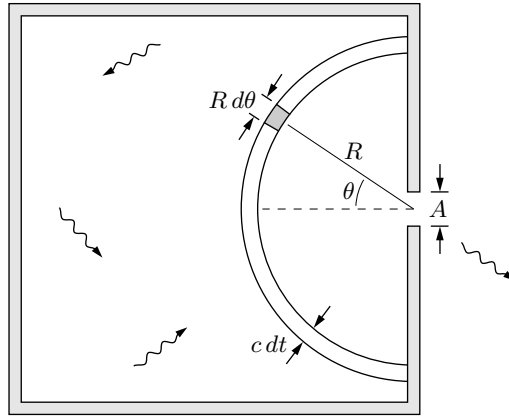


Figure 7.23. The photons that escape now were once somewhere within a hemispherical shell inside the box. From a given point in this shell, the probability of escape depends on the distance from the hole and the angle θ .

to the bottom, out of the page, and back to the top.

Now consider the shaded chunk of the shell shown Figure 7.23. Its volume is

$$\text{volume of chunk} = (R d\theta) \times (R \sin \theta d\phi) \times (c dt). \quad (7.90)$$

(The depth of the chunk, perpendicular to the page, is $R \sin \theta d\phi$, since $R \sin \theta$ is the radius of a ring of constant θ swept out as ϕ ranges from 0 to 2π .) The energy density of the photons within this chunk is given by equation 7.86:

$$\frac{U}{V} = \frac{8\pi^5}{15} \frac{(kT)^4}{(hc)^3}. \quad (7.91)$$

In what follows I'll simply call this quantity U/V ; the total energy in the chunk is thus

$$\text{energy in chunk} = \frac{U}{V} c dt R^2 \sin \theta d\theta d\phi. \quad (7.92)$$

But not all the energy in this chunk of space will escape through the hole, because most of the photons are pointed in the wrong direction. The probability of a photon being pointed in the *right* direction is equal to the apparent area of the hole, as viewed from the chunk, divided by the total area of an imaginary sphere of radius R centered on the chunk:

$$\text{probability of escape} = \frac{A \cos \theta}{4\pi R^2}. \quad (7.93)$$

Here A is the area of the hole, and $A \cos \theta$ is its foreshortened area, as seen from the chunk. The amount of energy that escapes from this chunk is therefore

$$\text{energy escaping from chunk} = \frac{A \cos \theta}{4\pi} \frac{U}{V} c dt \sin \theta d\theta d\phi. \quad (7.94)$$

To find the *total* energy that escapes through the hole in the time interval dt , we just integrate over θ and ϕ :

$$\begin{aligned}\text{total energy escaping} &= \int_0^{2\pi} d\phi \int_0^{\pi/2} d\theta \frac{A \cos \theta}{4\pi} \frac{U}{V} c dt \sin \theta \\ &= 2\pi \frac{A}{4\pi} \frac{U}{V} c dt \int_0^{\pi/2} \cos \theta \sin \theta d\theta \\ &= \frac{A}{4} \frac{U}{V} c dt.\end{aligned}\tag{7.95}$$

The amount of energy that escapes is naturally proportional to the area A of the hole, and also to the duration dt of the time interval. If we divide by these quantities we get the *power* emitted per unit area:

$$\text{power per unit area} = \frac{c}{4} \frac{U}{V}.\tag{7.96}$$

Aside from the factor of $1/4$, you could have guessed this result using dimensional analysis: To turn energy/volume into power/area, you have to multiply by something with units of distance/time, and the only relevant speed in the problem is the speed of light.

Plugging in formula 7.91 for the energy density inside the box, we obtain the more explicit result

$$\text{power per unit area} = \frac{2\pi^5}{15} \frac{(kT)^4}{h^3 c^2} = \sigma T^4,\tag{7.97}$$

where σ is known as the **Stefan-Boltzmann constant**,

$$\sigma = \frac{2\pi^5 k^4}{15 h^3 c^2} = 5.67 \times 10^{-8} \frac{\text{W}}{\text{m}^2 \text{K}^4}.\tag{7.98}$$

(This number isn't hard to memorize: Just think "5-6-7-8," and don't forget the minus sign.) The dependence of the power radiated on the fourth power of the temperature is known as **Stefan's law**, and was discovered empirically in 1879.

Radiation from Other Objects

Although I derived Stefan's law for photons emitted from a hole in a box, it also applies to photons emitted by any nonreflecting ("black") surface at temperature T . Such radiation is therefore called **blackbody radiation**. The proof that a black object emits photons exactly as does a hole in a box is amazingly simple.

Suppose you have a hole in a box, on one hand, and a black object, on the other hand, both at the same temperature, facing each other as in Figure 7.24. Each object emits photons, some of which are absorbed by the other. If the objects are the same size, each will absorb the same fraction of the other's radiation. Now suppose that the blackbody does *not* emit the same amount of power as the hole; perhaps

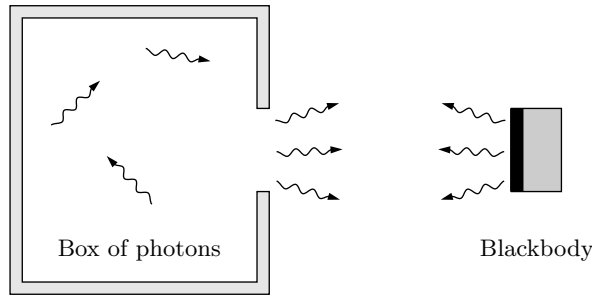


Figure 7.24. A thought experiment to demonstrate that a perfectly black surface emits radiation identical to that emitted by a hole in a box of thermal photons.

it emits somewhat less. Then more energy will flow from the hole to the blackbody than from the blackbody to the hole, and the blackbody will gradually get hotter. Oops! This process would violate the second law of thermodynamics. And if the blackbody emits *more* radiation than the hole, then the blackbody gradually cools off while the box with the hole gets hotter; again, this can't happen.

So the total power emitted by the blackbody, per unit area at any given temperature, must be the same as that emitted by the hole. But we can say more. Imagine inserting a filter, which allows only a certain range of wavelengths to pass through, between the hole and the blackbody. Again, if one object emits more radiation at these wavelengths than the other, its temperature will decrease while the other's temperature increases, in violation of the second law. Thus the entire spectrum of radiation emitted by the blackbody must be the same as for the hole.

If an object is *not* black, so that it reflects some photons instead of absorbing them, things get a bit more complicated. Let's say that out of every three photons (at some given wavelength) that hit the object, it reflects one back and absorbs the other two. Now, in order to remain in thermal equilibrium with the hole, it only needs to emit two photons, which join the reflected photon on its way back. More generally, if e is the fraction of photons absorbed (at some given wavelength), then e is also the fraction emitted, in comparison to a perfect blackbody. This number e is called the **emissivity** of the material. It equals 1 for a perfect blackbody, and equals 0 for a perfectly reflective surface. Thus, a good reflector is a poor emitter, and vice versa. Generally the emissivity depends upon the wavelength of the light, so the spectrum of radiation emitted will differ from a perfect blackbody spectrum. If we use a weighted average of e over all relevant wavelengths, then the total power radiated by an object can be written

$$\text{power} = \sigma e A T^4, \quad (7.99)$$

where A is the object's surface area.

Problem 7.51. The tungsten filament of an incandescent light bulb has a temperature of approximately 3000 K. The emissivity of tungsten is approximately 1/3, and you may assume that it is independent of wavelength.

- (a) If the bulb gives off a total of 100 watts, what is the surface area of its filament in square millimeters?
- (b) At what value of the photon energy does the peak in the bulb's spectrum occur? What is the wavelength corresponding to this photon energy?
- (c) Sketch (or use a computer to plot) the spectrum of light given off by the filament. Indicate the region on the graph that corresponds to visible wavelengths, between 400 and 700 nm.
- (d) Calculate the fraction of the bulb's energy that comes out as visible light. (Do the integral numerically on a calculator or computer.) Check your result qualitatively from the graph of part (c).
- (e) To increase the efficiency of an incandescent bulb, would you want to raise or lower the temperature? (Some incandescent bulbs *do* attain slightly higher efficiency by using a different temperature.)
- (f) Estimate the maximum possible efficiency (i.e., fraction of energy in the visible spectrum) of an incandescent bulb, and the corresponding filament temperature. Neglect the fact that tungsten melts at 3695 K.

Problem 7.52.

- (a) Estimate (roughly) the total power radiated by your body, neglecting any energy that is returned by your clothes and environment. (Whatever the color of your skin, its emissivity at infrared wavelengths is quite close to 1; almost any nonmetal is a near-perfect blackbody at these wavelengths.)
- (b) Compare the total energy radiated by your body in one day (expressed in kilocalories) to the energy in the food you eat. Why is there such a large discrepancy?
- (c) The sun has a mass of 2×10^{30} kg and radiates energy at a rate of 3.9×10^{26} watts. Which puts out more power *per unit mass*—the sun or your body?

Problem 7.53. A black hole is a blackbody if ever there was one, so it should emit blackbody radiation, called **Hawking radiation**. A black hole of mass M has a total energy of Mc^2 , a surface area of $16\pi G^2 M^2/c^4$, and a temperature of $hc^3/16\pi^2 kGM$ (as shown in Problem 3.7).

- (a) Estimate the typical wavelength of the Hawking radiation emitted by a one-solar-mass (2×10^{30} kg) black hole. Compare your answer to the size of the black hole.
- (b) Calculate the total power radiated by a one-solar-mass black hole.
- (c) Imagine a black hole in empty space, where it emits radiation but absorbs nothing. As it loses energy, its mass must decrease; one could say it “evaporates.” Derive a differential equation for the mass as a function of time, and solve this equation to obtain an expression for the lifetime of a black hole in terms of its initial mass.
- (d) Calculate the lifetime of a one-solar-mass black hole, and compare to the estimated age of the known universe (10^{10} years).
- (e) Suppose that a black hole that was created early in the history of the universe finishes evaporating today. What was its initial mass? In what part of the electromagnetic spectrum would most of its radiation have been emitted?

The Sun and the Earth

From the amount of solar radiation received by the earth (1370 W/m^2 , known as the **solar constant**) and the earth's distance from the sun (150 million kilometers), it's pretty easy to calculate the sun's total energy output or **luminosity**: 3.9×10^{26} watts. The sun's radius is a little over 100 times the earth's: $7.0 \times 10^8 \text{ m}$; so its surface area is $6.1 \times 10^{18} \text{ m}^2$. From this information, assuming an emissivity of 1 (which is not terribly accurate but good enough for our purposes), we can calculate the sun's surface temperature:

$$T = \left(\frac{\text{luminosity}}{\sigma A} \right)^{1/4} = 5800 \text{ K.} \quad (7.100)$$

Knowing the temperature, we can predict that the spectrum of sunlight should peak at a photon energy of

$$\epsilon = 2.82 kT = 1.41 \text{ eV,} \quad (7.101)$$

which corresponds to a wavelength of 880 nm, in the near infrared. This is a testable prediction, and it agrees with experiment: The sun's spectrum is approximately given by the Planck formula, with a peak at this energy. Since the peak is so close to the red end of the visible spectrum, much of the sun's energy is emitted as visible light. (If you've learned elsewhere that the sun's spectrum peaks in the middle of the visible spectrum at about 500 nm, and you're worried about the discrepancy, go back and work Problem 7.39.)

A tiny fraction of the sun's radiation is absorbed by the earth, warming the earth's surface to a temperature suitable for life. But the earth doesn't just keep getting hotter and hotter; it also *emits* radiation into space, at the same rate, on average. This balance between absorption and emission gives us a way to estimate the earth's equilibrium surface temperature.

As a first crude estimate, let's pretend that the earth is a perfect blackbody at all wavelengths. Then the power absorbed is the solar constant times the earth's cross-sectional area as viewed from the sun, πR^2 . The power emitted, meanwhile, is given by Stefan's law, with A being the full surface area of the earth, $4\pi R^2$, and T being the effective average surface temperature. Setting the power absorbed equal to the power emitted gives

$$\begin{aligned} (\text{solar constant}) \cdot \pi R^2 &= 4\pi R^2 \sigma T^4 \\ \Rightarrow T &= \left(\frac{1370 \text{ W/m}^2}{4 \cdot 5.67 \times 10^{-8} \text{ W/m}^2 \cdot \text{K}^4} \right)^{1/4} = 279 \text{ K.} \end{aligned} \quad (7.102)$$

This is extremely close to the measured average temperature of 288 K (15°C).

However, the earth is *not* a perfect blackbody. About 30% of the sunlight striking the earth is reflected directly back into space, mostly by clouds. Taking reflection into account brings the earth's predicted average temperature down to a frigid 255 K.

Since a poor absorber is also a poor emitter, you might think we could bring the earth's predicted temperature back up by taking the imperfect emissivity into account on the right-hand side of equation 7.102. Unfortunately, this doesn't work. There's no particular reason why the earth's emissivity should be the same for the infrared light emitted as for the visible light absorbed, and in fact, the earth's surface (like almost any nonmetal) is a very efficient emitter at infrared wavelengths. But there's another mechanism that saves us: Water vapor and carbon dioxide in earth's atmosphere make the atmosphere mostly opaque at wavelengths above a few microns, so if you look at the earth from space with an eye sensitive to infrared light, what you see is mostly the atmosphere, not the surface. The equilibrium temperature of 255 K applies (roughly) to the atmosphere, while the surface below is heated both by the incoming sunlight and by the atmospheric "blanket." If we model the atmosphere as a single layer that is transparent to visible light but opaque to infrared, we get the situation shown in Figure 7.25. Equilibrium requires that the energy of the incident sunlight (minus what is reflected) be equal to the energy emitted upward by the atmosphere, which in turn is equal to the energy radiated downward by the atmosphere. Therefore the earth's surface receives twice as much energy (in this simplified model) as it would from sunlight alone. According to equation 7.102, this mechanism raises the surface temperature by a factor of $2^{1/4}$, to 303 K. This is a bit high, but then, the atmosphere isn't just a single perfectly opaque layer. By the way, this mechanism is called the **greenhouse effect**, even though most greenhouses depend primarily on a different mechanism (namely, limiting convective cooling).

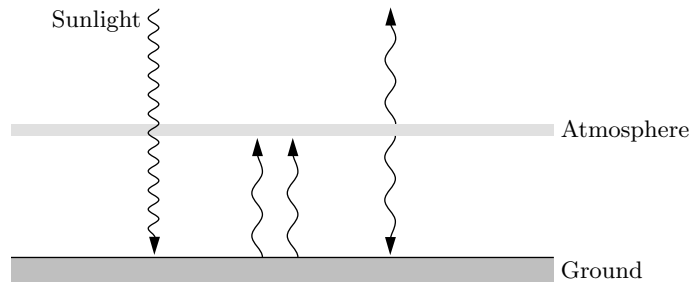


Figure 7.25. Earth's atmosphere is mostly transparent to incoming sunlight, but opaque to the infrared light radiated upward by earth's surface. If we model the atmosphere as a single layer, then equilibrium requires that earth's surface receive as much energy from the atmosphere as from the sun.

Problem 7.54. The sun is the only star whose size we can easily measure directly; astronomers therefore estimate the sizes of other stars using Stefan's law.

- (a) The spectrum of Sirius A, plotted as a function of energy, peaks at a photon energy of 2.4 eV, while Sirius A is approximately 24 times as luminous as the sun. How does the radius of Sirius A compare to the sun's radius?
- (b) Sirius B, the companion of Sirius A (see Figure 7.12), is only 3% as luminous as the sun. Its spectrum, plotted as a function of energy, peaks at about 7 eV. How does its radius compare to that of the sun?

- (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 100,000 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,

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

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 $T \rightarrow 0$, 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

$$\epsilon = hf = \frac{hc_s}{\lambda} = \frac{hc_s n}{2L}. \quad (7.104)$$

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:

$$\bar{n}_{\text{Pl}} = \frac{1}{e^{\epsilon/kT} - 1}. \quad (7.105)$$

(This \bar{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:

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

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 an eighth-sphere whose total volume is N . You can easily show that the radius of the sphere has to be

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

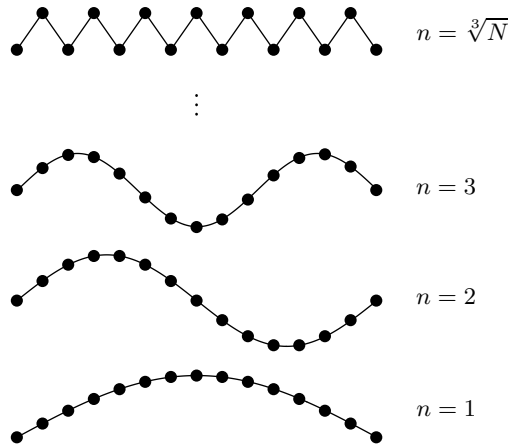


Figure 7.26. Modes of oscillation of a row of atoms in a crystal. If the crystal is a cube, then the number of atoms along any row is $\sqrt[3]{N}$. This is also the total number of modes along this direction, because each “bump” in the wave form must contain at least one atom.

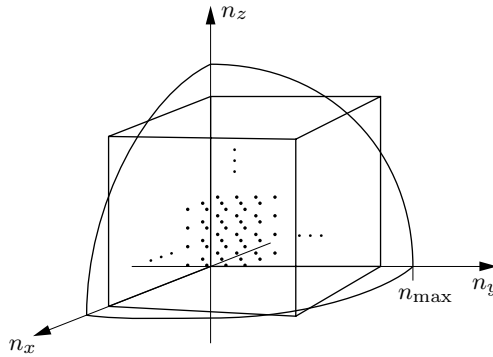


Figure 7.27. The sum in equation 7.106 is technically over a cube in n -space whose width is $\sqrt[3]{N}$. As an approximation, we instead sum over an eighth-sphere with the same total volume.

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

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

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

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

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

$$x = \frac{hc_s n}{2LkT}. \quad (7.110)$$

The upper limit on the integral will then be

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

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

$$U = \frac{9NkT^4}{T_D^3} \int_0^{T_D/T} \frac{x^3}{e^x - 1} dx. \quad (7.112)$$

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 $T \gg T_D$, 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 $\frac{1}{3}(T_D/T)^3$, leading to the final result

$$U = 3NkT \quad \text{when } T \gg T_D, \quad (7.113)$$

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

When $T \ll T_D$, 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

$$U = \frac{3\pi^4}{5} \frac{NkT^4}{T_D^3} \quad \text{when } T \ll T_D. \quad (7.114)$$

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

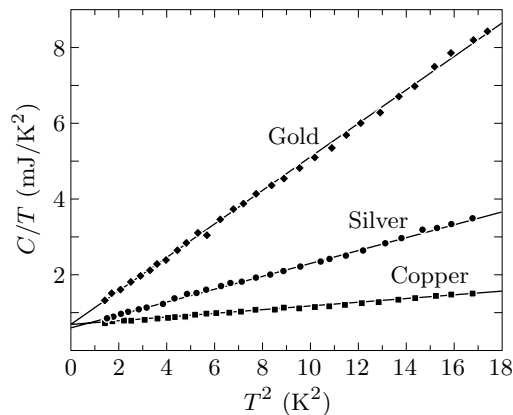
$$C_V = \frac{12\pi^4}{5} \left(\frac{T}{T_D} \right)^3 Nk \quad \text{when } T \ll T_D. \quad (7.115)$$

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

$$C = \gamma T + \frac{12\pi^4 Nk}{5T_D^3} T^3 \quad (\text{metal, } T \ll T_D), \quad (7.116)$$

where $\gamma = \pi^2 Nk^2/2\epsilon_F$ 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

$$C_V = 9Nk \left(\frac{T}{T_D} \right)^3 \int_0^{T_D/T} \frac{x^4 e^x}{(e^x - 1)^2} dx. \quad (7.117)$$

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 $T = T_D$, 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.

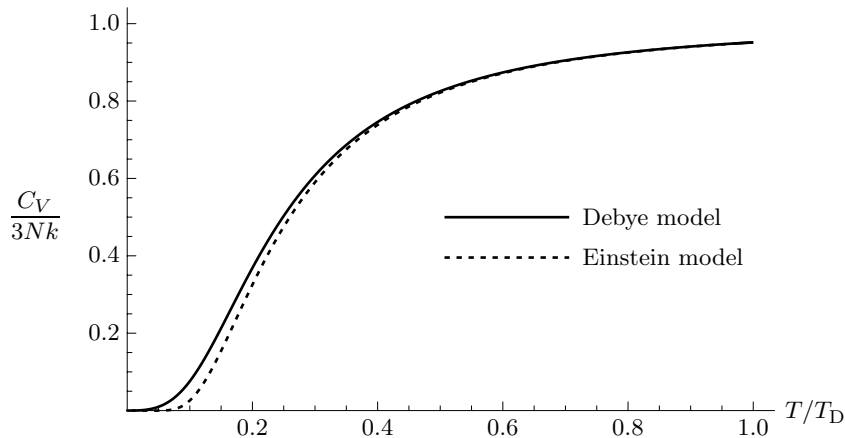


Figure 7.29. The Debye prediction for the heat capacity of a solid, with the prediction of the Einstein model plotted for comparison. The constant ϵ in the Einstein model has been chosen to obtain the best agreement with the Debye model at high temperatures. Note that the Einstein curve is much flatter 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 ^4He 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 ^4He 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 ^4He 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 $T = T_D$ and $T = 2T_D$.

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 $\sim 2\mu_B N$, 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 $\hbar/2\pi$, and therefore reduces the magnetization by $\sim 2\mu_B$. 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 $\epsilon = \hbar f$ and $p = \hbar/\lambda$ for any “particle,” the energy of a magnon is proportional

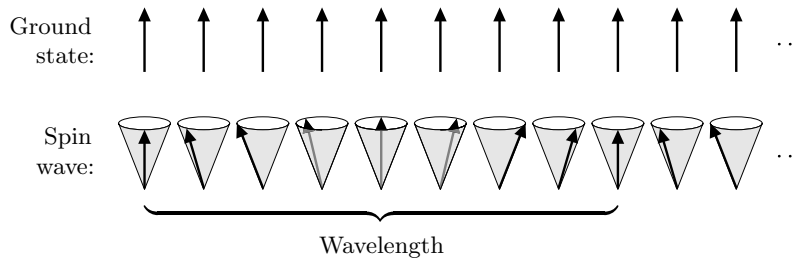


Figure 7.30. In the ground state of a ferromagnet, all the elementary dipoles point in the same direction. The lowest-energy excitations above the ground state are **spin waves**, in which the dipoles precess in a conical motion. A long-wavelength spin wave carries very little energy, because the difference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

7.6 Bose-Einstein Condensation

The previous two sections treated bosons (photons and phonons) that can be created in arbitrary numbers—whose total number is determined by the condition of thermal equilibrium. But what about more “ordinary” bosons, such as atoms with integer spin, whose number is fixed from the outset?

I’ve saved this case for last because it is more difficult. In order to apply the Bose-Einstein distribution we’ll have to determine the chemical potential, which (rather than being fixed at zero) is now a nontrivial function of the density and temperature. Determining μ will require some careful analysis, but is worth the trouble: We’ll find that it behaves in a most peculiar way, indicating that a gas of bosons will abruptly “condense” into the ground state as the temperature goes below a certain critical value.

It’s simplest to first consider the limit $T \rightarrow 0$. At zero temperature, all the atoms will be in the lowest-energy available state, and since arbitrarily many bosons are allowed in any given state, this means that *every* atom will be in the ground state. (Here again, when I say simply “state” I mean a single-particle state.) For atoms confined to a box of volume $V = L^3$, the energy of the ground state is

$$\epsilon_0 = \frac{h^2}{8mL^2}(1^2 + 1^2 + 1^2) = \frac{3h^2}{8mL^2}, \quad (7.118)$$

which works out to a *very* small energy provided that L is macroscopic. At any temperature, the average number of atoms in this state, which I’ll call N_0 , is given by the Bose-Einstein distribution:

$$N_0 = \frac{1}{e^{(\epsilon_0 - \mu)/kT} - 1}. \quad (7.119)$$

When T is sufficiently low, N_0 will be quite large. In this case, the denominator of this expression must be very small, which implies that the exponential is very close to 1, which implies that the exponent, $(\epsilon_0 - \mu)/kT$, is very small. We can therefore expand the exponential in a Taylor series and keep only the first two terms, to obtain

$$N_0 = \frac{1}{1 + (\epsilon_0 - \mu)/kT - 1} = \frac{kT}{\epsilon_0 - \mu} \quad (\text{when } N_0 \gg 1). \quad (7.120)$$

The chemical potential μ , therefore, must be equal to ϵ_0 at $T = 0$, and just a *tiny* bit less than ϵ_0 when T is nonzero but still sufficiently small that nearly all of the atoms are in the ground state. The remaining question is this: How low must the temperature be, in order for N_0 to be large?

The general condition that determines μ is that the sum of the Bose-Einstein distribution over *all* states must add up to the total number of atoms, N :

$$N = \sum_{\text{all } s} \frac{1}{e^{(\epsilon_s - \mu)/kT} - 1}. \quad (7.121)$$

In principle, we could keep guessing values of μ until this sum works out correctly

(and repeat the process for each value of T). In practice, it's usually easier to convert the sum to an integral:

$$N = \int_0^\infty g(\epsilon) \frac{1}{e^{(\epsilon-\mu)/kT} - 1} d\epsilon. \quad (7.122)$$

This approximation should be valid when $kT \gg \epsilon_0$, so that the number of terms that contribute significantly to the sum is large. The function $g(\epsilon)$ is the **density of states**: the number of single-particle states per unit energy. For spin-zero bosons confined in a box of volume V , this function is the same as what we used for electrons in Section 7.3 (equation 7.51) but divided by 2 because now there is only one spin orientation:

$$g(\epsilon) = \frac{2}{\sqrt{\pi}} \left(\frac{2\pi m}{h^2} \right)^{3/2} V \sqrt{\epsilon}. \quad (7.123)$$

Figure 7.31 shows graphs of the density of states, the Bose-Einstein distribution (drawn for μ slightly less than zero), and the product of the two, which is the distribution of particles as a function of energy.

Unfortunately, the integral 7.122 cannot be performed analytically. Therefore we must guess values of μ until we find one that works, doing the integral numerically each time. The most interesting (and easiest) guess is $\mu = 0$, which should work (to a good approximation) at temperatures that are low enough for N_0 to be large. Plugging in $\mu = 0$ and changing variables to $x = \epsilon/kT$ gives

$$\begin{aligned} N &= \frac{2}{\sqrt{\pi}} \left(\frac{2\pi m}{h^2} \right)^{3/2} V \int_0^\infty \frac{\sqrt{\epsilon} d\epsilon}{e^{\epsilon/kT} - 1} \\ &= \frac{2}{\sqrt{\pi}} \left(\frac{2\pi mkT}{h^2} \right)^{3/2} V \int_0^\infty \frac{\sqrt{x} dx}{e^x - 1}. \end{aligned} \quad (7.124)$$

The integral over x is equal to 2.315; combining this number with the factor of $2/\sqrt{\pi}$ yields the formula

$$N = 2.612 \left(\frac{2\pi mkT}{h^2} \right)^{3/2} V. \quad (7.125)$$

This result is obviously wrong: Everything on the right-hand side is independent

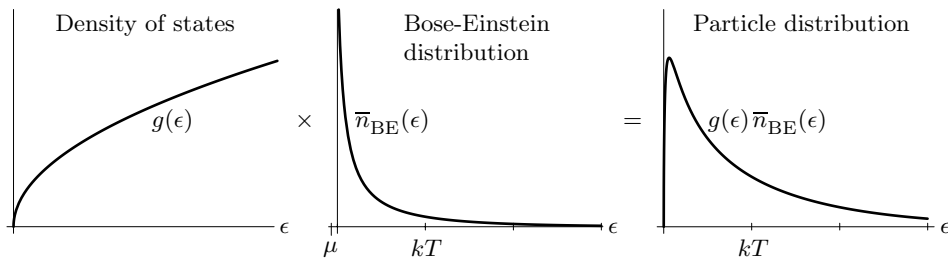


Figure 7.31. The distribution of bosons as a function of energy is the product of two functions, the density of states and the Bose-Einstein distribution.

of temperature except T , so it says that the number of atoms depends on the temperature, which is absurd. In fact, there can be only one particular temperature for which equation 7.125 is correct; I'll call this temperature T_c :

$$N = 2.612 \left(\frac{2\pi m k T_c}{h^2} \right)^{3/2} V, \quad \text{or} \quad k T_c = 0.527 \left(\frac{h^2}{2\pi m} \right) \left(\frac{N}{V} \right)^{2/3}. \quad (7.126)$$

But what's wrong with equation 7.125 when $T \neq T_c$? At temperatures *higher* than T_c , the chemical potential must be significantly less than zero; from equation 7.122 you can see that a negative value of μ will yield a result for N that is smaller than the right-hand side of equation 7.125, as desired. At temperatures *lower* than T_c , on the other hand, the solution to the paradox is more subtle; in this case, replacing the discrete sum 7.121 with the integral 7.122 is invalid.

Look carefully at the integrand in equation 7.124. As ϵ goes to zero, the density of states (proportional to $\sqrt{\epsilon}$) goes to zero while the Bose-Einstein distribution blows up (in proportion to $1/\epsilon$). Although the product is an integrable function, it is not at all clear that this infinite spike at $\epsilon = 0$ correctly represents the sum 7.121 over the actual discretely spaced states. In fact, we have already seen in equation 7.120 that the number of atoms in the ground state can be enormous when $\mu \approx 0$, and this enormous number is not included in our integral. On the other hand, the integral *should* correctly represent the number of particles in the vast majority of the states, away from the spike, where $\epsilon \gg \epsilon_0$. If we imagine cutting off the integral at a lower limit that is somewhat greater than ϵ_0 but much less than kT , we'll still obtain *approximately* the same answer,

$$N_{\text{excited}} = 2.612 \left(\frac{2\pi m k T}{h^2} \right)^{3/2} V \quad (\text{when } T < T_c). \quad (7.127)$$

This is then the number of atoms in excited states, *not* including the ground state. (Whether this expression correctly accounts for the few *lowest* excited states, just above the ground state in energy, is not completely clear. If we assume that the difference between N and the preceding expression for N_{excited} is sufficiently large, then it follows that μ must be much closer to the ground-state energy than to the energy of the first excited state, and therefore that no excited state contains anywhere near as many atoms as the ground state. However, there will be a narrow range of temperatures, just below T_c , where this condition is not met. When the total number of atoms is not particularly large, this range of temperatures might not even be so narrow. These issues are explored in Problem 7.66.)

So the bottom line is this: At temperatures higher than T_c , the chemical potential is negative and essentially all of the atoms are in excited states. At temperatures lower than T_c , the chemical potential is very close to zero and the number of atoms in excited states is given by equation 7.127; this formula can be rewritten more simply as

$$N_{\text{excited}} = \left(\frac{T}{T_c} \right)^{3/2} N \quad (T < T_c). \quad (7.128)$$

The rest of the atoms must be in the ground state, so

$$N_0 = N - N_{\text{excited}} = \left[1 - \left(\frac{T}{T_c} \right)^{3/2} \right] N \quad (T < T_c). \quad (7.129)$$

Figure 7.32 shows a graph of N_0 and N_{excited} as functions of temperature; Figure 7.33 shows the temperature dependence of the chemical potential.

The abrupt accumulation of atoms in the ground state at temperatures below T_c is called **Bose-Einstein condensation**. The transition temperature T_c is called the **condensation temperature**, while the ground-state atoms themselves are called the **condensate**. Notice from equation 7.126 that the condensation temperature is (aside from the factor of 2.612) precisely the temperature at which the quantum volume ($v_Q = (h^2/2\pi mkT)^{3/2}$) equals the average volume per particle (V/N). In other words, if we imagine the atoms being in wavefunctions that are as localized in space as possible (as in Figure 7.4), then condensation begins to occur

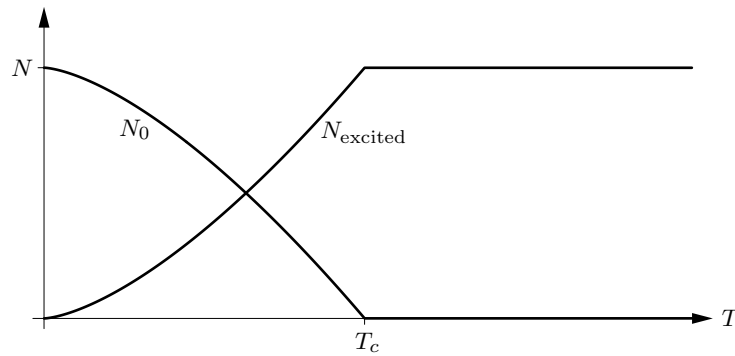


Figure 7.32. Number of atoms in the ground state (N_0) and in excited states, for an ideal Bose gas in a three-dimensional box. Below T_c the number of atoms in excited states is proportional to $T^{3/2}$.

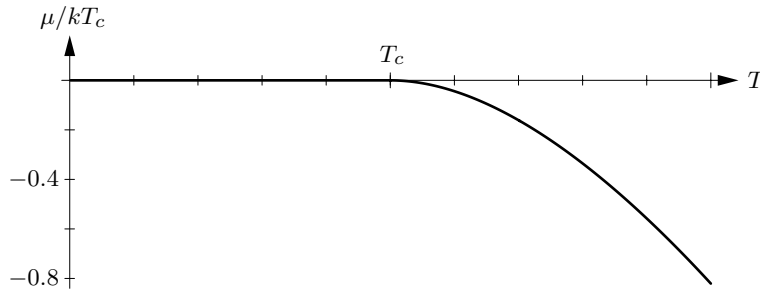


Figure 7.33. Chemical potential of an ideal Bose gas in a three-dimensional box. Below the condensation temperature, μ differs from zero by an amount that is too small to show on this scale. Above the condensation temperature μ becomes negative; the values plotted here were calculated numerically as described in Problem 7.69.

just as the wavefunctions begin to overlap significantly. (The condensate atoms themselves have wavefunctions that occupy the entire container, which I won't try to draw.)

Numerically, the condensation temperature turns out to be very small in all realistic experimental situations. However, it's not as low as we might have guessed. If you put a *single* particle into a box of volume V , it's reasonably likely to be found in the ground state only when kT is of order ϵ_0 or smaller (so that the excited states, which have energies of $2\epsilon_0$ and higher, are significantly less probable). However, if you put a *large* number of identical bosons into the same box, you can get most of them into the ground state at temperatures only somewhat less than T_c , which is much higher: From equations 7.118 and 7.126 we see that kT_c is greater than ϵ_0 by a factor of order $N^{2/3}$. The hierarchy of energy scales— $(\epsilon_0 - \mu) \ll \epsilon_0 \ll kT_c$ —is depicted schematically in Figure 7.34.

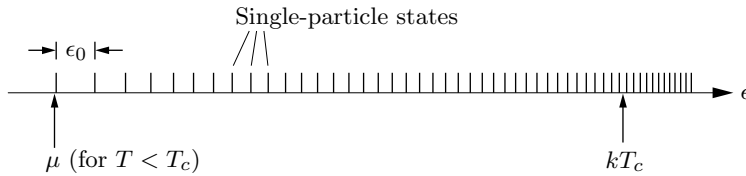


Figure 7.34. Schematic representation of the energy scales involved in Bose-Einstein condensation. The short vertical lines mark the energies of various single-particle states. (Aside from growing closer together (on average) with increasing energy, the locations of these lines are not quantitatively accurate.) The condensation temperature (times k) is many times larger than the spacing between the lowest energy levels, while the chemical potential, when $T < T_c$, is only a tiny amount below the ground-state energy.

Real-World Examples

Bose-Einstein condensation of a gas of weakly interacting atoms was first achieved in 1995, using rubidium-87.* In this experiment, roughly 10^4 atoms were confined (using the laser cooling and trapping technique described in Section 4.4) in a volume of order 10^{-15} m^3 . A large fraction of the atoms were observed to condense into the ground state at a temperature of about 10^{-7} K , a hundred times greater than the temperature at which a *single* isolated atom would have a good chance of being in the ground state. Figure 7.35 shows the velocity distribution of the atoms in this experiment, at temperatures above, just below, and far below the condensation temperature. As of 1999, Bose-Einstein condensation has also been achieved with dilute gases of atomic sodium, lithium, and hydrogen.

*For a beautiful description of this experiment see Carl E. Wieman, “The Richtmyer Memorial Lecture: Bose-Einstein Condensation in an Ultracold Gas,” *American Journal of Physics* **64**, 847–855 (1996).

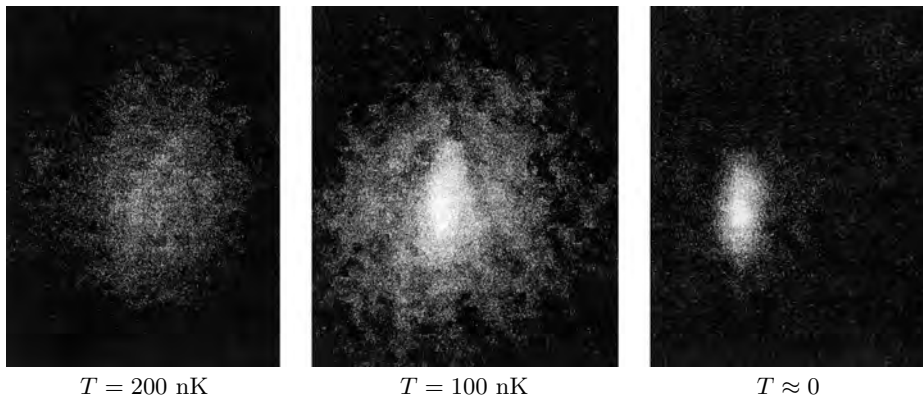


Figure 7.35. Evidence for Bose-Einstein condensation of rubidium-87 atoms. These images were made by turning off the magnetic field that confined the atoms, letting the gas expand for a moment, and then shining light on the expanded cloud to map its distribution. Thus, the positions of the atoms in these images give a measure of their *velocities* just before the field was turned off. Above the condensation temperature (left), the velocity distribution is broad and isotropic, in accord with the Maxwell-Boltzmann distribution. Below the condensation temperature (center), a substantial fraction of the atoms fall into a small, elongated region in velocity space. These atoms make up the condensate; the elongation occurs because the trap is narrower in the vertical direction, causing the ground-state wavefunction to be narrower in position space and thus wider in velocity space. At the lowest temperatures achieved (right), essentially all of the atoms are in the ground-state wavefunction. From Carl E. Wieman, *American Journal of Physics* **64**, 854 (1996).

Bose-Einstein condensation also occurs in systems where particle interactions are significant, so that the quantitative treatment of this section is not very accurate. The most famous example is liquid helium-4, which forms a **superfluid** phase, with essentially zero viscosity, at temperatures below 2.17 K (see Figure 5.13). More precisely, the liquid below this temperature is a mixture of normal and superfluid components, with the superfluid becoming more predominant as the temperature decreases. This behavior suggests that the superfluid component is a Bose-Einstein condensate; indeed, a naive calculation, ignoring interatomic forces, predicts a condensation temperature only slightly greater than the observed value (see Problem 7.68). Unfortunately, the superfluid property itself cannot be understood without accounting for interactions between the helium atoms.

If the superfluid component of helium-4 is a Bose-Einstein condensate, then you would think that helium-3, which is a fermion, would have no such phase. And indeed, it has no superfluid transition anywhere near 2 K. Below 3 *millikelvin*, however, ^3He turns out to have not one but *two* distinct superfluid phases.* How

*These phases were discovered in the early 1970s. To achieve such low temperatures the experimenters used a helium dilution refrigerator (see Section 4.4) in combination with the cooling technique described in Problem 5.34.

is this possible for a system of fermions? It turns out that the “particles” that condense are actually *pairs* of ^3He atoms, held together by the interaction of their nuclear magnetic moments with the surrounding atoms.* A pair of fermions has integer spin and is therefore a boson. An analogous phenomenon occurs in a superconductor, where pairs of electrons are held together through interactions with the vibrating lattice of ions. At low temperature these pairs “condense” into a superconducting state, yet another example of Bose-Einstein condensation.†

Why Does it Happen?

Now that I’ve shown you that Bose-Einstein condensation *does* happen, let me return to the question of *why* it happens. The derivation above was based entirely on the Bose-Einstein distribution function—a powerful tool, but not terribly intuitive. It’s not hard, though, to gain some understanding of this phenomenon using more elementary methods.

Suppose that, instead of a collection of identical bosons, we have a collection of N *distinguishable* particles all confined inside a box. (Perhaps they’re all painted different colors or something.) Then, if the particles don’t interact with each other, we can treat each one of them as a separate system using Boltzmann statistics. At temperature T , a given particle has a decent chance of occupying any single-particle state whose energy is of order kT , and the number of such states will be quite large under any realistic conditions. (This number is essentially equal to the single-particle partition function, Z_1 .) The probability of the particle being in the ground state is therefore very small, namely $1/Z_1$. Since this conclusion applies separately to each one of the N distinguishable particles, only a tiny fraction of the particles will be found in the ground state. There is no Bose-Einstein condensation.

It’s useful to analyze this same situation from a different perspective, treating the entire system all at once, rather than one particle at a time. From this viewpoint, each *system* state has its own probability and its own Boltzmann factor. The system state with all the particles in the ground state has a Boltzmann factor of 1 (taking the ground-state energy to be zero for simplicity), while a system state with total energy U has a Boltzmann factor of $e^{-U/kT}$. According to the conclusion of the previous paragraph, the dominant system states are those for which nearly all of the particles are in excited states with energies of order kT ; the total system energy is therefore $U \sim NkT$, so the Boltzmann factor of a typical system state is something like $e^{-NkT/kT} = e^{-N}$. This is a *very* small number! How can it be that the system prefers these states, rather than condensing into the ground state with its much larger Boltzmann factor?

The answer is that while any *particular* system state with energy of order NkT is highly improbable, the *number* of such states is so huge that taken together they

*For an overview of the physics of both isotopes of liquid helium, see Wilks and Betts (1987).

†For review articles on Bose-Einstein condensation in a variety of systems, see A. Griffin, D. W. Snoke, and S. Stringari, eds., *Bose-Einstein Condensation* (Cambridge University Press, Cambridge, 1995).

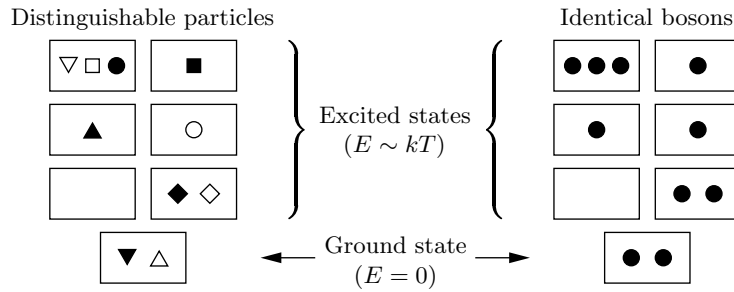


Figure 7.36. When most particles are in excited states, the Boltzmann factor for the entire system is always very small (of order e^{-N}). For distinguishable particles, the number of arrangements among these states is so large that system states of this type are still very probable. For identical bosons, however, the number of arrangements is much smaller.

are quite probable after all (see Figure 7.36). The number of ways of arranging N distinguishable particles among Z_1 single-particle states is Z_1^N , which overwhelms the Boltzmann factor e^{-N} provided that $Z_1 \gg 1$.

Now let's return to the case of identical bosons. Here again, if essentially all the particles are in single-particle states with energies of order kT , then the system state has a Boltzmann factor of order e^{-N} . But now, the *number* of such system states is much smaller. This number is essentially the number of ways of arranging N indistinguishable particles among Z_1 single-particle states, which is mathematically the same as the number of ways of arranging N units of energy among Z_1 oscillators in an Einstein solid:

$$\left(\begin{array}{c} \text{number of} \\ \text{system states} \end{array} \right) \sim \binom{N+Z_1-1}{N} \sim \begin{cases} (eZ_1/N)^N & \text{when } Z_1 \gg N; \\ (eN/Z_1)^{Z_1} & \text{when } Z_1 \ll N. \end{cases} \quad (7.130)$$

When the number of available single-particle states is much larger than the number of bosons, the combinatoric factor is again large enough to overwhelm the Boltzmann factor e^{-N} , so system states with essentially all the bosons in excited states will again predominate. On the other hand, when the number of available single-particle states is much smaller than the number of bosons, the combinatoric factor is not large enough to compensate for the Boltzmann factor, so these system states, even all taken together, will be exponentially improbable. (This last conclusion is not quite clear from looking at the formulas, but here is a simple numerical example: When $N = 100$ and $Z_1 = 25$, a system state with all the bosons in excited states has a Boltzmann factor of order $e^{-100} = 4 \times 10^{-44}$, while the number of such system states is only $\binom{124}{100} = 3 \times 10^{25}$.) In general, the combinatoric factor will be sufficiently large to get about one boson, on average, into each available excited state. Any remaining bosons condense into the ground state, because of the way the Boltzmann factor favors system states with lower energy.

So the explanation of Bose-Einstein condensation lies in the combinatorics of counting arrangements of identical particles: Since the number of distinct ways of arranging identical particles among the excited states is relatively small, the ground

state becomes much more favored than if the particles were distinguishable. You may still be wondering, though, how we *know* that bosons of a given species are truly identical and must therefore be counted in this way. Or alternatively, how do we *know* that the fundamental assumption, which gives all distinct states (of the system plus its environment) the same statistical weight, applies to systems of identical bosons? These questions have good theoretical answers, but the answers require an understanding of quantum mechanics that is beyond the scope of this book. Even then, the answers are not completely airtight—there is still the possibility that *some* undiscovered type of interaction may be able to distinguish supposedly identical bosons from each other, causing a Bose-Einstein condensate to spontaneously evaporate. So far, the experimental fact is that such interactions do not seem to exist. Let us therefore invoke Occam's Razor and conclude, if only tentatively, that bosons of a given species are truly indistinguishable; as David Griffiths has said,* even God cannot tell them apart.

Problem 7.65. Evaluate the integral in equation 7.124 numerically, to confirm the value quoted in the text.

Problem 7.66. Consider a collection of 10,000 atoms of rubidium-87, confined inside a box of volume $(10^{-5} \text{ m})^3$.

- Calculate ϵ_0 , the energy of the ground state. (Express your answer in both joules and electron-volts.)
- Calculate the condensation temperature, and compare kT_c to ϵ_0 .
- Suppose that $T = 0.9T_c$. How many atoms are in the ground state? How close is the chemical potential to the ground-state energy? How many atoms are in each of the (threefold-degenerate) first excited states?
- Repeat parts (b) and (c) for the case of 10^6 atoms, confined to the same volume. Discuss the conditions under which the number of atoms in the ground state will be much greater than the number in the first excited state.

Problem 7.67. In the first achievement of Bose-Einstein condensation with atomic hydrogen,[†] a gas of approximately 2×10^{10} atoms was trapped and cooled until its peak density was $1.8 \times 10^{14} \text{ atoms/cm}^3$. Calculate the condensation temperature for this system, and compare to the measured value of $50 \mu\text{K}$.

Problem 7.68. Calculate the condensation temperature for liquid helium-4, pretending that the liquid is a gas of noninteracting atoms. Compare to the observed temperature of the superfluid transition, 2.17 K. (The density of liquid helium-4 is 0.145 g/cm^3 .)

Problem 7.69. If you have a computer system that can do numerical integrals, it's not particularly difficult to evaluate μ for $T > T_c$.

- As usual when solving a problem on a computer, it's best to start by putting everything in terms of dimensionless variables. So define $t = T/T_c$,

**Introduction to Quantum Mechanics* (Prentice-Hall, Englewood Cliffs, NJ, 1995), page 179.

[†]Dale G. Fried et al., *Physical Review Letters* **81**, 3811 (1998).

$c = \mu/kT_c$, and $x = \epsilon/kT_c$. Express the integral that defines μ , equation 7.122, in terms of these variables. You should obtain the equation

$$2.315 = \int_0^\infty \frac{\sqrt{x} dx}{e^{(x-c)/t} - 1}.$$

- (b) According to Figure 7.33, the correct value of c when $T = 2T_c$ is approximately -0.8 . Plug in these values and check that the equation above is approximately satisfied.
- (c) Now vary μ , holding T fixed, to find the precise value of μ for $T = 2T_c$. Repeat for values of T/T_c ranging from 1.2 up to 3.0, in increments of 0.2. Plot a graph of μ as a function of temperature.

Problem 7.70. Figure 7.37 shows the heat capacity of a Bose gas as a function of temperature. In this problem you will calculate the shape of this unusual graph.

- (a) Write down an expression for the total energy of a gas of N bosons confined to a volume V , in terms of an integral (analogous to equation 7.122).
- (b) For $T < T_c$ you can set $\mu = 0$. Evaluate the integral numerically in this case, then differentiate the result with respect to T to obtain the heat capacity. Compare to Figure 7.37.
- (c) Explain why the heat capacity must approach $\frac{3}{2}Nk$ in the high- T limit.
- (d) For $T > T_c$ you can evaluate the integral using the values of μ calculated in Problem 7.69. Do this to obtain the energy as a function of temperature, then numerically differentiate the result to obtain the heat capacity. Plot the heat capacity, and check that your graph agrees with Figure 7.37.

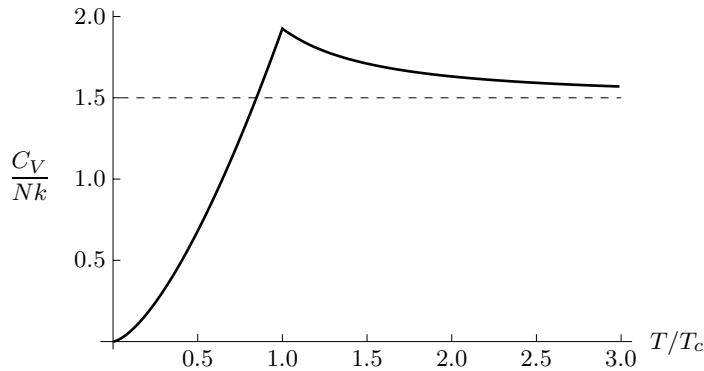


Figure 7.37. Heat capacity of an ideal Bose gas in a three-dimensional box.

Problem 7.71. Starting from the formula for C_V derived in Problem 7.70(b), calculate the entropy, Helmholtz free energy, and pressure of a Bose gas for $T < T_c$. Notice that the pressure is independent of volume; how can this be the case?

Problem 7.72. For a gas of particles confined inside a *two*-dimensional box, the density of states is constant, independent of ϵ (see Problem 7.28). Investigate the behavior of a gas of noninteracting bosons in a two-dimensional box. You should find that the chemical potential remains significantly less than zero as long as T is significantly greater than zero, and hence that there is no abrupt condensation of particles into the ground state. Explain how you know that this is the case, and describe what *does* happen to this system as the temperature decreases. What property must $g(\epsilon)$ have in order for there to be an abrupt Bose-Einstein condensation?

Problem 7.73. Consider a gas of N identical spin-0 bosons confined by an isotropic three-dimensional harmonic oscillator potential. (In the rubidium experiment discussed above, the confining potential was actually harmonic, though not isotropic.) The energy levels in this potential are $\epsilon = nhf$, where n is any nonnegative integer and f is the classical oscillation frequency. The degeneracy of level n is $(n+1)(n+2)/2$.

- Find a formula for the density of states, $g(\epsilon)$, for an atom confined by this potential. (You may assume $n \gg 1$.)
- Find a formula for the condensation temperature of this system, in terms of the oscillation frequency f .
- This potential effectively confines particles inside a volume of roughly the cube of the oscillation amplitude. The oscillation amplitude, in turn, can be estimated by setting the particle's total energy (of order kT) equal to the potential energy of the "spring." Making these associations, and neglecting all factors of 2 and π and so on, show that your answer to part (b) is roughly equivalent to the formula derived in the text for the condensation temperature of bosons confined inside a box with rigid walls.

Problem 7.74. Consider a Bose gas confined in an isotropic harmonic trap, as in the previous problem. For this system, because the energy level structure is much simpler than that of a three-dimensional box, it is feasible to carry out the sum in equation 7.121 *numerically*, without approximating it as an integral.*

- Write equation 7.121 for this system as a sum over energy levels, taking degeneracy into account. Replace T and μ with the dimensionless variables $t = kT/hf$ and $c = \mu/hf$.
- Program a computer to calculate this sum for any given values of t and c . Show that, for $N = 2000$, equation 7.121 is satisfied at $t = 15$ provided that $c = -10.534$. (Hint: You'll need to include approximately the first 200 energy levels in the sum.)
- For the same parameters as in part (b), plot the number of particles in each energy level as a function of energy.
- Now reduce t to 14, and adjust the value of c until the sum again equals 2000. Plot the number of particles as a function of energy.
- Repeat part (d) for $t = 13, 12, 11$, and 10. You should find that the required value of c increases toward zero but never quite reaches it. Discuss the results in some detail.

*This problem is based on an article by Martin Ligare, *American Journal of Physics* **66**, 185–190 (1998).

Problem 7.75. Consider a gas of noninteracting spin-0 bosons at *high* temperatures, when $T \gg T_c$. (Note that “high” in this sense can still mean below 1 K.)

- (a) Show that, in this limit, the Bose-Einstein distribution function can be written approximately as

$$\bar{n}_{\text{BE}} = e^{-(\epsilon - \mu)/kT} [1 + e^{-(\epsilon - \mu)/kT} + \dots].$$

- (b) Keeping only the terms shown above, plug this result into equation 7.122 to derive the first quantum correction to the chemical potential for a gas of bosons.
- (c) Use the properties of the grand free energy (Problems 5.23 and 7.7) to show that the pressure of any system is given by $P = (kT/V) \ln \mathcal{Z}$, where \mathcal{Z} is the grand partition function. Argue that, for a gas of noninteracting particles, $\ln \mathcal{Z}$ can be computed as the sum over all modes (or single-particle states) of $\ln \mathcal{Z}_i$, where \mathcal{Z}_i is the grand partition function for the i th mode.
- (d) Continuing with the result of part (c), write the sum over modes as an integral over energy, using the density of states. Evaluate this integral explicitly for a gas of noninteracting bosons in the high-temperature limit, using the result of part (b) for the chemical potential and expanding the logarithm as appropriate. When the smoke clears, you should find

$$P = \frac{NkT}{V} \left(1 - \frac{Nv_Q}{4\sqrt{2}V} \right),$$

again neglecting higher-order terms. Thus, quantum statistics results in a *lowering* of the pressure of a boson gas, as one might expect.

- (e) Write the result of part (d) in the form of the virial expansion introduced in Problem 1.17, and read off the second virial coefficient, $B(T)$. Plot the predicted $B(T)$ for a hypothetical gas of noninteracting helium-4 atoms.
- (f) Repeat this entire problem for a gas of spin-1/2 fermions. (Very few modifications are necessary.) Discuss the results, and plot the predicted virial coefficient for a hypothetical gas of noninteracting helium-3 atoms.

Ten percent or more of a complete stellar inventory consists of white dwarfs, just sitting there, radiating away the thermal (kinetic) energy of their carbon and oxygen nuclei from underneath very thin skins of hydrogen and helium. They will continue this uneventful course until the universe recontracts, their baryons decay, or they collapse to black holes by barrier penetration. (Likely time scales for these three outcomes are 10^{14} , 10^{33} , and $10^{10^{76}}$ —years for the first two and for the third one it doesn’t matter.)

—Virginia Trimble, *SLAC Beam Line*
21, 3 (fall, 1991).