Chapter 6

Many Particle Systems

©2009 by Harvey Gould and Jan Tobochnik
1 August 2009

We apply the general formalism of statistical mechanics to systems of many particles and discuss the semiclassical limit of the partition function, the equipartition theorem for classical systems, and the general applicability of the Maxwell velocity distribution. We then consider noninteracting quantum systems and discuss the single particle density of states, the Fermi-Dirac and Bose-Einstein distribution functions, the thermodynamics of ideal Fermi and Bose gases, blackbody radiation, and the specific heat of crystalline solids among other applications.

6.1 The Ideal Gas in the Semiclassical Limit

We first apply the canonical ensemble to an ideal gas in the semiclassical limit. Because the thermodynamic properties of a system are independent of the choice of ensemble, we will find the same thermal and pressure equations of state as we found in Section 4.5. Although we will not obtain any new results, this application will give us more experience in working with the canonical ensemble and again show the subtle nature of the semiclassical limit. In Section 6.6 we will derive the classical equations of state using the grand canonical ensemble without any ad hoc assumptions.

In Sections 4.4 and 4.5 we derived the thermodynamic properties of the ideal classical gas[1] using the microcanonical ensemble. If the gas is in thermal equilibrium with a heat bath at temperature T, it is more natural and convenient to treat the ideal gas in the canonical ensemble. Because the particles are not localized, they cannot be distinguished from each other as were the harmonic oscillators considered in Example 4.3 and the spins in Chapter 5. Hence, we cannot simply focus our attention on one particular particle. The approach we will take here is to treat the particles as distinguishable, and then correct for the error approximately.

As before, we will consider a system of noninteracting particles starting from their fundamental description according to quantum mechanics. If the temperature is sufficiently high, we expect

---

[1]The theme music for this section can be found at <www.classicalgas.com/>.

that we can treat the particles classically. To do so we cannot simply take the limit $\hbar \to 0$ wherever it appears because the counting of microstates is different in quantum mechanics and classical mechanics. That is, particles of the same type are indistinguishable according to quantum mechanics. So in the following we will consider the *semiclassical* limit and the particles will remain indistinguishable even in the limit of high temperatures.

To take the semiclassical limit the mean de Broglie wavelength $\overline{\lambda}$ of the particles must be smaller than any other length in the system. For an ideal gas the only two lengths are L, the linear dimension of the system, and the mean distance between particles. Because we are interested in the thermodynamic limit for which $L \gg \overline{\lambda}$, the first condition will always be satisfied. As shown in Problem 6.1, the mean distance between particles in three dimensions is $\rho^{-1/3}$. Hence, the semiclassical limit requires that

$$\overline{\lambda} \ll \rho^{-1/3} \text{ or } \rho\overline{\lambda}^3 \ll 1. \qquad \text{(semiclassical limit)} \qquad (6.1)$$

Problem 6.1. Mean distance between particles

(a) Consider a system of N particles confined to a line of length L. What is the definition of the particle density ρ? The mean distance between particles is L/N. How does this distance depend on ρ?

(b) Consider a system of N particles confined to a square of linear dimension L. How does the mean distance between particles depend on ρ?

(c) Use similar considerations to determine the density dependence of the mean distance between particles in three dimensions. □

To estimate the magnitude of $\overline{\lambda}$ we need to know the typical value of the momentum of a particle. For a nonrelativistic system in the semiclassical limit we know from (4.65) that $\overline{p^2}/2m = 3kT/2$. (We will rederive this result more generally in Section 6.2.1.) Hence $\overline{p^2} \sim mkT$ and $\overline{\lambda} \sim h/\sqrt{\overline{p^2}} \sim h/\sqrt{mkT}$. We will find it is convenient to define the *thermal de Broglie wavelength* λ as

$$\boxed{\lambda \equiv \left(\frac{h^2}{2\pi mkT}\right)^{1/2} = \left(\frac{2\pi\hbar^2}{mkT}\right)^{1/2}.} \qquad \text{(thermal de Broglie wavelength)} \qquad (6.2)$$

This form of λ with the factor of $\sqrt{2\pi}$ will allow us to express the partition function in a convenient form (see (6.11)).

The calculation of the partition function of an ideal gas in the semiclassical limit proceeds as follows. First, we assume that $\lambda \ll \rho^{-1/3}$ so that we can pick out one particle if we make the additional assumption that the particles are distinguishable. (If $\lambda \sim \rho^{-1/3}$, the wave functions of the particles would overlap.) Because identical particles are intrinsically indistinguishable, we will have to correct for the latter assumption later.

With these considerations in mind we now calculate Z_1, the partition function for one particle, in the semiclassical limit. As we found in (4.40), the energy eigenvalues of a particle in a cube of side L are given by

$$\epsilon_n = \frac{h^2}{8mL^2}(n_x{}^2 + n_y{}^2 + n_z{}^2), \qquad (6.3)$$

where the subscript n represents the set of quantum numbers n_x, n_y, and n_z, each of which can be any nonzero, positive integer. The corresponding partition function is given by

$$Z_1 = \sum_n e^{-\beta \epsilon_n} = \sum_{n_x=1}^{\infty} \sum_{n_y=1}^{\infty} \sum_{n_z=1}^{\infty} e^{-\beta h^2 (n_x{}^2 + n_y{}^2 + n_z{}^2)/8mL^2}. \tag{6.4}$$

Because the sum over each quantum number is independent of the sums, we can rewrite (6.4) as

$$Z_1 = \Big[\sum_{n_x=1}^{\infty} e^{-\alpha^2 n_x{}^2} \Big] \Big[\sum_{n_y=1}^{\infty} e^{-\alpha n_y{}^2} \Big] \Big[\sum_{n_z=1}^{\infty} e^{-\alpha n_z{}^2} \Big] = S^3, \tag{6.5}$$

where

$$S = \sum_{n_x=1}^{\infty} e^{-\alpha^2 n_x{}^2}. \tag{6.6}$$

and

$$\alpha^2 = \frac{\beta h^2}{8mL^2} = \frac{\pi}{4} \frac{\lambda^2}{L^2}, \tag{6.7}$$

It remains to evaluate the sum over n_x in (6.6). Because the linear dimension L of the container is of macroscopic size, we have $\lambda \ll L$ and α in (6.6) is much less than one. Hence because the difference between successive terms in the sum is very small, we can convert the sum in (6.6) to an integral:

$$S = \sum_{n_x=1}^{\infty} e^{-\alpha^2 n_x{}^2} = \sum_{n_x=0}^{\infty} e^{-\alpha^2 n_x{}^2} - 1 \rightarrow \int_0^{\infty} e^{-\alpha^2 n_x^2} \, dn_x - 1. \tag{6.8}$$

We have accounted for the fact that the sum over n_x in (6.6) is from $n_x = 1$ rather than $n_x = 0$. We next make a change of variables and write $u^2 = \alpha^2 n_x^2$. We have that

$$S = \frac{1}{\alpha} \int_0^{\infty} e^{-u^2} du - 1 = L \Big(\frac{2\pi m}{\beta h^2} \Big)^{1/2} - 1. \tag{6.9}$$

The Gaussian integral in (6.9) gives a factor of $\pi^{1/2}/2$ (see Appendix A). Because the first term in (6.9) is order $L/\lambda \gg 1$, we can ignore the second term, and hence we obtain

$$Z_1 = S^3 = V \Big(\frac{2\pi m}{\beta h^2} \Big)^{3/2}. \tag{6.10}$$

The result (6.10) is the partition function associated with the translational motion of one particle in a box. Note that Z_1 can be conveniently expressed as

$$Z_1 = \frac{V}{\lambda^3}. \tag{6.11}$$

It is straightforward to find the mean pressure and energy for one particle in a box. We take the logarithm of both sides of (6.10) and find

$$\ln Z_1 = \ln V - \frac{3}{2} \ln \beta + \frac{3}{2} \ln \frac{2\pi m}{h^2}. \tag{6.12}$$

The mean pressure due to one particle is given by

$$\overline{p} = \frac{1}{\beta}\frac{\partial \ln Z_1}{\partial V}\bigg|_{T,N} = \frac{1}{\beta V} = \frac{kT}{V}, \tag{6.13}$$

and the mean energy is

$$\overline{e} = -\frac{\partial \ln Z_1}{\partial \beta}\bigg|_{V,N} = \frac{3}{2\beta} = \frac{3}{2}kT. \tag{6.14}$$

The mean energy and pressure of an ideal gas of N particles is N times that of the corresponding quantities for one particle. Hence, we obtain for an ideal classical gas the equations of state

$$\overline{P} = \frac{NkT}{V}, \tag{6.15}$$

and

$$\overline{E} = \frac{3}{2}NkT. \tag{6.16}$$

In the following we will usually omit the bar on mean quantities. The heat capacity at constant volume of an ideal gas of N particles is

$$C_V = \frac{\partial E}{\partial T}\bigg|_V = \frac{3}{2}Nk. \tag{6.17}$$

We have derived the mechanical and thermal equations of state for an ideal classical gas for a second time! The derivation of the equations of state is much easier in the canonical ensemble than in the microcanonical ensemble. The reason is that we were able to consider the partition function of one particle because the only constraint is that the temperature is fixed instead of the total energy.

Problem 6.2. Independence of the partition function on the shape of the box

The volume dependence of Z_1 should be independent of the shape of the box. Show that the same result for Z_1 is obtained if the box has linear dimensions L_x, L_y, and L_z with $V = L_x L_y L_z$.   □

Problem 6.3. Semiclassical limit of the single particle partition function

We obtained the semiclassical limit of the partition function Z_1 for one particle in a box by writing it as a sum over single particle states and then converting the sum to an integral. Show that the semiclassical partition function Z_1 for a particle in a one-dimensional box can be expressed as

$$Z_1 = \iint \frac{dp\,dx}{h}\, e^{-\beta p^2/2m}. \tag{6.18}$$

The integral over p in (6.18) extends from $-\infty$ to $+\infty$.   □

The entropy of an ideal classical gas of N particles. Although it is straightforward to calculate the mean energy and pressure of an ideal classical gas by considering the partition function for one particle, the calculation of the entropy is more subtle. To understand the difficulty, consider the calculation of the partition function of an ideal gas of two particles. Because there are no

microstate s	red	blue	E_s
1	ϵ_a	ϵ_a	$2\epsilon_a$
2	ϵ_b	ϵ_b	$2\epsilon_b$
3	ϵ_c	ϵ_c	$2\epsilon_c$
4	ϵ_a	ϵ_b	$\epsilon_a + \epsilon_b$
5	ϵ_b	ϵ_a	$\epsilon_a + \epsilon_b$
6	ϵ_a	ϵ_c	$\epsilon_a + \epsilon_c$
7	ϵ_c	ϵ_a	$\epsilon_a + \epsilon_c$
8	ϵ_b	ϵ_c	$\epsilon_b + \epsilon_c$
9	ϵ_c	ϵ_b	$\epsilon_b + \epsilon_c$

Table 6.1: The nine microstates of a system of two noninteracting distinguishable particles (red and blue). Each particle can be in one of three microstates with energy ϵ_a, ϵ_b, or ϵ_c.

interactions between the particles, we can write the total energy as a sum of the single particle energies $\epsilon_1 + \epsilon_2$, where ϵ_i is the energy of the ith particle. The partition function Z_2 is

$$Z_2 = \sum_{\text{all states}} e^{-\beta(\epsilon_1 + \epsilon_2)}. \tag{6.19}$$

The sum over all microstates in (6.19) is over the microstates of the two particle system. If the two particles were distinguishable, there would be no restriction on the number of particles that could be in any single particle microstate, and we could sum over the possible microstates of each particle separately. Hence, the partition function for a system of two distinguishable particles has the form

$$Z_{2,\text{distinguishable}} = Z_1^2. \tag{6.20}$$

It is instructive to show the origin of the relation (6.20) for a specific example. Suppose the two particles are red and blue and are in equilibrium with a heat bath at temperature T. For simplicity, we assume that each particle can be in one of three microstates with energies ϵ_a, ϵ_b, and ϵ_c. The partition function for one particle is given by

$$Z_1 = e^{-\beta\epsilon_a} + e^{-\beta\epsilon_b} + e^{-\beta\epsilon_c}. \tag{6.21}$$

In Table 6.1 we list the $3^2 = 9$ possible microstates of this system of two distinguishable particles. The corresponding partition function is given by

$$\begin{aligned} Z_{2,\text{distinguishable}} = {} & e^{-2\beta\epsilon_a} + e^{-2\beta\epsilon_b} + e^{-2\beta\epsilon_c} \\ & + 2\big[e^{-\beta(\epsilon_a + \epsilon_b)} + e^{-\beta(\epsilon_a + \epsilon_c)} + e^{-\beta(\epsilon_b + \epsilon_c)}\big]. \end{aligned} \tag{6.22}$$

It is easy to see that Z_2 in (6.22) can be factored and expressed as in (6.20).

In contrast, if the two particles are indistinguishable, many of the microstates shown in Table 6.1 cannot be counted as separate microstates. In this case we cannot assign the microstates of the particles independently, and the sum over all microstates in (6.19) cannot be factored as in (6.20). For example, the microstate a, b cannot be distinguished from the microstate b, a.

As discussed in Section 4.3.6, the semiclassical limit assumes that microstates with multiple occupancy such as a, a and b, b can be ignored because there are many more single particle states

than there are particles (see Problem 4.14, page 191). (In our simple example, each particle can be in one of only three microstates, and the number of microstates is comparable to the number of particles.) If we assume that the particles are indistinguishable and that microstates with multiple occupancy can be ignored, then Z_2 is given by

$$Z_2 = e^{-\beta(\epsilon_a+\epsilon_b)} + e^{-\beta(\epsilon_a+\epsilon_c)} + e^{-\beta(\epsilon_b+\epsilon_c)}. \quad \text{(indistinguishable, no multiple occupancy)} \quad (6.23)$$

We see that if we ignore multiple occupancy there are three microstates for indistinguishable particles and six microstates for distinguishable particles. Hence, in the semiclassical limit we can write $Z_2 = Z_1^2/2!$ where the factor of 2! corrects for overcounting. For three particles (each of which can be in one of three possible microstates) and no multiple occupancy, there would be one microstate of the system for indistinguishable particles and no multiple occupancy, namely the microstate a, b, c. However, there would be six such microstates for distinguishable particles. Thus if we count microstates assuming that the particles are distinguishable, we would overcount the number of microstates by $N!$, the number of permutations of N particles.

We conclude that if we begin with the fundamental quantum mechanical description of matter, then identical particles are indistinguishable at all temperatures. If we make the assumption that single particle microstates with multiple occupancy can be ignored, we can express the partition function of N noninteracting identical particles as

$$Z_N = \frac{Z_1{}^N}{N!}. \qquad \text{(ideal gas, semiclassical limit)} \qquad (6.24)$$

We substitute for Z_1 from (6.10) and obtain the partition function of an ideal gas of N particles in the semiclassical limit:

$$Z_N = \frac{V^N}{N!}\left(\frac{2\pi mkT}{h^2}\right)^{3N/2}. \qquad (6.25)$$

If we take the logarithm of both sides of (6.25) and use Stirling's approximation (3.102), we can write the free energy of a noninteracting classical gas as

$$F = -kT\ln Z_N = -kTN\left[\ln\frac{V}{N} + \frac{3}{2}\ln\left(\frac{2\pi mkT}{h^2}\right) + 1\right]. \qquad (6.26)$$

In Section 6.6 we will use the grand canonical ensemble to obtain the entropy of an ideal classical gas without any ad hoc assumptions such as assuming that the particles are distinguishable and then correcting for overcounting by including the factor of $N!$. That is, in the grand canonical ensemble we will be able to automatically satisfy the condition that the particles are indistguishable.

Problem 6.4. Equations of state of an ideal classical gas

Use the result (6.26) to find the pressure equation of state and the mean energy of an ideal gas. Do the equations of state depend on whether the particles are indistinguishable or distinguishable? □

Problem 6.5. Entropy of an ideal classical gas

(a) The entropy can be found from the relations $F = E - TS$ or $S = -\partial F/\partial T$. Show that

$$S(T,V,N) = Nk\left[\ln\frac{V}{N} + \frac{3}{2}\ln\left(\frac{2\pi mkT}{h^2}\right) + \frac{5}{2}\right]. \qquad (6.27)$$

The form of S in (6.27) is known as the *Sackur-Tetrode equation* (see Problem 4.20, page 198). Is this form of S applicable for low temperatures?

(b) Express kT in terms of E and show that $S(E, V, N)$ can be expressed as

$$S(E, V, N) = Nk\left[\ln\frac{V}{N} + \frac{3}{2}\ln\left(\frac{4\pi mE}{3Nh^2}\right) + \frac{5}{2}\right], \tag{6.28}$$

in agreement with the result (4.63) found using the microcanonical ensemble. □

Problem 6.6. The chemical potential of an ideal classical gas

(a) Use the relation $\mu = \partial F/\partial N$ and the result (6.26) to show that the chemical potential of an ideal classical gas is given by

$$\mu = -kT\ln\left[\frac{V}{N}\left(\frac{2\pi mkT}{h^2}\right)^{3/2}\right]. \tag{6.29}$$

(b) We will see in Chapter 7 that if two systems are placed into contact with different initial chemical potentials, particles will go from the system with high chemical potential to the system with low chemical potential. (This behavior is analogous to energy going from high to low temperatures.) Does "high" chemical potential for an ideal classical gas imply "high" or "low" density?

(c) Calculate the entropy and chemical potential of one mole of helium gas at standard temperature and pressure. Take $V = 2.24 \times 10^{-2}\,\text{m}^3$, $N = 6.02 \times 10^{23}$, $m = 6.65 \times 10^{-27}\,\text{kg}$, and $T = 273\,\text{K}$.

(d) Consider one mole of an ideal classical gas at standard temperature and pressure. Assume that only single particle microstates with $p^2/2m < 3kT/2$ are occupied. What fraction of these microstates are actually occupied by the gas? □

Problem 6.7. Entropy as an extensive quantity

(a) Because the entropy is an extensive quantity, we know that if we double the volume and double the number of particles (thus keeping the density constant), the entropy must double. This condition can be written formally as

$$S(T, \lambda V, \lambda N) = \lambda S(T, V, N). \tag{6.30}$$

Although this behavior of the entropy is completely general, there is no guarantee that an approximate calculation of S will satisfy this condition. Show that the Sackur-Tetrode form of the entropy of an ideal gas of identical particles, (6.27), satisfies this general condition.

(b) Show that if the $N!$ term were absent from (6.25) for Z_N, S would be given by

$$S = Nk\left[\ln V + \frac{3}{2}\ln\left(\frac{2\pi mkT}{h^2}\right) + \frac{3}{2}\right]. \tag{6.31}$$
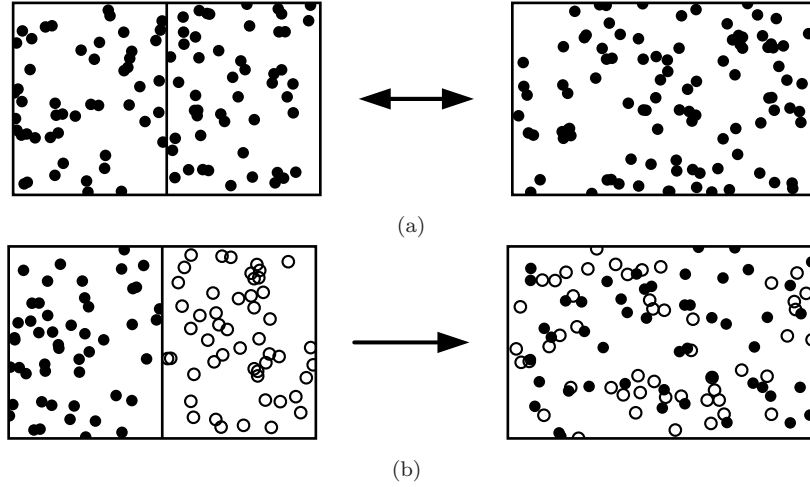
Is this form of S extensive?

(a)

(b)

Figure 6.1: (a) A composite system is prepared such that there are N argon atoms in container A and N argon atoms in container B. The two containers are at the same temperature T and have the same volume V. What is the change of the entropy of the composite system if the partition separating the two containers is removed and the two gases are allowed to mix? (b) A composite system is prepared such that there are N argon atoms in container A and N helium atoms in container B. The other conditions are the same as before. The change in the entropy when the partition is removed is equal to $2Nk \ln 2$.

(c) The fact that (6.31) yields an entropy that is not extensive does *not* indicate that identical particles must be indistinguishable. Instead the problem arises from our identification of S with $\ln Z$ as mentioned in Section 4.6, page 200. Recall that we considered a system with fixed N and made the identification that (see (4.106))

$$dS/k = d(\ln Z + \beta E). \tag{6.32}$$

It is straightforward to integrate (6.32) and obtain

$$S = k(\ln Z + \beta E) + g(N), \tag{6.33}$$

where $g(N)$ is an arbitrary function only of N. Although we usually set $g(N) = 0$, it is important to remember that $g(N)$ is arbitrary. What must be the form of $g(N)$ in order that the entropy of an ideal classical gas be extensive? □

Entropy of mixing. Consider two containers A and B each of volume V with two identical gases of N argon atoms each at the same temperature T. What is the change of the entropy of the combined system if we remove the partition separating the two containers and allow the two gases to mix (see Figure 6.1)(a)? Because the argon atoms are identical, nothing has really changed and no information has been lost, we know that $\Delta S = 0$.

In contrast, suppose that one container is composed of N argon atoms and the other is composed of N helium atoms (see Figure 6.1)(b)). What is the change of the entropy of the

combined system if we remove the partition separating them and allow the two gases to mix? Because argon atoms are distinguishable from helium atoms, we lose information about the system, and therefore we know that the entropy must increase. Alternatively, we know that the entropy must increase because removing the partition between the two containers is an irreversible process. (Reinserting the partition would not separate the two gases.) We conclude that the entropy of mixing is nonzero:

$$\Delta S > 0 \qquad \text{(entropy of mixing)} \tag{6.34}$$

In the following, we will derive these results for the special case of an ideal classical gas.

Consider two ideal gases at the same temperature T with N_A and N_B particles in containers of volume V_A and V_B, respectively. The gases are initially separated by a partition. We use (6.27) for the entropy and find

$$S_A = N_A k \left[\ln \frac{V_A}{N_A} + f(T, m_A) \right], \tag{6.35a}$$

$$S_B = N_B k \left[\ln \frac{V_B}{N_B} + f(T, m_B) \right], \tag{6.35b}$$

where the function $f(T, m) = 3/2 \ln(2\pi mkT/h^2) + 5/2$, and m_A and m_B are the particle masses in system A and system B, respectively. We then allow the particles to mix so that they fill the entire volume $V = V_A + V_B$. If the particles are identical and have mass m, the total entropy after the removal of the partition is given by

$$S = k(N_A + N_B) \left[\ln \frac{V_A + V_B}{N_A + N_B} + f(T, m) \right], \tag{6.36}$$

and the change in the value of S, the *entropy of mixing*, is given by

$$\Delta S = k \left[(N_A + N_B) \ln \frac{V_A + V_B}{N_A + N_B} - N_A \ln \frac{V_A}{N_A} - N_B \ln \frac{V_B}{N_B} \right]. \qquad \text{(identical gases)} \tag{6.37}$$

Problem 6.8. Entropy of mixing of identical particles

(a) Use (6.37) to show that $\Delta S = 0$ if the two gases have equal densities before separation. Write $N_A = \rho V_A$ and $N_B = \rho V_B$.

(b) Why is the entropy of mixing nonzero if the two gases initially have different densities even though the particles are identical? ◻

If the two gases are not identical, the total entropy after mixing is

$$S = k \left[N_A \ln \frac{V_A + V_B}{N_A} + N_B \ln \frac{V_A + V_B}{N_B} + N_A f(T, m_A) + N_B f(T, m_B) \right]. \tag{6.38}$$

Then the entropy of mixing becomes

$$\Delta S = k \left[N_A \ln \frac{V_A + V_B}{N_A} + N_B \ln \frac{V_A + V_B}{N_B} - N_A \ln \frac{V_A}{N_A} - N_B \ln \frac{V_B}{N_B} \right]. \tag{6.39}$$

For the special case of $N_A = N_B = N$ and $V_A = V_B = V$, we find

$$\Delta S = 2Nk \ln 2. \tag{6.40}$$

Problem 6.9. More on the entropy of mixing

(a) Explain the result (6.40) for nonidentical particles in simple terms.

(b) Consider the special case $N_A = N_B = N$ and $V_A = V_B = V$ and show that if we use the result (6.31) instead of (6.27), the entropy of mixing for identical particles is nonzero. This incorrect result is known as *Gibbs' paradox*. Does it imply that classical physics, which assumes that particles of the same type are distinguishable, is incorrect? □

6.2 Classical Statistical Mechanics

From our discussions of the ideal gas in the semiclassical limit we found that approaching the classical limit must be done with care. Planck's constant appears in the expression for the entropy even for the simple case of an ideal gas, and the indistinquishability of the particles is not a classical concept.

If we started entirely within the framework of classical mechanics, we would replace the sum over microstates in the partition function by an integral over phase space, that is,

$$Z_{N,\,\text{classical}} = C_N \int e^{-\beta E(\mathbf{r}_1,\ldots,\mathbf{r}_N,\mathbf{p}_1,\ldots,\mathbf{p}_N)}\, d\mathbf{r}_1 \ldots d\mathbf{r}_N\, d\mathbf{p}_1 \ldots d\mathbf{p}_N. \tag{6.41}$$

The constant C_N cannot be determined from classical mechanics. From our counting of microstates for a single particle and the harmonic oscillator in Section 4.3 and the arguments for including the factor of $1/N!$ on page 297 we see that we can obtain results consistent with starting from quantum mechanics if we choose the constant C_N to be

$$C_N = \frac{1}{N! h^{3N}}. \tag{6.42}$$

Thus the partition function of a system of N particles in the semiclassical limit can be written as

$$\boxed{Z_{N,\,\text{classical}} = \frac{1}{N!} \int e^{-\beta E(\mathbf{r}_1,\ldots,\mathbf{r}_N,\mathbf{p}_1,\ldots,\mathbf{p}_N)}\, \frac{d\mathbf{r}_1 \ldots d\mathbf{r}_N\, d\mathbf{p}_1 \ldots d\mathbf{p}_N}{h^{3N}}}. \tag{6.43}$$

We obtained a special case of the form (6.43) in Problem 6.3. In the following three subsections we integrate over phase space as in (6.43) to find some general properties of classical systems of many particles.

6.2.1 The equipartition theorem

We have used the microcanonical and canonical ensembles to show that the energy of an ideal classical gas in three dimensions is given by $E = 3kT/2$. Similarly, we have found that the energy of a one-dimensional harmonic oscillator is given by $E = kT$ in the high temperature limit. These results are special cases of the *equipartition theorem* which can be stated as follows:

For a classical system in equilibrium with a heat bath at temperature T, the mean value of each contribution to the total energy that is quadratic in a coordinate equals $\frac{1}{2}kT$.

Note that the equipartition theorem holds regardless of the coefficients of the quadratic terms and is valid only for a classical system. If all the contributions to the energy are quadratic, the mean energy is distributed equally to each term (hence the name "equipartition").

To see how to calculate averages according to classical statistical mechanics, we first consider a single particle subject to a potential energy $U(\mathbf{r})$ in equilibrium with a heat bath at temperature T. Classically, the probability of finding the particle in a small volume $d\mathbf{r}$ about $\mathbf{r}$ with a momentum in a small volume $d\mathbf{p}$ about $\mathbf{p}$ is proportional to the Boltzmann factor and the volume $d\mathbf{r} \, d\mathbf{p}$ in phase space:

$$p(\mathbf{r}, \mathbf{p})d\mathbf{r} \, d\mathbf{p} = A e^{-\beta(p^2/2m + U(\mathbf{r}))} d\mathbf{r} \, d\mathbf{p}. \tag{6.44}$$

To normalize the probability and determine the constant A we have to integrate over all the possible values of $\mathbf{r}$ and $\mathbf{p}$.

We next consider a classical system of N particles in the canonical ensemble. The probability density of a particular microstate is proportional to the Boltzmann probability $e^{-\beta E}$, where E is the energy of the microstate. Because a microstate is defined classically by the positions and momenta of every particle, we can express the average of any physical quantity $f(\mathbf{r}, \mathbf{p})$ in a classical system as

$$\overline{f} = \frac{\int f(\mathbf{r}_1, \ldots, \mathbf{r}_N, \mathbf{p}_1, \ldots, \mathbf{p}_N) \, e^{-\beta E(\mathbf{r}_1, \ldots, \mathbf{r}_N, \mathbf{p}_1, \ldots, \mathbf{p}_N)} \, d\mathbf{r}_1 \ldots d\mathbf{r}_N \, d\mathbf{p}_1 \ldots d\mathbf{p}_N}{\int e^{-\beta E(\mathbf{r}_1, \ldots, \mathbf{r}_N, \mathbf{p}_1, \ldots, \mathbf{p}_N)} \, d\mathbf{r}_1 \ldots d\mathbf{r}_N \, d\mathbf{p}_1 \ldots d\mathbf{p}_N}. \tag{6.45}$$

Note that the sum over quantum states has been replaced by an integration over phase space. We could divide the numerator and denominator by h^{3N} so that we would obtain the correct number of microstates in the semiclassical limit, but this factor cancels in calculations of average quantities. We have already seen that the mean energy and mean pressure do not depend on whether the factors of h^{3N} and $1/N!$ are included in the partition function.

Suppose that the total energy can be written as a sum of quadratic terms. For example, the kinetic energy of one particle in three dimensions in the nonrelativistic limit can be expressed as $(p_x^2 + p_y^2 + p_z^2)/2m$. Another example is the one-dimensional harmonic oscillator for which the total energy is $p_x^2/2m + kx^2/2$. For simplicity let's consider a one-dimensional system of two particles, and suppose that the energy of the system can be written as

$$E = \epsilon_1(p_1) + \tilde{E}(x_1, x_2, p_2), \tag{6.46}$$

where $\epsilon_1 = bp_1^2$ with b equal to a constant. We have separated out the quadratic dependence of the energy of particle one on its momentum. We use (6.45) and express the mean value of ϵ_1 as

$$\overline{\epsilon}_1 = \frac{\int_{-\infty}^{\infty} \epsilon_1 \, e^{-\beta E(x_1, x_2, p_1, p_2)} \, dx_1 dx_2 \, dp_1 dp_2}{\int_{-\infty}^{\infty} e^{-\beta E(x_1, x_2, p_1, p_2)} \, dx_1 dx_2 \, dp_1 dp_2} \tag{6.47a}$$

$$= \frac{\int_{-\infty}^{\infty} \epsilon_1 \, e^{-\beta[\epsilon_1 + \tilde{E}(x_1, x_2, p_2)]} \, dx_1 dx_2 \, dp_1 dp_2}{\int_{-\infty}^{\infty} e^{-\beta[\epsilon_1 + \tilde{E}(x_1, x_2, p_2, p_2)]} \, dx_1 dx_2 dp_1 dp_2} \tag{6.47b}$$

$$= \frac{\int_{-\infty}^{\infty} \epsilon_1 \, e^{-\beta \epsilon_1} dp_1 \int e^{-\beta \tilde{E}} \, dx_1 dx_2 \, dp_2}{\int_{-\infty}^{\infty} e^{-\beta \epsilon_1} dp_1 \int e^{-\beta \tilde{E}} \, dx_1 dx_2 \, dp_2}. \tag{6.47c}$$

The integrals over all the coordinates except p_1 cancel, and we have

$$\overline{\epsilon}_1 = \frac{\int_{-\infty}^{\infty} \epsilon_1 \, e^{-\beta \epsilon_1} \, dp_1}{\int_{-\infty}^{\infty} e^{-\beta \epsilon_1} \, dp_1}. \tag{6.48}$$

As we have done in other contexts (see (4.84), page 203) we can write $\overline{\epsilon}_1$ as

$$\overline{\epsilon}_1 = -\frac{\partial}{\partial \beta} \ln \left(\int_{-\infty}^{\infty} e^{-\beta \epsilon_1} \, dp_1 \right). \tag{6.49}$$

If we substitute $\epsilon_1 = ap_1^2$, the integral in (6.49) becomes

$$I(\beta) = \int_{-\infty}^{\infty} e^{-\beta \epsilon_1} dp_1 = \int_{-\infty}^{\infty} e^{-\beta a p_1^2} \, dp_1 \tag{6.50a}$$

$$= (\beta a)^{-1/2} \int_{-\infty}^{\infty} e^{-u^2} du, \tag{6.50b}$$

where we have let $u^2 = \beta ap^2$. Note that the integral in (6.50b) is independent of β, and its numerical value is irrelevant. Hence

$$\overline{\epsilon}_1 = -\frac{\partial}{\partial \beta} \ln I(\beta) = \frac{1}{2}kT. \tag{6.51}$$

Equation (6.51) is an example of the equipartition theorem of classical statistical mechanics.

The equipartition theorem is not really a new result, is applicable only when the system can be described classically, and is applicable only to each term in the energy that is proportional to a coordinate squared. This coordinate must take on a continuum of values from $-\infty$ to $+\infty$.

Applications of the equipartition theorem. A system of particles in three dimensions has $3N$ quadratic contributions to the kinetic energy, three for each particle. From the equipartition theorem, we know that the mean kinetic energy is $3NkT/2$, independent of the nature of the interactions, if any, between the particles. Hence, the heat capacity at constant volume of an ideal classical monatomic gas is given by $C_V = 3Nk/2$ as we have found previously.

Another application of the equipartition function is to the one-dimensional harmonic oscillator in the classical limit. In this case there are two quadratic contributions to the total energy and

hence the mean energy of a one-dimensional classical harmonic oscillator in equilibrium with a heat bath at temperature T is kT. In the harmonic model of a crystal each atom feels a harmonic or spring-like force due to its neighboring atoms (see Section 6.9.1). The N atoms independently perform simple harmonic oscillations about their equilibrium positions. Each atom contributes three quadratic terms to the kinetic energy and three quadratic terms to the potential energy. Hence, in the high temperature limit the energy of a crystal of N atoms is $E = 6NkT/2$ and the heat capacity at constant volume is

$$C_V = 3Nk. \qquad \text{(law of Dulong and Petit)} \qquad (6.52)$$

The result (6.52) is known as the law of Dulong and Petit. This result was first discovered empirically and is valid only at sufficiently high temperatures. At low temperatures a quantum treatment is necessary and the independence of C_V on T breaks down. The heat capacity of an insulating solid at low temperatures is discussed in Section 6.9.2.

We next consider an ideal gas consisting of diatomic molecules (see Figure 6.5 on page 347). Its pressure equation of state is still given by $PV = NkT$, because the pressure depends only on the translational motion of the center of mass of each molecule. However, its heat capacity differs from that of a ideal monatomic gas because a diatomic molecule has additional energy associated with its vibrational and rotational motion. Hence, we would expect that C_V for an ideal diatomic gas is greater than C_V for an ideal monatomic gas. The temperature-dependence of the heat capacity of an ideal diatomic gas is explored in Problem 6.47.

6.2.2 The Maxwell velocity distribution

So far we have used the tools of statistical mechanics to calculate macroscopic quantities of interest in thermodynamics such as the pressure, the temperature, and the heat capacity. We now apply statistical mechanics arguments to gain more detailed information about classical systems of particles by calculating the velocity distribution of the particles.

Consider a classical system of particles in equilibrium with a heat bath at temperature T. We know that the total energy can be written as the sum of two parts: the kinetic energy $K(\mathbf{p}_1, \ldots, \mathbf{p}_N)$ and the potential energy $U(\mathbf{r}_1, \ldots, \mathbf{r}_N)$. The kinetic energy is a quadratic function of the momenta $\mathbf{p}_1, \ldots, \mathbf{p}_N$ (or velocities), and the potential energy is a function of the positions $\mathbf{r}_1, \ldots, \mathbf{r}_N$ of the particles. The total energy is $E = K + U$. The probability density of a microstate of N particles defined by $\mathbf{r}_1, \ldots, \mathbf{r}_N, \mathbf{p}_1, \ldots, \mathbf{p}_N$ is given in the canonical ensemble by

$$p(\mathbf{r}_1, \ldots, \mathbf{r}_N; \mathbf{p}_1, \ldots, \mathbf{p}_N) = A \, e^{-[K(\mathbf{p}_1, \mathbf{p}_2, \ldots, \mathbf{p}_N) + U(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N)]/kT} \qquad (6.53\text{a})$$

$$= A \, e^{-K(\mathbf{p}_1, \mathbf{p}_2, \ldots, \mathbf{p}_N)/kT} e^{-U(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N)/kT}, \qquad (6.53\text{b})$$

where A is a normalization constant. The probability density p is a product of two factors, one that depends only on the particle positions and the other that depends only on the particle momenta. This factorization implies that the probabilities of the momenta and positions are independent. The momentum of a particle is not influenced by its position and vice versa. The probability of the positions of the particles can be written as

$$f(\mathbf{r}_1, \ldots, \mathbf{r}_N) \, d\mathbf{r}_1 \ldots d\mathbf{r}_N = B \, e^{-U(\mathbf{r}_1, \ldots, \mathbf{r}_N)/kT} d\mathbf{r}_1 \ldots d\mathbf{r}_N, \qquad (6.54)$$

and the probability of the momenta is given by

$$f(\mathbf{p}_1, \ldots, \mathbf{p}_N) \, d\mathbf{p}_1 \ldots d\mathbf{p}_N = C \, e^{-K(\mathbf{p}_1, \ldots, \mathbf{p}_N)/kT} d\mathbf{p}_1 \ldots d\mathbf{p}_N. \tag{6.55}$$

For notational simplicity, we have denoted the two probability densities by f, even though their meaning is different in (6.54) and (6.55). The constants B and C in (6.54) and (6.55) can be found by requiring that each probability be normalized.

We stress that the probability distribution for the momenta does not depend on the nature of the interaction between the particles and is the same for all classical systems at the same temperature. This statement might seem surprising because it might seem that the velocity distribution should depend on the density of the system. An external potential also does not affect the velocity distribution. These statements do not hold for quantum systems, because in this case the position and momentum operators do not commute. That is, $e^{-\beta(\hat{K}+\hat{U})} \neq e^{-\beta\hat{K}} e^{-\beta\hat{U}}$ for quantum systems, where we have used the symbol ˆ to denote operators in quantum mechanics.

Because the total kinetic energy is a sum of the kinetic energy of each of the particles, the probability density $f(\mathbf{p}_1, \ldots, \mathbf{p}_N)$ is a product of terms that each depend on the momenta of only one particle. This factorization implies that the momentum probabilities of the various particles are independent, that is, the momentum of one particle does not affect the momentum of any other particle. These considerations imply that we can write the probability that a particle has momentum $\mathbf{p}$ in the range $d\mathbf{p}$ as

$$f(p_x, p_y, p_z) \, dp_x dp_y dp_z = c \, e^{-(p_x^2 + p_y^2 + p_z^2)/2mkT} dp_x dp_y dp_z. \tag{6.56}$$

The constant c is given by the normalization condition

$$c \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} e^{-(p_x^2 + p_y^2 + p_z^2)/2mkT} dp_x dp_y dp_z = c \Big[\int_{-\infty}^{\infty} e^{-p^2/2mkT} dp \Big]^3 = 1. \tag{6.57}$$

If we use the fact that $\int_{-\infty}^{\infty} e^{-\alpha x^2} dx = (\pi/\alpha)^{1/2}$ (see Appendix A), we find that $c = (2\pi mkT)^{-3/2}$. Hence the momentum probability distribution can be expressed as

$$f(p_x, p_y, p_z) \, dp_x dp_y dp_z = \frac{1}{(2\pi mkT)^{3/2}} \, e^{-(p_x^2 + p_y^2 + p_z^2)/2mkT} dp_x dp_y dp_z. \tag{6.58}$$

The corresponding velocity probability distribution is given by

$$f(v_x, v_y, v_z) \, dv_x dv_y dv_z = \Big(\frac{m}{2\pi kT} \Big)^{3/2} e^{-m(v_x^2 + v_y^2 + v_z^2)/2kT} dv_x dv_y dv_z. \tag{6.59}$$

Equation (6.59) is known as the *Maxwell velocity distribution*. Note that its form is a Gaussian. The probability distribution for the speed is discussed in Section 6.2.3.

Because $f(v_x, v_y, v_z)$ is a product of three independent factors, the probability of the velocity of a particle in a particular direction is independent of the velocity in any other direction. For example, the probability that a particle has a velocity in the x-direction in the range v_x to $v_x + dv_x$ is

$$f(v_x) \, dv_x = \Big(\frac{m}{2\pi kT} \Big)^{1/2} e^{-mv_x^2/2kT} dv_x. \tag{6.60}$$

Many textbooks derive the Maxwell velocity distribution for an ideal classical gas and give the misleading impression that the distribution applies only if the particles are noninteracting. We stress that the Maxwell velocity (and momentum) distribution applies to any classical system regardless of the interactions, if any, between the particles.

Problem 6.10. Is there an upper limit to the velocity?

The upper limit to the velocity of a particle is the velocity of light. Yet the Maxwell velocity distribution imposes no upper limit to the velocity. Does this contradiction lead to difficulties? □

Problem 6.11. Simulations of the Maxwell velocity distribution

(a) Program `LJ2DFluidMD` simulates a system of particles interacting via the Lennard-Jones potential (1.1) in two dimensions by solving Newton's equations of motion numerically. The program computes the distribution of velocities in the x-direction among other quantities. Compare the form of the velocity distribution to the form of the Maxwell velocity distribution in (6.60). How does its width depend on the temperature?

(b) Program `TemperatureMeasurementIdealGas` implements the demon algorithm for an ideal classical gas in one dimension (see Section 4.9). All the particles have the same initial velocity. The program computes the distribution of velocities among other quantities. What is the form of the velocity distribution? Give an argument based on the central limit theorem (see Section 3.7) why the distribution has the observed form. Is this form consistent with (6.60)?

6.2.3 The Maxwell speed distribution

We have found that the distribution of velocities in a classical system of particles is a Gaussian and is given by (6.59). To determine the distribution of speeds for a three-dimensional system we need to know the number of microstates between v and $v + \Delta v$. This number is proportional to the volume of a spherical shell of width Δv or $4\pi(v + \Delta v)^3/3 - 4\pi v^3/3 \rightarrow 4\pi v^2 \Delta v$ in the limit $\Delta v \rightarrow 0$. Hence, the probability that a particle has a speed between v and $v + dv$ is given by

$$f(v)dv = 4\pi A v^2 e^{-mv^2/2kT} dv, \qquad (6.61)$$

where A is a normalization constant which we calculate in Problem 6.12.

Problem 6.12. Maxwell speed distribution

(a) Compare the form of the Maxwell speed distribution (6.61) with the form of the Maxwell velocity distribution (6.59).

(b) Use the normalization condition $\int_0^\infty f(v)dv = 1$ to calculate A and show that

$$f(v)dv = 4\pi v^2 \left(\frac{m}{2\pi kT}\right)^{3/2} e^{-mv^2/2kT} dv. \qquad \text{(Maxwell speed distribution)} \qquad (6.62)$$

(c) Calculate the mean speed $\overline{v}$, the most probable speed $\tilde{v}$, and the root-mean square speed v_{rms} and discuss their relative magnitudes.
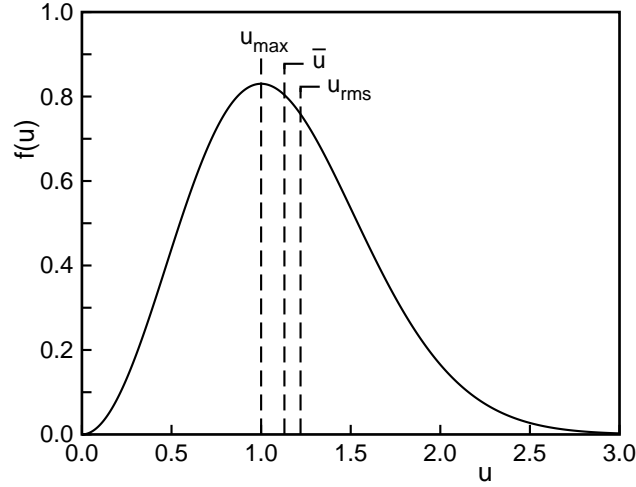
Figure 6.2: The probability density $f(u) = 4/\sqrt{\pi}u^2 e^{-u^2}$ that a particle has a dimensionless speed u. Note the difference between the most probable speed $\tilde{u} = 1$, the mean speed $\overline{u} \approx 1.13$, and the root-mean-square speed $u_{\text{rms}} \approx 1.22$. The dimensionless speed u is defined by $u \equiv v/(2kT/m)^{1/2}$.

(d) Make the change of variables $u = v/\sqrt{(2kT/m)}$ and show that

$$f(v)dv = f(u)du = (4/\sqrt{\pi})u^2 e^{-u^2}du, \tag{6.63}$$

where we have again used same the same notation for two different, but physically related probability densities. The (dimensionless) speed probability density $f(u)$ is shown in Figure 6.2. ∎

Problem 6.13. Maxwell speed distribution in one or two dimensions

Find the Maxwell speed distribution for particles restricted to one and two dimensions. □

6.3 Occupation Numbers and Bose and Fermi Statistics

We now develop the formalism for calculating the thermodynamic properties of ideal gases for which quantum effects are important. We have already noted that the absence of interactions between the particles of an ideal gas enables us to reduce the problem of determining the energy levels of the gas as a whole to determining $\epsilon_{\mathbf{k}}$, the energy levels of a single particle. Because the particles are indistinguishable, we cannot specify the microstate of each particle. Instead a microstate of an ideal gas is specified by the *occupation numbers* $n_{\mathbf{k}}$, the number of particles in the single particle state $\mathbf{k}$ with energy $\epsilon_{\mathbf{k}}$.[2] If we know the value of the occupation number for each

---

[2]The relation of $\mathbf{k}$ to the quantum numbers labeling the single particle microstates is given in (4.35) and in (6.93). In the following we will use $\mathbf{k}$ to label single particle microstates.

single particle microstate, we can write the total energy of the system in microstate s as

$$E_s = \sum_{\mathbf{k}} n_{\mathbf{k}} \, \epsilon_{\mathbf{k}}. \tag{6.64}$$

The set of $n_{\mathbf{k}}$ completely specifies a microstate of the system.

The partition function for an ideal gas can be expressed in terms of the occupation numbers as

$$Z(V,T,N) = \sum_{\{n_{\mathbf{k}}\}} e^{-\beta \sum_{\mathbf{k}} n_{\mathbf{k}} \epsilon_{\mathbf{k}}}, \tag{6.65}$$

where the occupation numbers $n_{\mathbf{k}}$ satisfy the condition

$$N = \sum_{\mathbf{k}} n_{\mathbf{k}}. \tag{6.66}$$

The condition (6.66) is difficult to satisfy in practice, and we will later use the grand canonical ensemble for which the condition of a fixed number of particles is relaxed.

As discussed in Section 4.3.6 one of the fundamental results of relativistic quantum mechanics is that all particles can be classified into two groups. Particles with zero or integral spin such as ^{4}He are *bosons* and have wave functions that are symmetric under the exchange of any pair of particles. Particles with half-integral spin such as electrons, protons, and neutrons are *fermions* and have wave functions that are antisymmetric under particle exchange. The Bose or Fermi character of composite objects can be found by noting that composite objects that have an even number of fermions are bosons and those containing an odd number of fermions are themselves fermions. For example, an atom of ^{3}He is composed of an odd number of particles: two electrons, two protons, and one neutron each of spin $\frac{1}{2}$. Hence, ^{3}He has half-integral spin making it a fermion. An atom of ^{4}He has one more neutron so there are an even number of fermions and ^{4}He is a boson.

It is remarkable that all particles fall into one of two mutually exclusive classes with different spin. It is even more remarkable that there is a connection between the spin of a particle and its statistics. Why are particles with half-integral spin fermions and particles with integral spin bosons? The answer lies in the requirements imposed by Lorentz invariance on quantum field theory. This requirement implies that the form of quantum field theory must be the same in all inertial reference frames. Although many physicists believe that the relation between spin and statistics must have a simpler explanation, no such explanation yet exists.[3]

The difference between fermions and bosons is specified by the possible values of $n_{\mathbf{k}}$. For fermions we have

$$n_{\mathbf{k}} = 0 \text{ or } 1. \qquad \text{(fermions)} \tag{6.67}$$

The restriction (6.67) is a statement of the Pauli exclusion principle for noninteracting particles – two identical fermions cannot be in the same single particle microstate. In contrast, the occupation numbers $n_{\mathbf{k}}$ for identical bosons can take any positive integer value:

$$n_{\mathbf{k}} = 0, 1, 2, \cdots \qquad \text{(bosons)} \tag{6.68}$$

We will see in the following sections that the nature of the statistics of a many particle system can have a profound effect on its properties.

---

[3]In spite of its fundamental importance, it is only a slight exaggeration to say that "everyone knows the spin-statistics theorem, but no one understands it." See the text by Ian Duck and E. C. G. Sudarshan.

n_1	n_2	n_3	n_4
0	1	1	1
1	0	1	1
1	1	0	1
1	1	1	0

Table 6.2: The possible states of a three particle fermion system with four single particle energy microstates. The quantity n_1 represents the number of particles in the single particle microstate labeled 1, etc. Note that we have not specified which particle is in a particular microstate.

Example 6.1. Calculate the partition function of an ideal gas of $N = 3$ identical fermions in equilibrium with a heat bath at temperature T. Assume that each particle can be in one of four possible microstates with energies, $\epsilon_1, \epsilon_2, \epsilon_3$, and ϵ_4.

Solution. The possible microstates of the system are summarized in Table 6.2. The spin of the fermions is neglected. Is it possible to reduce this problem to a one body problem as we did for a noninteracting classical system?

From Table 6.2 we see that the partition function is given by

$$Z_3 = e^{-\beta(\epsilon_2+\epsilon_3+\epsilon_4)} + e^{-\beta(\epsilon_1+\epsilon_3+\epsilon_4)} + e^{-\beta(\epsilon_1+\epsilon_2+\epsilon_4)} + e^{-\beta(\epsilon_1+\epsilon_2+\epsilon_3)}. \tag{6.69}$$

$\diamond$

Problem 6.14. Calculate $\overline{n}_1$, the mean number of fermions in the single particle microstate 1 with energy ϵ_1, for the system in Example 6.1. □

Problem 6.15. Mean energy of a toy model of an ideal Bose gas

(a) Calculate the mean energy of an ideal gas of $N = 2$ identical bosons in equilibrium with a heat bath at temperature T, assuming that each particle can be in one of three microstates with energies, 0, Δ, and 2Δ.

(b) Calculate the mean energy for $N = 2$ distinguishable particles assuming that that each particle can be in one of three possible microstates.

(c) If $\bar{E}_1$ is the mean energy for one particle and $\bar{E}_2$ is the mean energy for the two particle system, is $\bar{E}_2 = 2\bar{E}_1$ for either bosons or distinguishable particles? □

6.4 Distribution Functions of Ideal Bose and Fermi Gases

The calculation of the partition function for an ideal gas in the semiclassical limit was done by choosing a single particle as the system. This choice is not possible for an ideal gas at low temperatures where the quantum nature of the particles cannot be ignored. So we need a different strategy. The key idea is that it is possible to distinguish the subset of all particles in a *given single particle microstate* from the particles in all other single particle states. For this reason we

divide the system of interest into subsystems each of which is the *set of all particles that are in a given single particle microstate.* Because the number of particles in a given microstate varies, we need to use the grand canonical ensemble and assume that each subsystem is coupled to a heat bath and a particle reservoir independently of the other single particle microstates.

Because we have not yet applied the grand canonical ensemble, we review it here. The thermodynamic potential in the grand canonical ensemble is denoted by $\Omega(T, V, \mu)$ and is equal to $-PV$ (see (2.168)). The relation of thermodynamics to statistical mechanics is given by $\Omega = -kT \ln Z_G$, where the grand partition function Z_G is given by

$$Z_G = \sum_s e^{-\beta(E_s - \mu N_s)}, \tag{6.70}$$

where E_s is the energy of microstate s and N_s is the number of particles in microstate s. The goal is to calculate Z_G, then Ω and the pressure equation of state $-PV$ (in terms of T, V, and μ), and then determine S from the relation

$$S = -\left(\frac{\partial \Omega}{\partial T}\right)_{V, \mu}, \tag{6.71}$$

and the mean number of particles from the relation

$$\overline{N} = -\left(\frac{\partial \Omega}{\partial \mu}\right)_{T, V} \tag{6.72}$$

The probability of a particular microstate is given by

$$P_s = \frac{1}{Z_G} e^{-\beta(E_s - \mu N_s)}. \qquad \text{(Gibbs distribution)} \tag{6.73}$$

Because we can treat an ideal gas as a collection of independent subsystems where each subsystem is a single particle microstate, Z_G reduces to the product of $Z_{G, \mathbf{k}}$ for each subsystem. Thus, the first step is to calculate the grand partition function $Z_{G, \mathbf{k}}$ for each subsystem. We write the energy of the $n_{\mathbf{k}}$ particles in the single particle microstate $\mathbf{k}$ as $n_{\mathbf{k}} \epsilon_{\mathbf{k}}$ and write $Z_{G, \mathbf{k}}$ as

$$Z_{G, \mathbf{k}} = \sum_{n_{\mathbf{k}}} e^{-\beta n_{\mathbf{k}}(\epsilon_{\mathbf{k}} - \mu)}, \tag{6.74}$$

where the sum is over the possible values of $n_{\mathbf{k}}$. For fermions this sum is straightforward because $n_{\mathbf{k}} = 0$ and 1 (see (6.67)). Hence

$$Z_{G, \mathbf{k}} = 1 + e^{-\beta(\epsilon_{\mathbf{k}} - \mu)}. \tag{6.75}$$

The corresponding thermodynamic or Landau potential $\Omega_{\mathbf{k}}$ is given by

$$\Omega_{\mathbf{k}} = -kT \ln Z_{G, \mathbf{k}} = -kT \ln[1 + e^{-\beta(\epsilon_{\mathbf{k}} - \mu)}]. \tag{6.76}$$

We use the relation $\overline{n}_{\mathbf{k}} = -\partial \Omega_{\mathbf{k}}/\partial \mu$ (see (6.72)) to find the mean number of particles in microstate $\mathbf{k}$. The result is

$$\overline{n}_{\mathbf{k}} = -\frac{\partial \Omega_{\mathbf{k}}}{\partial \mu} = \frac{e^{-\beta(\mu - \epsilon_{\mathbf{k}})}}{1 + e^{-\beta(\mu - \epsilon_{\mathbf{k}})}}, \tag{6.77}$$

or

$$\overline{n}_{\mathbf{k}} = \frac{1}{e^{\beta(\epsilon_{\mathbf{k}} - \mu)} + 1}. \qquad \text{(Fermi-Dirac distribution)} \qquad (6.78)$$

The result (6.78) for the mean number of particles in single particle microstate $\mathbf{k}$ is known as the *Fermi-Dirac distribution*.

The integer values of $n_{\mathbf{k}}$ are unrestricted for bosons. We write (6.74) as

$$Z_{\mathrm{G},\,\mathbf{k}} = 1 + e^{-\beta(\epsilon_{\mathbf{k}} - \mu)} + e^{-2\beta(\epsilon_{\mathbf{k}} - \mu)} + \cdots = \sum_{n_{\mathbf{k}}=0}^{\infty} \left[e^{-\beta(\epsilon_{\mathbf{k}} - \mu)} \right]^{n_{\mathbf{k}}}. \qquad (6.79)$$

The geometric series in (6.79) is convergent for $e^{-\beta(\epsilon_{\mathbf{k}} - \mu)} < 1$. Because this condition must be satisfied for all values of $\epsilon_{\mathbf{k}}$, we require that $e^{\beta \mu} < 1$ or

$$\mu < 0. \qquad \text{(bosons)} \qquad (6.80)$$

In contrast, the chemical potential may be either positive or negative for fermions. The summation of the geometric series in (6.79) gives

$$Z_{\mathrm{G},\,\mathbf{k}} = \frac{1}{1 - e^{-\beta(\epsilon_{\mathbf{k}} - \mu)}}, \qquad (6.81)$$

and hence we obtain

$$\Omega_{\mathbf{k}} = kT \ln \left[1 - e^{-\beta(\epsilon_{\mathbf{k}} - \mu)} \right]. \qquad (6.82)$$

The mean number of particles in single particle microstate $\mathbf{k}$ is given by

$$\overline{n}_{\mathbf{k}} = -\frac{\partial \Omega_{\mathbf{k}}}{\partial \mu} = \frac{e^{-\beta(\epsilon_{\mathbf{k}} - \mu)}}{1 - e^{-\beta(\epsilon_{\mathbf{k}} - \mu)}}, \qquad (6.83)$$

or

$$\overline{n}_{\mathbf{k}} = \frac{1}{e^{\beta(\epsilon_{\mathbf{k}} - \mu)} - 1}. \qquad \text{(Bose-Einstein distribution)} \qquad (6.84)$$

The form (6.84) is known as the *Bose-Einstein distribution*.

It is frequently convenient to group the Fermi-Dirac and Bose-Einstein distributions together and to write

$$\boxed{\overline{n}_{\mathbf{k}} = \frac{1}{e^{\beta(\epsilon_{\mathbf{k}} - \mu)} \pm 1}. \qquad \begin{cases} + \text{ Fermi-Dirac distribution} \\ - \text{ Bose-Einstein distribution} \end{cases}} \qquad (6.85)$$

The convention is that the upper sign corresponds to Fermi statistics and the lower sign to Bose statistics.

Because the (grand) partition function Z_G is a product, $Z_G = \prod_{\mathbf{k}} Z_{\mathrm{G},\,\mathbf{k}}$, the Landau potential for the ideal gas is given by

$$\Omega(T, V, \mu) = \sum_{\mathbf{k}} \Omega_{\mathbf{k}} = \mp kT \sum_{\mathbf{k}} \ln \left[1 \pm e^{-\beta(\epsilon_{\mathbf{k}} - \mu)} \right]. \qquad (6.86)$$

The classical limit. The Fermi-Dirac and Bose-Einstein distributions must reduce to the classical limit under the appropriate conditions. In the classical limit $\overline{n}_{\mathbf{k}} \ll 1$ for all $\mathbf{k}$; that is, the mean

number of particles in any single particle microstate must be small. Hence $e^{\beta(\epsilon_\mathbf{k}-\mu)} \gg 1$ and in this limit both the Fermi-Dirac and Bose-Einstein distributions reduce to

$$\overline{n}_\mathbf{k} = e^{-\beta(\epsilon_\mathbf{k}-\mu)} \qquad \text{(Maxwell-Boltzmann distribution)} \tag{6.87}$$

This result (6.87) is known as the *Maxwell-Boltzmann distribution*.

6.5 Single Particle Density of States

To find the various thermodynamic quantities we need to calculate various sums. For example, to obtain the mean number of particles in the system we need to sum (6.85) over all single particle states:

$$\overline{N}(T, V, \mu) = \sum_\mathbf{k} \overline{n}_\mathbf{k} = \sum_\mathbf{k} \frac{1}{e^{\beta(\epsilon_\mathbf{k}-\mu)} \pm 1}. \tag{6.88}$$

For a given temperature T and volume V, (6.88) is an implicit equation for the chemical potential μ in terms of the mean number of particles. That is, the chemical potential determines the mean number of particles just as the temperature determines the mean energy. Similarly, we can write the mean energy of the system as

$$\overline{E}(T, V, \mu) = \sum_\mathbf{k} \overline{n}_\mathbf{k}\, \epsilon_\mathbf{k}. \tag{6.89}$$

For a macroscopic system the number of particles and the energy are well defined, and we will usually replace $\overline{N}$ and $\overline{E}$ by N and E respectively.

Because we have described the microscopic states at the most fundamental level, that is, by using quantum mechanics, the macroscopic averages of interest such as (6.88), (6.89) and (6.86) involve sums over the microscopic states. However, because the systems of interest are macroscopic, the volume of the system is so large that the energies of the discrete microstates are very close together and for practical purposes indistinguishable from a continuum. As usual, it is easier to do integrals than to do sums over a very large number of microstates, and we will replace the sums in (6.88)–(6.86) by integrals. For example, we will write for an arbitrary function $f(\epsilon)$

$$\sum_\mathbf{k} f(\epsilon_\mathbf{k}) \to \int_0^\infty f(\epsilon)\, g(\epsilon) d\epsilon, \tag{6.90}$$

where $g(\epsilon)\, d\epsilon$ is the number of single particle microstates between ϵ and $\epsilon + d\epsilon$. The quantity $g(\epsilon)$ is known as the *density of states*, although a better term would be the density of *single* particle microstates.

Although we have calculated the density of states $g(\epsilon)$ for a single particle in a box (see Section 4.3), we review the calculation here to emphasize its generality and the common aspects of the calculation for blackbody radiation, elastic waves in a solid, and electron waves. For convenience, we choose the box to be a cube of linear dimension L and assume that there are standing waves that vanish at the faces of the cube. The condition for a standing wave in one dimension is that the wavelength satisfies the condition

$$\lambda = \frac{2L}{n}, \qquad (n = 1,\ 2,\ \ldots) \tag{6.91}$$

where n is a nonzero positive integer. It is useful to define the *wave number k* as

$$k = \frac{2\pi}{\lambda}, \qquad (6.92)$$

and write the standing wave condition as $k = n\pi/L$. Because the waves in the x, y, and z directions satisfy similar conditions, we can treat the wave number as a vector whose components satisfy the condition

$$\mathbf{k} = (n_x, n_y, n_z)\frac{\pi}{L}, \qquad (6.93)$$

where n_x, n_y, n_z are positive nonzero integers.

Not all values of $\mathbf{k}$ are permissible and each combination of $\{n_x, n_y, n_z\}$ corresponds to a different microstate. In the "number space" defined by the three perpendicular axes labeled by n_x, n_y, and n_z, the possible values of the microstates lie at the centers of cubes of unit edge length. Because the energy of a wave depends only on the magnitude of $\mathbf{k}$, we want to know the number of microstates between k and $k + dk$. As we did in Section 4.3, it is easier to first find $\Gamma(k)$, the number of microstates with wave number less than or equal to k. We know that the volume in n-space of a single particle microstate is one, and hence the number of single particle microstates in number space that are contained in the positive octant of a sphere of radius n is given by $\Gamma(n) = \frac{1}{8}(4\pi n^3/3)$, where $n^2 = n_x^2 + n_y^2 + n_z^2$. Because $\mathbf{k} = \pi\mathbf{n}/L$, the number of single particle microstates with wave vector less than or equal to k is

$$\Gamma(k) = \frac{1}{8}\frac{4\pi k^3/3}{(\pi/L)^3}. \qquad (6.94)$$

If we use the relation

$$g(k)\,dk = \Gamma(k + dk) - \Gamma(k) = \frac{d\Gamma(k)}{dk}\,dk, \qquad (6.95)$$

we obtain

$$g(k)\,dk = V\frac{k^2 dk}{2\pi^2}, \qquad (6.96)$$

where the volume $V = L^3$. Equation (6.96) gives the density of states in k-space between k and $k + dk$.

Although we obtained the result (6.96) for a cube, the result is independent of the shape of the enclosure and the nature of the boundary conditions (see Problem 6.58). That is, if the box is sufficiently large, the surface effects introduced by the box do not affect the physical properties of the system.

Problem 6.16. Single particle density of states in one and two dimensions

Find the form of the density of states in k-space for standing waves in a two-dimensional and in a one-dimensional box. □

6.5.1 Photons

The result (6.96) for the density of states in k-space holds for any wave in a three-dimensional enclosure. We next determine the number of states $g(\epsilon)\,d\epsilon$ as a function of the energy ϵ. For

simplicity, we adopt the same symbol to represent the density of states in k-space and in ϵ-space because the meaning of g will be clear from the context.

The nature of the dependence of $g(\epsilon)$ on the energy ϵ is determined by the form of the function $\epsilon_{\mathbf{k}}$. For electromagnetic waves of frequency ν we know that $\lambda\nu = c$, $\omega = 2\pi\nu$, and $k = 2\pi/\lambda$. Hence, $\omega = 2\pi c/\lambda$ or

$$\omega = ck. \tag{6.97}$$

The energy ϵ of a photon of frequency ω is

$$\epsilon = \hbar\omega = \hbar ck. \tag{6.98}$$

Because $k = \epsilon/\hbar c$, we find from (6.96) that

$$g(\epsilon)\,d\epsilon = V\frac{\epsilon^2}{2\pi^2\hbar^3 c^3}\,d\epsilon. \tag{6.99}$$

The result (6.99) requires one modification. The state of an electromagnetic wave or photon depends not only on its wave vector or momentum, but also on its polarization. There are two mutually perpendicular directions of polarization (right circularly polarized and left circularly polarized) for each electromagnetic wave of wave number $\mathbf{k}$.[4] Thus the number of photon microstates in which the photon has an energy in the range ϵ to $\epsilon + d\epsilon$ is given by

$$g(\epsilon)\,d\epsilon = V\frac{\epsilon^2 d\epsilon}{\pi^2\hbar^3 c^3}. \qquad \text{(photons)} \tag{6.100}$$

We will use (6.100) frequently in the following.

6.5.2 Nonrelativistic particles

For a nonrelativistic particle of mass m we know that

$$\epsilon = \frac{p^2}{2m}. \tag{6.101}$$

From the relations $p = h/\lambda$ and $k = 2\pi/\lambda$, we find that the momentum p of a particle is related to its wave vector k by $p = \hbar k$. Hence, the energy can be expressed as

$$\epsilon = \frac{\hbar^2 k^2}{2m}, \tag{6.102}$$

and

$$d\epsilon = \frac{\hbar^2 k}{m}dk. \tag{6.103}$$

If we use (6.96) and the relations (6.102) and (6.103), we find that the number of microstates in the interval ϵ to $\epsilon + d\epsilon$ is given by

$$g(\epsilon)\,d\epsilon = n_s\frac{V}{4\pi^2\hbar^3}(2m)^{3/2}\,\epsilon^{1/2}\,d\epsilon. \tag{6.104}$$

---

[4]In the language of quantum mechanics we say that the photon has spin one and two helicity states. The fact that the photon has spin $S = 1$ and two helicity states rather than $(2S + 1) = 3$ states is a consequence of special relativity for massless particles.

We have included a factor of n_s, the number of spin states for a given value of k or ϵ. Because electrons have spin $1/2$, $n_s = 2$, and we can write (6.104) as

$$g(\epsilon)\, d\epsilon = \frac{V}{2\pi^2\hbar^3}(2m)^{3/2}\,\epsilon^{1/2}\, d\epsilon. \qquad \text{(electrons)} \qquad (6.105)$$

Because it is common to choose units such that $\hbar = 1$, we will express most of our results in the remainder of this chapter in terms of $\hbar$ instead of h.

Problem 6.17. Density of states in one and two dimensions

Calculate the density of states $g(\epsilon)$ for a nonrelativistic particle of mass m in in one and two dimensions (see Problem 6.16). Sketch $g(\epsilon)$ on one graph for $d = 1$, 2, and 3 and comment on the different dependence of $g(\epsilon)$ on ϵ for different spatial dimensions. $\qquad\square$

Problem 6.18. Relativistic particles

Calculate the density of states $g(\epsilon)$ in three dimensions for a relativistic particle of rest mass m for which $\epsilon^2 = p^2 c^2 + m^2 c^4$. Don't try to simplify your result. $\qquad\square$

Problem 6.19. Relation between the energy and pressure equations of state for a nonrelativistic ideal gas

The mean energy E is given by

$$E = \int_0^\infty \epsilon \overline{n}(\epsilon)\, g(\epsilon)\, d\epsilon \qquad (6.106a)$$

$$= n_s \frac{V}{4\pi^2\hbar^3}(2m)^{3/2} \int_0^\infty \frac{\epsilon^{3/2} d\epsilon}{e^{\beta(\epsilon-\mu)} + 1}. \qquad (6.106b)$$

Use (6.86) for the Landau potential and (6.104) for the density of states of nonrelativistic particles in three dimensions to show that Ω can be expressed as

$$\Omega = \mp kT \int_0^\infty g(\epsilon)\, \ln[1 \pm e^{-\beta(\epsilon-\mu)}]\, d\epsilon, \qquad (6.107)$$

$$= \mp kT \frac{n_s V}{4\pi^2\hbar^3}(2m)^{3/2} \int_0^\infty \epsilon^{1/2} \ln[1 \pm e^{-\beta(\epsilon-\mu)}]\, d\epsilon. \qquad (6.108)$$

Integrate (6.108) by parts with $u = \ln[1 \pm e^{-\beta(\epsilon-\mu)}]$ and $dv = \epsilon^{1/2}\, d\epsilon$ and show that

$$\Omega = -\frac{2}{3}n_s \frac{V}{4\pi^2\hbar^3}(2m)^{3/2} \int_0^\infty \frac{\epsilon^{3/2}\, d\epsilon}{e^{\beta(\epsilon-\mu)} + 1}. \qquad (6.109)$$

The form (6.106b) for E is the same as the general result (6.109) for Ω except for the factor of $-\frac{2}{3}$. Use the relation $\Omega = -PV$ (see (2.168)) to show that

$$PV = \frac{2}{3}E. \qquad (6.110)$$

The relation (6.110) is exact and holds for an ideal gas with any statistics at any temperature T, and depends only on the nonrelativistic relation, $\epsilon = p^2/2m$. $\qquad\square$

Problem 6.20. Relation between the energy and pressure equations of state for photons
Use similar considerations as in Problem 6.19 to show that for photons:

$$PV = \frac{1}{3}E. \tag{6.111}$$

Equation (6.111) holds at any temperature and is consistent with Maxwell's equations. Thus, the pressure due to electromagnetic radiation is related to the energy density by $P = u(T)/3$. □

6.6 The Equation of State of an Ideal Classical Gas: Application of the Grand Canonical Ensemble

We have already seen how to obtain the equations of state and other thermodynamic quantities for the ideal classical gas in the microcanonical ensemble (fixed E, T, and N) and in the canonical ensemble (fixed T, V, and N). We now discuss how to use the grand canonical ensemble (fixed T, V, and μ) to find the analogous quantities under conditions for which the Maxwell-Boltzmann distribution is applicable. The calculation in the grand canonical ensemble will automatically satisfy the condition that the particles are indistinguishable.

As an example, we first calculate the chemical potential given that the mean number of particles is $\overline{N}$. We use the Maxwell distribution (6.87) and the density of states (6.104) for particles of mass m and set $n_s = 1$ for simplicity. The result is

$$\overline{N} = \sum_{\mathbf{k}} \overline{n}_{\mathbf{k}} \rightarrow \int_0^\infty \overline{n}(\epsilon)\, g(\epsilon)\, d\epsilon \tag{6.112a}$$

$$= \frac{V}{4\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2} \int_0^\infty e^{-\beta(\epsilon-\mu)}\, \epsilon^{1/2}\, d\epsilon. \tag{6.112b}$$

We make the change of variables $u = \beta\epsilon$ and write (6.112b) as

$$\overline{N} = \frac{V}{4\pi^2}\left(\frac{2m}{\hbar^2\beta}\right)^{3/2} e^{\beta\mu} \int_0^\infty e^{-u}\, u^{1/2}\, du. \tag{6.113}$$

The integral in (6.113) can be done analytically (make the change of variables $u = y^2$) and has the value $\pi^{1/2}/2$ (see Appendix A). Hence, the mean number of particles is given by

$$\overline{N}(T, V, \mu) = V\left(\frac{m}{2\pi\hbar^2\beta}\right)^{3/2} e^{\beta\mu}. \tag{6.114}$$

Because we cannot easily measure μ, it is of more interest to find the value of μ that yields the desired value of $\overline{N}$. The solution of (6.114) for the chemical potential is

$$\mu = kT \ln\left[\frac{\overline{N}}{V}\left(\frac{2\pi\hbar^2\beta}{m}\right)^{3/2}\right]. \tag{6.115}$$

What is the difference, if any, between (6.114) and the result (6.29) for μ found in the canonical ensemble?

Problem 6.21. The chemical potential

(a) Estimate the chemical potential of one mole of a ideal monatomic classical gas at standard temperature and pressure and show that $\mu \ll 0$.

(b) Show that $\overline{N}$ can be expressed as (see (6.114))

$$\overline{N} = \frac{V}{\lambda^3}\, e^{\beta\mu}, \tag{6.116}$$

and hence

$$\mu(T, V) = -kT \ln \frac{1}{\rho\lambda^3}, \tag{6.117}$$

where $\rho = \overline{N}/V$.

(c) In Section 6.1 we argued that the semiclassical limit $\lambda \ll \rho^{-1/3}$ (see (6.1)) implies that $\overline{n}_{\mathbf{k}} \ll 1$; that is, the mean number of particles in any single particle energy state is very small. Use the expression (6.117) for μ and (6.87) for $\overline{n}_{\mathbf{k}}$ to show that the condition $\overline{n}_{\mathbf{k}} \ll 1$ implies that $\lambda \ll \rho^{-1/3}$. □

As we saw in Section 2.21, the chemical potential is the change in any of the thermodynamic potentials when a particle is added. It might be expected that $\mu > 0$, because it should cost energy to add a particle. But because the particles do not interact, perhaps $\mu = 0$? So why is $\mu \ll 0$ for an ideal classical gas? The reason is that we have to include the contribution of the entropy. In the canonical ensemble the change in the free energy due to the addition of a particle at constant temperature is $\Delta F = \Delta E - T\Delta S \approx kT - T\Delta S$. The number of places where the additional particle can be located is approximately V/λ^3, and hence $\Delta S \sim k \ln V/\lambda^3$. Because $V/\lambda^3 \gg 1$, $\Delta S \gg \Delta E$, and thus $\Delta F \ll 0$, which implies that $\mu = \Delta F/\Delta N \ll 0$.

The example calculation of $\overline{N}(T, V, \mu)$ leading to (6.114) was not necessary because we can calculate all thermodynamic quantities directly from the Landau potential Ω. We calculate Ω from (6.86) by noting that $e^{\beta\mu} \ll 1$ and approximating the logarithm as $\ln(1 \pm x) \approx \pm x$. We find that

$$\Omega = \mp kT \sum_{\mathbf{k}} \ln\left[1 \pm e^{-\beta(\epsilon_{\mathbf{k}} - \mu)}\right] \tag{6.118a}$$

$$\to -kT \sum_{\mathbf{k}} e^{-\beta(\epsilon_{\mathbf{k}} - \mu)}. \qquad \text{(semiclassical limit)} \tag{6.118b}$$

As expected, the form of Ω in (6.118b) is independent of whether we started with Bose or Fermi statistics.

As usual, we replace the sum over the single particle states by an integral over the density of states and find

$$\Omega = -kT\, e^{\beta\mu} \int_0^\infty g(\epsilon)\, e^{-\beta\epsilon}\, d\epsilon \tag{6.119a}$$

$$= -kT\, \frac{V}{4\pi^2\hbar^3} \left(\frac{2m}{\beta}\right)^{3/2} e^{\beta\mu} \int_0^\infty x^{1/2} e^{-u}\, du \tag{6.119b}$$

$$= -\frac{V}{\beta^{5/2}} \left(\frac{m}{2\pi\hbar^2}\right)^{3/2} e^{\beta\mu}. \tag{6.119c}$$

If we substitute $\lambda = (2\pi\beta\hbar^2/m)^{1/2}$, we find

$$\Omega = -kT\frac{V}{\lambda^3}\,e^{\beta\mu}. \tag{6.120}$$

From the relation $\Omega = -PV$ (see (2.168)), we obtain

$$P = \frac{kT}{\lambda^3}\,e^{\beta\mu}. \tag{6.121}$$

If we use the thermodynamic relation (6.72), we obtain

$$\overline{N} = -\frac{\partial\Omega}{\partial\mu}\Big|_{V,T} = \frac{V}{\lambda^3}\,e^{\beta\mu}. \tag{6.122}$$

The classical equation of state, $PV = \overline{N}kT$, is obtained by using (6.122) to eliminate μ. The simplest way of finding the energy is to use the relation (6.110).

We can find the entropy $S(T,V,\mu)$ using (6.120) and (6.71):

$$S(T,V,\mu) = -\frac{\partial\Omega}{\partial T}\Big|_{V,\mu} = k\beta^2\,\frac{\partial\Omega}{\partial\beta} \tag{6.123a}$$

$$= Vk\beta^2\Big[\frac{5}{2\beta^{7/2}} - \frac{\mu}{\beta^{5/2}}\Big]\Big(\frac{m}{2\pi\hbar^2}\Big)^{3/2} e^{\beta\mu}. \tag{6.123b}$$

We eliminate μ from (6.123b) using (6.115) and obtain the Sackur-Tetrode expression for the entropy of an ideal gas:

$$S(T,V,N) = Nk\Big[\frac{5}{2} - \ln\frac{N}{V} - \ln\Big(\frac{2\pi\hbar^2}{mkT}\Big)^{3/2}\Big]. \tag{6.124}$$

We have written N rather than $\overline{N}$ in (6.124). Note that we did not have to introduce any extra factors of $N!$ as we did in Section 6.1, because we already correctly counted the number of microstates.

Problem 6.22. Ideal gas equations of state

Show that $E = (3/2)NkT$ and $PV = NkT$ from the results of this section. $\qquad\qquad\square$

6.7 Blackbody Radiation

We can regard electromagnetic radiation as equivalent to a system of noninteracting bosons (photons), each of which has an energy $h\nu$, where ν is the frequency of the radiation. If the radiation is in an enclosure, equilibrium will be established and maintained by the interactions of the photons with the atoms of the wall in the enclosure. Because the atoms emit and absorb photons, the total number of photons is not conserved.

If a body in thermal equilibrium emits electromagnetic radiation, this radiation is described as blackbody radiation and the object is said to be a blackbody. This statement does not mean that the body is actually black. The word "black" indicates that the radiation is perfectly absorbed and

re-radiated by the object. The frequency spectrum of light radiated by such an idealized body is described by a universal spectrum called the Planck spectrum, which we will derive in the following (see (6.133)). The nature of the spectrum depends only on the temperature T of the radiation.

We can derive the Planck radiation law using either the canonical or grand canonical ensemble because the photons are continuously absorbed and emitted by the walls of the container and hence their number is not conserved. This lack of a conservation law for the number of particles implies that the chemical potential vanishes. Hence the Bose-Einstein distribution in (6.85) reduces to

$$\overline{n}_{\mathbf{k}} = \frac{1}{e^{\beta \epsilon_{\mathbf{k}}} - 1} \qquad \text{(Planck distribution)} \qquad (6.125)$$

for blackbody radiation.

The result (6.125) can be understood by simple considerations. As we have mentioned, equilibrium is established and maintained by the interactions between the photons and the atoms of the wall in the enclosure. The number N of photons in the cavity cannot be imposed externally on the system and is fixed by the temperature T of the walls and the volume V enclosed. Hence, the free energy F for photons cannot depend on N because the latter is not a thermodynamic variable, and we have $\mu = \partial F / \partial N = 0$. If we substitute $\mu = 0$ into the general result (6.84) for the Bose-Einstein distribution, we find that the mean number of photons in single particle state $\mathbf{k}$ is given by

$$\overline{n}_{\mathbf{k}} = \frac{1}{e^{\beta \epsilon_{\mathbf{k}}} - 1}, \qquad (6.126)$$

in agreement with (6.125).

To see how (6.126) follows from the canonical ensemble, consider a system in equilibrium with a heat bath at temperature T. Because there is no constraint on the total number of photons, the number of photons in each single particle microstate is independent of the number of photons in all the other single particle microstates. Thus, the partition function is the product of the single particle state partition functions $Z_{\mathbf{k}}(T, V)$ for each state in the same way as the partition function for a collection of noninteracting spins is the product of the partition functions for each spin. We have

$$Z_{\mathbf{k}}(T, V) = \sum_{n_{\mathbf{k}}=0}^{\infty} e^{-\beta n_{\mathbf{k}} \epsilon_{\mathbf{k}}}. \qquad (6.127)$$

Because the sum in brackets in (6.127) is a geometric series, we obtain

$$Z_{\mathbf{k}}(T, V) = \frac{1}{1 - e^{-\beta \epsilon_{\mathbf{k}}}}. \qquad (6.128)$$

In the canonical ensemble the mean number of photons in the single particle microstate $\mathbf{k}$ is given by

$$\overline{n}_{\mathbf{k}} = \frac{\sum_{n_{\mathbf{k}}=0}^{\infty} n_{\mathbf{k}} e^{-\beta n_{\mathbf{k}} \epsilon_{\mathbf{k}}}}{\sum_{n_{\mathbf{k}}=0}^{\infty} e^{-\beta n_{\mathbf{k}} \epsilon_{\mathbf{k}}}} \qquad (6.129\text{a})$$

$$= \frac{\partial \ln Z_{\mathbf{k}}}{\partial(-\beta \epsilon_{\mathbf{k}})}. \qquad (6.129\text{b})$$

We have from (6.128) and (6.129b)

$$\overline{n}_{\mathbf{k}} = \frac{\partial}{\partial(-\beta\epsilon_{\mathbf{k}})}\Big[-\ln\left(1 - e^{-\beta\epsilon_{\mathbf{k}}}\right)\Big] \tag{6.130a}$$

$$= \frac{e^{-\beta\epsilon_{\mathbf{k}}}}{1 - e^{-\beta\epsilon_{\mathbf{k}}}} = \frac{1}{e^{\beta\epsilon_{\mathbf{k}}} - 1}. \tag{6.130b}$$

Planck's theory of blackbody radiation follows from the form of the density of states for photons found in (6.100). The number of photons with energy in the range ϵ to $\epsilon + d\epsilon$ is given by

$$N(\epsilon)\,d\epsilon = \overline{n}(\epsilon)g(\epsilon)\,d\epsilon = \frac{V}{\pi^2\hbar^3c^3}\frac{\epsilon^2\,d\epsilon}{e^{\beta\epsilon} - 1}. \tag{6.131}$$

If we substitute $\epsilon = h\nu$ on the right-hand side of (6.131), we find that the number of photons in the frequency range ν to $\nu + d\nu$ is given by

$$N(\nu)\,d\nu = \frac{8\pi V}{c^3}\frac{\nu^2\,d\nu}{e^{\beta h\nu} - 1}. \tag{6.132}$$

The distribution of radiated energy is obtained by multiplying (6.132) by $h\nu$:

$$E(\nu)d\nu = h\nu N(\nu)\,d\nu = \frac{8\pi h V\nu^3}{c^3}\frac{d\nu}{e^{\beta h\nu} - 1}. \tag{6.133}$$

Equation (6.133) gives the energy radiated by a blackbody of volume V in the frequency range between ν and $\nu + d\nu$. The energy per unit volume $u(\nu)$ is given by

$$u(\nu) = \frac{8\pi h\nu^3}{c^3}\frac{1}{e^{\beta h\nu} - 1}. \qquad \text{(Planck's radiation law)} \tag{6.134}$$

We can change variables to $\epsilon = h\nu$ and write the energy density as

$$u(\epsilon) = \frac{8\pi}{(hc)^3}\frac{\epsilon^3}{e^{\epsilon/kT} - 1}. \tag{6.135}$$

The physical system that most closely gives the spectrum of a black body is the spectrum of the cosmic microwave background, which fits the theoretical spectrum of a blackbody better than the best blackbody spectrum that can be made in a laboratory. In contrast, a piece of hot, glowing firewood is not really in thermal equilibrium, and the spectrum of glowing embers is only a crude approximation to blackbody spectrum. The existence of the cosmic microwave background spectrum and its fit to the blackbody spectrum is compelling evidence that the universe experienced a Big Bang.[5]

---

[5]The universe is filled with electromagnetic radiation with a distribution of frequencies given by (6.133) with $T \approx 2.725\,\text{K}$. The existence of the background radiation is a remnant from a time when the universe was composed primarily of electrons and protons at a temperature of about $3000\,\text{K}$. This plasma of electrons and protons interacted strongly with the electromagnetic radiation over a wide range of frequencies, so that the matter and radiation reached thermal equilibrium. As the universe expanded, the plasma cooled until it became energetically favorable for electrons and protons to combine to form hydrogen atoms. Atomic hydrogen interacts with radiation only at the frequencies of the hydrogen spectral lines. As a result most of the radiation energy was effectively decoupled from matter so that its temperature is independent of the temperature of the hydrogen atoms. The background radiation is now at about $2.725\,\text{K}$ because of the expansion of the universe. This expansion causes the radiation to be redshifted. The temperature of the cosmic radiation background will continue to decrease as the universe expands.

Problem 6.23. Wien's displacement law

The maximum of $u(\nu)$ shifts to higher frequencies with increasing temperature. Show that the maximum of u can be found by solving the equation

$$(3 - x)e^x = 3, \tag{6.136}$$

where $x = \beta h\nu_{\max}$. Solve (6.136) numerically for x and show that

$$\frac{h\nu_{\max}}{kT} = 2.822. \qquad \text{(Wien's displacement law)} \tag{6.137}$$

$\square$

Problem 6.24. Derivation of the Rayleigh-Jeans and Wien's laws

(a) Do a change of variables in (6.134) to find the energy emitted by a blackbody at a wavelength between λ and $\lambda + d\lambda$.

(b) Determine the limiting behavior of your result in part (a) for long wavelengths. This limit is called the Rayleigh-Jeans law and is given by

$$u(\lambda)d\lambda = \frac{8\pi kT}{\lambda^4}d\lambda. \tag{6.138}$$

Does this form involve Planck's constant? The result in (6.138) was originally derived from purely classical considerations.

(c) Classical theory predicts what is known as the ultraviolet catastrophe, namely that an infinite amount of energy is radiated at high frequencies or short wavelengths. Explain how (6.138) would give an infinite result for the total radiated energy, and thus the classical result cannot be correct for all wavelengths.

(d) Determine the limiting behavior of $u(\lambda)$ for short wavelengths. This behavior is known as Wien's law after Wilhelm Wien who found it by finding a mathematical form to fit the experimental data. $\square$

Problem 6.25. Thermodynamics of blackbody radiation

Use the various thermodynamic relations to show that

$$E = V \int_0^\infty u(\nu)\, d\nu = \frac{4\sigma}{c}VT^4. \tag{6.139a}$$

$$\Omega = F = -\frac{4\sigma}{3c}VT^4. \tag{6.139b}$$

$$S = \frac{16\sigma}{3c}VT^3. \tag{6.139c}$$

$$P = \frac{4\sigma}{3c}T^4 = \frac{1}{3}\frac{E}{V}. \tag{6.139d}$$

$$G = F + PV = 0. \tag{6.139e}$$

The free energy F in (6.139b) can be calculated from Z starting from (6.128) and using (6.100). The Stefan-Boltzmann constant σ is given by

$$\sigma = \frac{2\pi^5 k^4}{15 h^3 c^2}. \tag{6.140}$$

The integral

$$\int_0^\infty \frac{x^3\,dx}{e^x - 1} = \frac{\pi^4}{15}. \tag{6.141}$$

is evaluated in Appendix A. $\qquad\square$

The relation (6.139a) between the total energy and the temperature is known as the Stefan-Boltzmann law. It was derived based on thermodynamic considerations in Section 2.21.

Problem 6.26. Mean number of photons

Show that the total mean number of photons in an enclosure of volume V is given by

$$N = \frac{V}{\pi^2 c^3} \int_0^\infty \frac{\omega^2 d\omega}{e^{\hbar\omega/kT} - 1} = \frac{V(kT)^3}{\pi^2 c^3 \hbar^3} \int_0^\infty \frac{x^2 dx}{e^x - 1}. \tag{6.142}$$

The integral in (6.142) can be expressed in terms of known functions (see Appendix A). The result is

$$\int_0^\infty \frac{x^2 dx}{e^x - 1} = 2 \times 1.202. \tag{6.143}$$

Hence N depends on T as

$$N = 0.244 V \left(\frac{kT}{\hbar c}\right)^3. \tag{6.144}$$

$\qquad\square$

6.8   The Ideal Fermi Gas

The low temperature properties of metals are dominated by the behavior of the conduction electrons. Given that there are Coulomb interactions between the electrons as well as interactions between the electrons and the positive ions of the lattice, it is remarkable that the *free electron model* in which the electrons are treated as an ideal gas of fermions near zero temperature is an excellent model of the conduction electrons in a metal under most circumstances.[6] In the following, we investigate the properties of an ideal Fermi gas and briefly discuss its applicability as a model of electrons in metals.

As we will see in Problem 6.27, the thermal de Broglie wavelength of the electrons in a typical metal is much larger than the mean interparticle spacing, and hence we must treat the electrons using Fermi statistics. When a system is dominated by quantum mechanical effects, it is said to be *degenerate*.

---

[6]The idea that a system of interacting electrons at low temperatures can be understood as a noninteracting gas of quasiparticles is due to Lev Landau (1908–1968), the same Landau for whom the thermodynamic potential in the grand canonical ensemble is named. Landau worked in many fields including low temperature physics, atomic and nuclear physics, condensed matter physics, and plasma physics. He was awarded the 1962 Nobel Prize for Physics for his work on superfluidity. He was also the co-author of ten widely used graduate-level textbooks on various areas of theoretical physics.
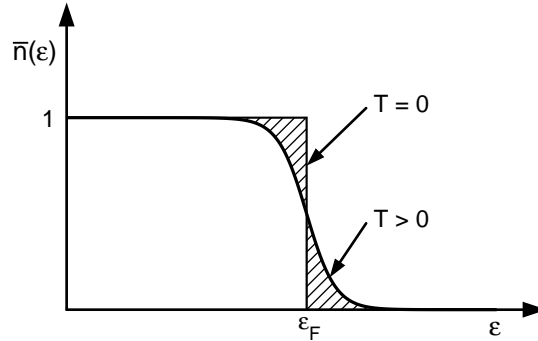
Figure 6.3: The Fermi-Dirac distribution at $T = 0$ (dotted line) and $T \ll T_F$ (solid line). The form of $\overline{n}(\epsilon)$ for $T > 0$ is based on the assumption that μ is unchanged for $T \ll T_F$. Note that the area under the dotted line ($\overline{n}(\epsilon)$ at $T = 0$) is approximately equal to the area under the solid line ($\overline{n}(\epsilon)$ for $T \ll T_F$).

6.8.1 Ground-state properties

We first discuss the noninteracting Fermi gas at $T = 0$. From (6.78) we see that the zero temperature limit ($\beta \to \infty$) of the Fermi-Dirac distribution is

$$\overline{n}(\epsilon) = \begin{cases} 1 & \text{for } \epsilon < \mu \\ 0 & \text{for } \epsilon > \mu. \end{cases} \tag{6.145}$$

That is, all states whose energies are below the chemical potential are occupied, and all states whose energies are above the chemical potential are unoccupied. The Fermi distribution at $T = 0$ is shown in Figure 6.3.

The consequences of (6.145) are easy to understand. At $T = 0$, the system is in its *ground state*, and the particles are distributed among the single particle states so that the total energy of the gas is a minimum. Because we may place no more than one particle in each state, we need to construct the ground state of the system by adding a particle into the lowest available energy state until we have placed all the particles. To find the value of $\mu(T = 0)$, we write

$$N = \int_0^\infty \overline{n}(\epsilon)g(\epsilon)\,d\epsilon \xrightarrow[T \to 0]{} \int_0^{\mu(T=0)} g(\epsilon)\,d\epsilon = V \int_0^{\mu(T=0)} \frac{(2m)^{3/2}}{2\pi^2\hbar^3}\epsilon^{1/2}\,d\epsilon. \tag{6.146}$$

We have substituted the electron density of states (6.105) in (6.146). The chemical potential at $T = 0$ is determined by requiring the integral to give the desired number of particles N. Because the value of the chemical potential at $T = 0$ will have special importance, it is common to denote it by ϵ_F:

$$\epsilon_F \equiv \mu(T = 0), \tag{6.147}$$

where ϵ_F, the energy of the highest occupied state, is called the *Fermi energy*.

The integral on the right-hand side of (6.146) gives

$$N = \frac{V}{3\pi^2}\left(\frac{2m\epsilon_F}{\hbar^2}\right)^{3/2}. \tag{6.148}$$

From (6.148) we have that

$$\epsilon_F = \frac{\hbar^2}{2m}(3\pi^2\rho)^{2/3}, \qquad \text{(Fermi energy)} \tag{6.149}$$

where the density $\rho = N/V$. It is convenient to write $\epsilon_F = p_F^2/2m$ where p_F is known as the *Fermi momentum*. It follows that the Fermi momentum p_F is given by

$$p_F = (3\pi^2\rho)^{1/3}\hbar. \qquad \text{(Fermi momentum)} \tag{6.150}$$

The Fermi momentum can be estimated by using the de Broglie relation $p = h/\overline{\lambda}$ and taking $\overline{\lambda} \sim \rho^{-1/3}$, the mean distance between particles. That is, the particles are "localized" within a distance of order $\rho^{-1/3}$.

At $T = 0$ all the states with momentum less that p_F are occupied and all the states above this momentum are unoccupied. The boundary in momentum space between occupied and unoccupied states at $T = 0$ is called the *Fermi surface*. For an ideal Fermi gas in three dimensions the Fermi surface is the surface of a sphere with radius p_F.

We can understand why the chemical potential at $T = 0$ is positive by reasoning similar to that given on page 319 for an ideal classical gas. At $T = 0$ the contribution of $T\Delta S$ to the free energy vanishes, and no particle can be added with energy less than $\mu(T = 0)$. Thus, $\mu(T = 0) > 0$. In contrast, we argued that $\mu(T > 0)$ is much less than zero for an ideal classical gas due to the large change in the entropy when adding (or removing) a particle.

We will find it convenient in the following to introduce a characteristic temperature, the Fermi temperature T_F, by

$$T_F = \epsilon_F/k. \tag{6.151}$$

The values of T_F for typical metals is given in Table 6.3.

A direct consequence of the fact that the density of states in three dimensions is proportional to $\epsilon^{1/2}$ is that the mean energy per particle at $T = 0$ is $3\epsilon_F/5$:

$$\frac{\overline{E}}{N} = \frac{\int_0^{\epsilon_F} \epsilon \, g(\epsilon) \, d\epsilon}{\int_0^{\epsilon_F} g(\epsilon) \, d\epsilon} = \frac{\int_0^{\epsilon_F} \epsilon^{3/2} d\epsilon}{\int_0^{\epsilon_F} \epsilon^{1/2} d\epsilon} \tag{6.152a}$$

$$= \frac{\frac{2}{5}\epsilon_F^{5/2}}{\frac{2}{3}\epsilon_F^{3/2}} = \frac{3}{5}\epsilon_F. \tag{6.152b}$$

The total energy is given by

$$E = \frac{3}{5}N\epsilon_F = \frac{3}{5}N(3\pi^2)^{2/3}\frac{\hbar^2}{2m}\rho^{2/3}. \tag{6.153}$$

The pressure can be immediately found from the general relation $PV = 2E/3$ (see (6.110)) for an nonrelativistic ideal gas at any temperature. Alternatively, the pressure can be found from the relation

$$P = -\frac{\partial F}{\partial V} = \frac{2}{3}\frac{E}{V}, \tag{6.154}$$

element	ϵ_F (eV)	T_F (10^4 K)
Li	4.7	5.5
Na	3.2	3.8
Al	11.7	13.6
Cu	7	8.2
Ag	5.5	6.4

Table 6.3: Values of the Fermi energy and Fermi temperature for several metals at room temperature and atmospheric pressure.

because the free energy is equal to the total energy at $T = 0$. The result is that the pressure at $T = 0$ is given by

$$P = \frac{2}{5}\rho\epsilon_F. \tag{6.155}$$

The fact that the pressure is nonzero even at zero temperature is a consequence of the Pauli exclusion principle, which allows only one particle to have zero momentum (two electrons if the spin is considered). All other particles have finite momentum and hence give rise to a nonzero pressure at $T = 0$.

Another way to understand the relation (6.155) is to recall the classical pressure equation of state, $P = \rho kT$, which would predict that the pressure is zero at zero temperature. However, if we replace T by the Fermi temperature T_F, then $P \propto \rho kT_F = \rho\epsilon_F$, which is the same as (6.155) except for a numerical factor.

Problem 6.27. Order of magnitude estimates

(a) Verify that the values of ϵ_F given in electon volts (eV) leads to the values of T_F in Table 6.3.

(b) Compare the values of T_F in Table 6.3 to room temperature. What is the value of kT in eV at room temperatures?

(c) Given the data in Table 6.3 verify that the electron density for Li and Cu is $\rho = 4.7 \times 10^{28}\,\mathrm{m}^{-3}$ and $\rho = 8.6 \times 10^{28}\,\mathrm{m}^{-3}$, respectively.

(d) What is the mean distance between the electrons for Li and Cu?

(e) Use the fact that the mass of an electron is $9.1 \times 10^{-31}\,\mathrm{kg}$ to estimate the de Broglie wavelength corresponding to an electron with energy comparable to the Fermi energy.

(f) Compare your result for the de Broglie wavelength which you found in part (e) to the mean interparticle spacing which you found in part (d). ◻

Problem 6.28. Landau potential at zero temperature

From (6.107) the Landau potential for an ideal Fermi gas at arbitrary T can be expressed as

$$\Omega = -kT \int_0^\infty g(\epsilon) \ln[1 + e^{-\beta(\epsilon-\mu)}]\, d\epsilon. \tag{6.156}$$

To obtain the $T = 0$ limit of Ω, we have that $\epsilon < \mu$ in (6.156), $\beta \to \infty$, and hence $\ln[1 + e^{-\beta(\epsilon-\mu)}] \to \ln e^{-\beta(\epsilon-\mu)} = -\beta(\epsilon - \mu)$. Hence, show that

$$\Omega = \frac{(2m)^{3/2}V}{2\pi^2\hbar^2}\int_0^{\epsilon_F} d\epsilon\, \epsilon^{1/2}\big(\epsilon - \epsilon_F\big). \tag{6.157}$$

Calculate Ω and determine the pressure at $T = 0$. $\qquad\square$

Problem 6.29. Show that the limit (6.145) for $\overline{n}(\epsilon)$ at $T = 0$ follows only if $\mu > 0$. $\qquad\square$

6.8.2   Low temperature properties

One of the greatest successes of the free electron model and Fermi-Dirac statistics is the explanation of the temperature dependence of the heat capacity of a metal. If the electrons behaved like a classical noninteracting gas, we would expect a contribution to the heat capacity equal to $3Nk/2$ as $T \to 0$. Instead, we typically find a very small contribution to the heat capacity which is linear in the temperature, a result that cannot be explained by classical statistical mechanics. Before we derive this result, we first give a qualitative argument for the low temperature dependence of the heat capacity of an ideal Fermi gas.

As we saw in Table 6.3, room temperature is much less than the Fermi temperature of the conduction electrons in a metal, that is, $T \ll T_F$. Hence we should be able to understand the behavior of an ideal Fermi gas at room temperature in terms of its behavior at zero temperature. Because there is only one characteristic energy in the system (the Fermi energy), the criterion for low temperature is that $T \ll T_F$. Hence the conduction electrons in a metal may be treated as if they are effectively near zero temperature even though the metal is at room temperature.

For $0 < T \ll T_F$, the electrons that are within order kT below the Fermi surface have enough energy to occupy the microstates with energies that are order kT above the Fermi energy. In contrast, the electrons that are deep within the Fermi surface do not have enough energy to be excited to microstates above the Fermi energy. Hence, only a small fraction of order T/T_F of the N electrons have a reasonable probability of being excited, and the remainder of the electrons remain unaffected as the temperature is increased from $T = 0$. This reasoning leads us to write the heat capacity of the electrons as $C_V \sim N_{\text{eff}}k$, where N_{eff} is the number of electrons that can be excited by exchanging energy with the heat bath. For a classical system, $N_{\text{eff}} = N$, but for a Fermi system at $T \ll T_F$, we have that $N_{\text{eff}} \sim N(T/T_F)$. Hence, we expect that the temperature dependence of the heat capacity is given by

$$C_V \sim Nk\frac{T}{T_F}. \qquad (T \ll T_F) \tag{6.158}$$

From (6.158) we see that the contribution to the heat capacity from the electrons is much smaller than the prediction of the equipartition theorem and is linear in T as is found empirically. As an example, the measured specific heat of copper for $T < 1\,\text{K}$ is dominated by the contribution of the electrons and is given by $C_V/kN = 0.8 \times 10^{-4}\,T$.

Our qualitative argument for the low temperature behavior of C_V implicitly assumes that $\mu(T)$ is unchanged for $T \ll T_F$. We can understand why $\mu(T)$ remains unchanged as T is increased

slightly from $T = 0$ by the following reasoning. The probability that a single particle state is empty is

$$1 - \overline{n}(\epsilon) = 1 - \frac{1}{e^{\beta(\epsilon-\mu)} + 1} = \frac{1}{e^{\beta(\mu-\epsilon)} + 1}. \tag{6.159}$$

We see from (6.159) that for a given distance from μ, the probability that a particle is lost from a previously occupied single particle state below μ equals the probability that a previously empty single particle state is occupied: $\overline{n}(\epsilon - \mu) = 1 - \overline{n}(\mu - \epsilon)$. This property implies that the area under the step function at $T = 0$ is nearly the same as the area under $\overline{n}(\epsilon)$ for $T \ll T_F$ (see Figure 6.3). That is, $\overline{n}(\epsilon)$ is symmetrical about $\epsilon = \mu$. If we make the additional assumption that the density of states changes very little in the region where $\overline{n}$ departs from a step function, we see that the mean number of particles *lost* from the previously occupied states just balances the mean number *gained* by the previously empty states. Hence, we conclude that for $T \ll T_F$, we still have the correct number of particles without any need to change the value of μ.

Similar reasoning implies that $\mu(T)$ must decrease slightly as T is increased from zero. Suppose that μ were to remain constant as T is increased. Because the density of states is an increasing function of ϵ, the number of electrons with energy $\epsilon > \mu$ would be greater than the number lost with $\epsilon < \mu$. As a result, we would increase the number of electrons by increasing T. To prevent such an nonsensical increase, μ has to reduce slightly. In addition, we know that because $\mu \ll 0$ for high temperatures where the system behaves like an ideal classical gas, $\mu(T)$ must pass through zero. At what temperature would you estimate that $\mu(T) \approx 0$?

In Problem 6.30 we will determine $\mu(T)$ by evaluating the integral in (6.160) numerically. Then we will evaluate the integral analytically for $T \ll T_F$ and show that $\mu(T) - \mu(T = 0) \sim (T/T_F)^2$. Hence to first order in T/T_F, μ is unchanged.

Problem 6.30. Numerical evaluation of the chemical potential for an ideal Fermi gas

To find the chemical potential for $T > 0$, we need to find the value of μ that yields the desired mean number of particles. We have

$$N = \int_0^\infty \overline{n}(\epsilon)g(\epsilon)d\epsilon = \frac{V(2m)^{3/2}}{2\pi^2\hbar^3} \int_0^\infty \frac{\epsilon^{1/2}d\epsilon}{e^{\beta(\epsilon-\mu)} + 1}, \tag{6.160}$$

where we have used (6.105) for $g(\epsilon)$. It is convenient to let $\epsilon = x\epsilon_F$, $\mu = \mu^*\epsilon_F$, and $T^* = kT/\epsilon_F$, and rewrite (6.160) as

$$\rho = \frac{N}{V} = \frac{(2m)^{3/2}}{2\pi^2\hbar^3}\epsilon_F^{3/2} \int_0^\infty \frac{x^{1/2}\, dx}{e^{(x-\mu^*)/T^*} + 1}, \tag{6.161}$$

or

$$1 = \frac{3}{2} \int_0^\infty \frac{x^{1/2}\, dx}{e^{(x-\mu^*)/T^*} + 1}, \tag{6.162}$$

where we have substituted (6.149) for ϵ_F. To find the dependence of μ^* on T^* and hence μ on T use program `IdealFermiGasIntegral` to evaluate the integral on the right-hand side of (6.162) numerically.

(a) Start with $T^* = 0.2$ and find μ^* such that (6.162) is satisfied. (Recall that $\mu^* = 1$ at $T^* = 0$.) Does μ^* initially increase or decrease as T is increased from zero? What is the sign of μ^* for $T^* \gg 1$?

(b) At what value of T^* is $\mu^* \approx 0$?

(c) Given the value of $\mu^*(T^*)$, the program computes the numerical value of $E(T)$. Describe its qualitative T-dependence and the T-dependence of C_V. □

We now derive a quantitative expression for C_V that is applicable for temperatures $T \ll T_F$.[7] The increase $\Delta E = E(T) - E(T = 0)$ in the total energy is given by

$$\Delta E = \int_0^\infty \epsilon \, \overline{n}(\epsilon) g(\epsilon) \, d\epsilon - \int_0^{\epsilon_F} \epsilon \, g(\epsilon) \, d\epsilon, \tag{6.163a}$$

which we rewrite as

$$= \int_0^{\epsilon_F} \epsilon [\overline{n}(\epsilon) - 1] g(\epsilon) \, d\epsilon + \int_{\epsilon_F}^\infty \epsilon \, \overline{n}(\epsilon) g(\epsilon) \, d\epsilon. \tag{6.163b}$$

We multiply the identity

$$N = \int_0^\infty \overline{n}(\epsilon) g(\epsilon) d\epsilon = \int_0^{\epsilon_F} g(\epsilon) \, d\epsilon \tag{6.164}$$

by ϵ_F and write the integral on the left-hand side as a sum of two contributions to obtain

$$\int_0^{\epsilon_F} \epsilon_F \, \overline{n}(e) g(\epsilon) \, d\epsilon + \int_{\epsilon_F}^\infty \epsilon_F \, \overline{n}(e) g(\epsilon) \, d\epsilon = \int_0^{\epsilon_F} \epsilon_F \, g(\epsilon) \, d\epsilon, \tag{6.165a}$$

or

$$\int_0^{\epsilon_F} \epsilon_F [\overline{n}(\epsilon) - 1] g(\epsilon) \, d\epsilon + \int_{\epsilon_F}^\infty \epsilon_F \overline{n}(\epsilon) g(\epsilon) \, d\epsilon = 0. \tag{6.165b}$$

We can use (6.165b) to rewrite (6.163b) as

$$\Delta E = \int_{\epsilon_F}^\infty (\epsilon - \epsilon_F) \overline{n}(\epsilon) g(\epsilon) d\epsilon + \int_0^{\epsilon_F} (\epsilon_F - \epsilon)[1 - \overline{n}(\epsilon)] g(\epsilon) d\epsilon. \tag{6.166}$$

The heat capacity is found by differentiating ΔE with respect to T. The only temperature-dependent term in (6.166) is $\overline{n}(\epsilon)$. Hence, we can write C_V as

$$C_V = \int_0^\infty (\epsilon - \epsilon_F) \frac{d\overline{n}(\epsilon)}{dT} g(\epsilon) d\epsilon. \tag{6.167}$$

For $T \ll T_F$, the derivative $d\overline{n}/dT$ is large only for ϵ near ϵ_F. Hence it is a good approximation to evaluate the density of states $g(\epsilon)$ at $\epsilon = \epsilon_F$ and take it outside the integral:

$$C_V = g(\epsilon_F) \int_0^\infty (\epsilon - \epsilon_F) \frac{d\overline{n}}{dT} d\epsilon. \tag{6.168}$$

We can also ignore the temperature-dependence of μ in $\overline{n}(\epsilon)$ and replace μ by ϵ_F. With this approximation we have

$$\frac{d\overline{n}}{dT} = \frac{d\overline{n}}{d\beta} \frac{d\beta}{dT} = \frac{1}{kT^2} \frac{(\epsilon - \epsilon_F) e^{\beta(\epsilon - \epsilon_F)}}{[e^{\beta(\epsilon - \mu)} + 1]^2}. \tag{6.169}$$

---

[7] The following derivation is adapted from Kittel.

We next let $x = (\epsilon - \epsilon_F)/kT$ and use (6.168) and (6.169) to write C_V as

$$C_V = k^2 T g(\epsilon_F) \int_{-\beta\epsilon_F}^{\infty} \frac{x^2 e^x}{(e^x + 1)^2} dx. \tag{6.170}$$

We can replace the lower limit by $-\infty$ because the factor e^x in the integrand is negligible at $x = -\beta\epsilon_F$ for low temperatures. If we use the integral

$$\int_{-\infty}^{\infty} \frac{x^2 e^x}{(e^x + 1)^2} dx = \frac{\pi^2}{3}, \tag{6.171}$$

we can write the heat capacity of an ideal Fermi gas as

$$C_V = \frac{1}{3}\pi^2 g(\epsilon_F) k^2 T. \tag{6.172}$$

It is straightforward to show that

$$g(\epsilon_F) = \frac{3N}{2\epsilon_F} = \frac{3N}{2kT_F}, \tag{6.173}$$

and we arrive at the desired result

$$C_V = \frac{\pi^2}{2} Nk \frac{T}{T_F}. \qquad (T \ll T_F) \tag{6.174}$$

A more detailed discussion of the low temperature properties of an ideal Fermi gas is given in Section 6.11.2. For convenience, we summarize the main results here:

$$\Omega = -\frac{2}{3} \frac{2^{1/2} V m^{3/2}}{\pi^2 \hbar^3} \left[\frac{2}{5} \mu^{5/2} + \frac{\pi^2}{4} (kT)^2 \mu^{1/2} \right]. \tag{6.175}$$

$$\overline{N} = -\frac{\partial \Omega}{\partial \mu} = \frac{V(2m)^{3/2}}{3\pi^2 \hbar^3} \left[\mu^{3/2} + \frac{\pi^2}{8} (kT)^2 \mu^{-1/2} \right]. \tag{6.176}$$

The results (6.175) and (6.176) are in the grand canonical ensemble in which the chemical potential is fixed. However, most experiments are done on a sample with a fixed number of electrons, and hence μ must change with T to keep $\overline{N}$ fixed. To find this dependence we rewrite (6.176) as

$$\frac{3\pi^2 \hbar^3 \rho}{(2m)^{3/2}} = \mu^{3/2} \left[1 + \frac{\pi^2}{8} (kT)^2 \mu^{-2} \right], \tag{6.177}$$

where $\rho = \overline{N}/V$. If we raise both sides of (6.177) to the 2/3 power and use (6.149), we have

$$\mu = \frac{3^{2/3} \pi^{4/3} \hbar^2 \rho^{2/3}}{2m} \left[1 + \frac{\pi^2}{8} (kT)^2 \mu^{-2} \right]^{-2/3}, \tag{6.178a}$$

$$= \epsilon_F \left[1 + \frac{\pi^2}{8} (kT)^2 \mu^{-2} \right]^{-2/3}. \tag{6.178b}$$

In the limit of $T \to 0$, $\mu = \epsilon_F$ as expected. From (6.178b) we see that the first correction for low temperatures is given by

$$\mu(T) = \epsilon_F \left[1 - \frac{2}{3} \frac{\pi^2}{8} \frac{(kT)^2}{\mu^2} \right] = \epsilon_F \left[1 - \frac{\pi^2}{12} \left(\frac{T}{T_F} \right)^2 \right], \tag{6.179}$$

where we have made the expansion $(1+x)^n \approx 1 + nx$ and replaced μ on the right-hand side by $\epsilon_F = kT_F$.

From (6.179) we see that the chemical potential decreases with temperature to keep N fixed, but the decrease is second order in T/T_F (rather than first order), consistent with our earlier qualitative considerations. The explanation for the decrease in $\mu(T)$ is that more particles move from energy states below the Fermi energy to energy states above the Fermi energy as the temperature increases. Because the density of states increases with energy, it is necessary to decrease the chemical potential to keep the number of particles constant. As the temperature becomes larger than the Fermi temperature, the chemical potential changes sign and becomes negative (see in Problem 6.30).

Problem 6.31. Low temperature behavior

(a) Fill in the missing steps in (6.163)–(6.174).

(b) Use (6.175) and (6.179) to show that the mean pressure for $T \ll T_F$ is given by

$$P = \frac{2}{5} \rho \epsilon_F \left[1 + \frac{5\pi^2}{12} \left(\frac{T}{T_F} \right)^2 + \dots \right]. \tag{6.180}$$

(c) Use the general relation between E and PV to show that

$$E = \frac{3}{5} N \epsilon_F \left[1 + \frac{5\pi^2}{12} \left(\frac{T}{T_F} \right)^2 + \dots \right]. \tag{6.181}$$

(d) For completeness, show that the low temperature behavior of the entropy is given by

$$S = \frac{\pi^2}{2} N k \frac{T}{T_F}. \tag{6.182}$$

We see from (6.174) that the conduction electrons of a metal contribute a linear term to the heat capacity. In Section 6.9 we shall see that the contribution from lattice vibrations contributes a term proportional to T^3 to C_V at low T. Thus for sufficiently low temperature, the linear term due to the conduction electrons dominates.

Problem 6.32. Effective electron mass

From Table 6.3 we see that $T_F = 8.5 \times 10^4$ K for copper. Use (6.174) to find the predicted value of C/NkT for copper. How does this value compare with the experimental value $C/NkT = 8 \times 10^{-5}$? It is remarkable that the theoretical prediction agrees so well with the experimental result based on the free electron model. Show that the small discrepancy can be removed by defining an effective mass m^* of the conduction electrons equal to $\approx 1.3 \, m_e$, where m_e is the mass of the electron. What factors might account for the effective mass being greater than m_e? ☐

Problem 6.33. Temperature dependence of the chemical potential in two dimensions

Consider a system of electrons restricted to a two-dimensional surface of area A. Show that the mean number of electrons can be written as

$$\overline{N} = \frac{mA}{\pi\hbar^2} \int_0^\infty \frac{d\epsilon}{e^{\beta(\epsilon-\mu)}+1}. \tag{6.183}$$

The integral in (6.183) can be evaluated in closed form using

$$\int \frac{dx}{1+ae^{bx}} = \frac{1}{b} \ln \frac{e^{bx}}{1+ae^{bx}} + \text{constant.} \tag{6.184}$$

(a) Show that

$$\mu(T) = kT \ln \left[e^{\rho\pi\hbar^2/mkT} - 1 \right], \tag{6.185}$$

where $\rho = \overline{N}/A$.

(b) What is the value of the Fermi energy $\epsilon_F = \mu(T=0)$? What is the value of μ for $T \gg T_F$?

(c) Plot μ versus T and discuss its qualitative dependence on T. □

6.9   The Heat Capacity of a Crystalline Solid

The free electron model of a metal successfully explains the temperature dependence of the contribution to the heat capacity from the electrons. What about the contribution from the ions? In a crystal each ion is localized about its lattice site and oscillates due to spring-like forces between nearest-neighbor atoms. Classically, we can regard each atom of the solid as having six quadratic contributions to the energy, three of which contribute $\frac{1}{2}kT$ to the mean kinetic energy and three contribute $\frac{1}{2}kT$ to the mean potential energy. Hence, the heat capacity at constant volume of a homogeneous isotropic solid is given by $C_V = 3Nk$, independent of the nature of the solid. This behavior of C_V agrees with experiment remarkably well at high temperatures. (The meaning of high temperature will be defined later in terms of the parameters of the solid.) At low temperatures the classical behavior is an overestimate of the experimentally measured heat capacity for crystalline solids, which is found to be proportional to T^3. To understand this low temperature behavior, we first consider the Einstein model and then the more sophisticated Debye model of a solid.

6.9.1   The Einstein model

The reason why the heat capacity decreases at low temperature is that the oscillations of the crystal must be treated quantum mechanically rather than classically. The simplest model of a solid, proposed by Einstein in 1906, is that each atom behaves like three independent harmonic oscillators each of frequency ω. Because the $3N$ identical oscillators are independent and are associated with distinguishable sites, we need only to find the thermodynamic functions of one of them. The partition function for one oscillator in one dimension is (see (4.129))

$$Z_1 = \frac{e^{-\beta\hbar\omega/2}}{1 - e^{-\beta\hbar\omega}}. \tag{6.186}$$

Other thermodynamic properties of one oscillator are given by

$$f = -kT \ln Z_1 = \frac{\hbar\omega}{2} + kT \ln[1 - e^{-\beta\hbar\omega}] \tag{6.187}$$

$$s = -\frac{\partial f}{\partial T} = -k \ln[1 - e^{-\beta\hbar\omega}] + k\beta\hbar\omega \frac{1}{e^{\beta\hbar\omega} - 1} \tag{6.188}$$

$$e = f + Ts = (\overline{n} + 1/2)\hbar\omega, \tag{6.189}$$

where

$$\overline{n} = \frac{1}{e^{\beta\hbar\omega} - 1}. \tag{6.190}$$

Note the form of $\overline{n}$, which is identical to the Bose-Einstein distribution with $\mu = 0$. We can think of $\overline{n}$ as the mean number of quanta (phonons). Because the number of phonons is not conserved, $\mu = 0$ in the Bose-Einstein distribution. To obtain extensive quantities such as F, S, and E, we multiply the single particle values by $3N$. For example, the heat capacity of an Einstein solid is given by

$$C_V = \left(\frac{\partial E}{\partial T}\right)_V = 3N\left(\frac{\partial e}{\partial T}\right)_V = 3Nk(\beta\hbar\omega)^2 \frac{e^{\beta\hbar\omega}}{[e^{\beta\hbar\omega} - 1]^2}. \tag{6.191}$$

It is convenient to introduce the Einstein temperature

$$kT_E = \hbar\omega, \tag{6.192}$$

and express C_V as

$$C_V = 3Nk\left(\frac{T_E}{T}\right)^2 \frac{e^{T_E/T}}{[e^{T_E/T} - 1]^2}. \tag{6.193}$$

The limiting behaviors of C_V from (6.191) or (6.193) is

$$C_V \to 3Nk, \qquad\qquad (T \gg T_E) \tag{6.194a}$$

and

$$C_V \to 3Nk\left(\frac{\hbar\omega}{kT}\right)^2 e^{-\hbar\omega/kT}. \qquad\qquad (T \ll T_E) \tag{6.194b}$$

The calculated heat capacity as $T \to 0$ is consistent with the third law of thermodynamics and is not very different from the heat capacity actually observed for insulating solids. However, it decreases too quickly at low temperatures and does not agree with the observed low temperature behavior $C_V \propto T^3$ satisfied by all insulating solids.

Problem 6.34. Limiting behavior of the heat capacity in the Einstein model

Derive the limiting behavior of C_V given in (6.194). $\qquad\qquad\qquad\qquad\qquad\qquad$ □

6.9.2   Debye theory

The Einstein model is based on the idea that each atom behaves like an harmonic oscillator whose motion is independent of the other atoms. A better approximation was made by Debye (1912) who observed that solids can carry sound waves. Because waves are inherently a collective phenomena

and are not associated with the oscillations of a single atom, it is better to think of a crystalline solid in terms of the collective motion rather than the independent motions of the atoms. The collective or cooperative motion corresponds to the $3N$ normal modes of the system, each with its own frequency.

For each value of the wavevector $\vec{k}$ there are three sound waves in a solid – one longitudinal with velocity c_ℓ and two transverse with velocity c_t. (Note that c_t and c_ℓ are speeds of sound, not light.) The density of states of each mode is determined by the same analysis as for photons. From (6.99) we see that the density of states of the system is given by

$$g(\omega)d\omega = (2g_t + g_\ell)d\omega = \frac{V\omega^2 d\omega}{2\pi^2}\left(\frac{2}{c_t^3} + \frac{1}{c_\ell^3}\right). \tag{6.195}$$

It is convenient to define a mean speed of sound $\overline{c}$ by the relation

$$\frac{3}{\overline{c}^3} = \frac{2}{c_t^3} + \frac{1}{c_\ell^3}, \tag{6.196}$$

so that the density of states can be written as

$$g(\omega)\,d\omega = \frac{3V\omega^2 d\omega}{2\pi^2\overline{c}^3}. \tag{6.197}$$

The total energy is given by

$$E = \int \hbar\omega\,\overline{n}(\omega)g(\omega)\,d\omega, = \frac{3V\hbar}{2\pi^2\overline{c}^3}\int\frac{\omega^3\,d\omega}{e^{\beta\hbar\omega} - 1}. \tag{6.198}$$

Equation (6.198) does not take into account the higher frequency modes that do not satisfy the linear relation $\omega = kc$. For reasons that we will discuss shortly we will use a high frequency cutoff at $\omega = \omega_D$ such that for the frequencies included $\omega \approx kc$. Because the low temperature heat capacity depends only on the low frequency modes, which we have treated correctly using (6.197), it follows that we can obtain a good approximation to the heat capacity by extending the integral in (6.197) to a maximum frequency ω_D which is determined by requiring that the total number of modes be $3N$. That is, we assume that $g(\omega) \propto \omega^2$ for $\omega < \omega_D$ such that

$$3N = \int_0^{\omega_D} g(\omega)\,d\omega. \tag{6.199}$$

If we substitute (6.197) into (6.199), we find that

$$\omega_D = 2\pi\overline{c}\left(\frac{3\rho}{4\pi}\right)^{1/3}. \tag{6.200}$$

It is convenient to relate the maximum frequency ω_D to a characteristic temperature, the Debye temperature T_D, by the relation

$$\hbar\omega_D = kT_D. \tag{6.201}$$

The thermal energy can now be expressed as

$$E = \frac{3V\hbar}{2\pi^2 c^3}\int_0^{kT_D/\hbar}\frac{\omega^3\,d\omega}{e^{\beta\hbar\omega} - 1} \tag{6.202a}$$

$$= 9NkT\left(\frac{T}{T_D}\right)^3\int_0^{T_D/T}\frac{x^3\,dx}{e^x - 1}. \tag{6.202b}$$

In the high temperature limit, $T_D/T \to 0$, and the important contribution to the integral in (6.202) comes from small x. Because the integrand is proportional x^2 for small x, the integral is proportional to $(T/T_D)^{-3}$, and hence the energy is proportional to T. Thus in the high temperature limit, the heat capacity is independent of the temperature, consistent with the law of Dulong and Petit. In the low temperature limit, $T_D/T \to \infty$, and the integral in (6.202) is independent of temperature. Hence in the limit $T \to 0$, the energy is proportional to T^4 and the heat capacity is proportional to T^3, consistent with experimental results at low temperatures.

Problem 6.35. More on the Einstein and Debye theories

(a) Determine the wavelength λ_D corresponding to ω_D and show that this wavelength is approximately equal to a lattice spacing. This equality provides another justification for a high frequency cutoff because the atoms in a crystal cannot oscillate with a wavelength smaller than a lattice spacing.

(b) Show explicity that that the energy in (6.202) is independent of T for high temperatures and proportional to T^4 for low temperatures.

(c) Plot the temperature dependence of the mean energy as given by the Einstein and Debye theories on the same graph and compare their predictions.

(d) Derive an expression for the mean energy analogous to (6.202) for one- and two-dimensional crystals. Then find explicit expressions for the high and low temperature dependence of the specific heat on the temperature. □

6.10 The Ideal Bose Gas and Bose Condensation

The historical motivation for discussing the ideal Bose gas is that this idealized system exhibits Bose-Einstein condensation. The original prediction of Bose-Einstein condensation by Satyendra Nath Bose and Albert Einstein in 1924 was considered by some to be a mathematical artifact or even a mistake. In the 1930s Fritz London realized that superfluid liquid helium could be understood in terms of Bose-Einstein condensation. However, the analysis of superfluid liquid helium is complicated by the fact that the helium atoms in a liquid strongly interact with one another. For many years scientists tried to create a Bose condensate in a less complicated system. In 1995 several groups used laser and magnetic traps to create a Bose-Einstein condensate of alkali atoms at approximately 10^{-6} K. In these systems the interaction between the atoms is very weak so that the ideal Bose gas is a good approximation and is no longer only a textbook example.[8]

Although the form of the Landau potential for the ideal Bose gas and the ideal Fermi gas differs only superficially (see (6.86)), the two systems behave very differently at low temperatures. The main reason is the difference in the ground states; that is, for a Bose system there is no limit to the number of particles in a single particle state.

---

[8]The 2001 Nobel Prize for Physics was awarded to Eric Cornell, Wolfgang Ketterle, and Carl Wieman for achieving Bose-Einstein condensation in dilute gases of alkali atoms and for early fundamental studies of the properties of the condensate.

The ground state of an ideal Bose gas is easy to construct. We can minimize the total energy by putting all the particles into the single particle state of lowest energy:

$$\epsilon_0 = \frac{\pi^2 \hbar^2}{2mL^2}(1^2 + 1^2 + 1^2) = \frac{3\pi^2 \hbar^2}{2mL^2}. \tag{6.203}$$

The energy of the ground state is given by $N\epsilon_0$. For convenience, we will choose the energy scale such that the ground state energy is zero. The behavior of the system cannot depend on the choice of the zero of energy.

The behavior of an ideal Bose gas can be understood by considering the temperature dependence of $\overline{N}(T, V, \mu)$:

$$\overline{N} = \sum_{\mathbf{k}} \frac{1}{e^{\beta(\epsilon_{\mathbf{k}}-\mu)} - 1} \to \int_0^\infty \overline{n}(\epsilon)g(\epsilon)d\epsilon \tag{6.204}$$

$$= \frac{V}{4\pi^2\hbar^3}(2m)^{3/2}\int_0^\infty \frac{\epsilon^{1/2}\,d\epsilon}{e^{\beta(\epsilon-\mu)} - 1}. \tag{6.205}$$

For simplicity, we will assume that the gas of bosons has zero spin, the same value of the spin as the helium isotope ^{4}He.

To understand the nature of an ideal Bose gas at low temperatures, we will assume that the mean density of the system is fixed and consider the effect of lowering the temperature. The correct choice of μ gives the desired value of ρ when substituted into (6.206).

$$\rho = \frac{\overline{N}}{V} = \frac{(2m)^{3/2}}{4\pi^2\hbar^3}\int_0^\infty \frac{\epsilon^{1/2}\,d\epsilon}{e^{\beta(\epsilon-\mu)} - 1}. \tag{6.206}$$

We know that the chemical potential μ of an ideal Bose gas must be negative at all temperatures (see (6.80)). We also know that for high temperatures, μ reduces to the semiclassical limit given by (6.29), which is large in magnitude and negative. To see how μ must change in (6.206) to keep the density ρ constant as we decrease the temperature, we make the change of variables $\beta\epsilon = x$ and let $\mu \to -|\mu|$:

$$\rho = \frac{(2mkT)^{3/2}}{4\pi^2\hbar^3}\int_0^\infty \frac{x^{1/2}\,dx}{e^{(x+\beta|\mu|)} - 1}. \tag{6.207}$$

As we decrease the temperature, the factor in front of the integral in (6.207) decreases and hence the integral must increase to compensate so that the density remains fixed. Hence $\beta|\mu|$ must become smaller, which implies that $|\mu|$ must become smaller. Because μ is negative for Bose-Einstein statistics, μ becomes less negative. The integral is finite for all values of $\beta|\mu|$ and has its maximum value when $|\mu| = 0$. Thus, there is a minimum value of T such that the right-hand side of (6.207) equals the given value of ρ. We denote this temperature by T_c and determine its value by solving (6.207) with $\mu = 0$:

$$\rho = \frac{(2mkT_c)^{3/2}}{4\pi^2\hbar^3}\int_0^\infty \frac{x^{1/2}\,dx}{e^x - 1}. \tag{6.208}$$

The definite integral in (6.208) can be written in terms of known functions (see Appendix A) and has the value:

$$\int_0^\infty \frac{x^{1/2}\,dx}{e^x - 1} = 2.612\frac{\pi^{1/2}}{2}. \tag{6.209}$$

Hence, we obtain

$$kT_c = \frac{1}{2.612^{2/3}} \frac{2\pi\hbar^2}{m} \rho^{2/3}. \tag{6.210}$$

Problem 6.36. Relation of T_c to the zero point energy

Express (6.210) in terms of the zero point energy associated with localizing a particle of mass m in a volume a^3, where $a = \rho^{-1/3}$ is the mean interparticle spacing. □

Problem 6.37. Numerical evaluation of μ for an ideal Bose gas

In this problem we study the behavior of μ as a function of the temperature. Program `IdealBose-GasIntegral` numerically evaluates the integral on the right-hand side of (6.206) for particular values of β and μ. The goal is to find the value of μ for a given value of β that yields the desired value of ρ.

To put (6.206) in a convenient form we introduce dimensionless variables and let $\epsilon = kT_c y$, $T = T_c T^*$, and $\mu = kT_c \mu^*$ and rewrite (6.206) as

$$1 = \frac{2}{2.612\sqrt{\pi}} \int_0^\infty \frac{y^{1/2}dy}{e^{(y-\mu^*)/T^*} - 1}, \tag{6.211a}$$

or

$$0.432 \int_0^\infty \frac{y^{1/2}dy}{e^{(y-\mu^*)/T^*} - 1} = 1, \tag{6.211b}$$

where we have used (6.210).

(a) Fill in the missing steps and derive (6.211).

(b) The program evaluates the left-hand side of (6.211b). The idea is to find μ^* for a given value of T^* such the left-hand side of (6.211b) equals one. Begin with $T^* = 10$. First choose $\mu^* = -10$ and find the value of the integral. Do you have to increase or decrease the value of μ^* to make the numerical value of the left-hand side of (6.211b) closer to one? Change μ^* by trial and error until you find the desired result. You should find that $\mu^* \approx -25.2$.

(c) Next choose $T^* = 5$ and find the value of μ^* so that the left-hand side of (6.211b) equals one. Does μ increase or decrease in magnitude? You can generate a plot of μ^* versus T^* by clicking on the `Accept parameters` button each time you find an approximately correct value of μ. □

(d) Discuss the qualitative behavior of μ as a function of T for fixed density.

(e) Use `IdealBoseGasIntegral` to find the numerical value of T at which $\mu = 0$ for $\rho^* = 1$. Confirm that your numerical value is consistent with (6.210).

Problem 6.38. Use similiar reasoning to show that the maximum density for a given temperature is given by

$$\rho_c = \frac{2.612}{\lambda^3}, \tag{6.212}$$
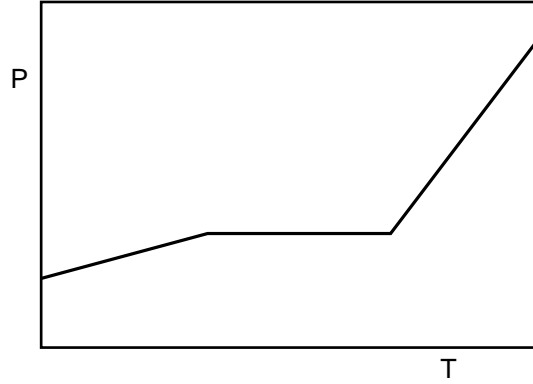
where λ is given by (6.2). □

Figure 6.4: Sketch of the dependence of the pressure P on the temperature T for a typical gas and liquid.

Problem 6.39. Show that the thermal de Broglie wavelength is comparable to the interparticle spacing at $T = T_c$. What is the implication of this result? □

There is no physical reason why we cannot continue lowering the temperature at fixed density (or increasing the density at fixed temperature). Before discussing how we can resolve this difficulty, consider a familiar situation in which an analogous phenomena occurs. Suppose that we put argon atoms into a container of fixed volume at a given temperature. If the temperature is high enough and the density is low enough, the argon atoms will be a gas and obey the ideal gas equation of state which we write as $P = NkT/V$. If we now decrease the temperature, we expect that the pressure will decrease. However at some temperature, this dependence will abruptly break down, and P will stop changing as indicated in Figure 6.4. We will study this behavior of P in Chapter 7, but you will probably recognize this behavior as a signature of the condensation of the vapor and the existence of a phase transition from gas to liquid. That is, at a certain temperature for a fixed density, droplets of liquid argon will begin to form in the container. As the temperature is lowered further, the liquid droplets will grow, but the pressure will remain constant because most of the extra particles will go into the denser liquid state.

We can describe the ideal Bose gas in the same terms, that is, in terms of a phase transition. At a special value of T, the chemical potential stops decreasing in magnitude and reaches its limit of $\mu = 0$. Beyond this point, the relation (6.205) is no longer able to keep track of all the particles.

Because the particles cannot appear or disappear when we change the temperature, (6.206) cannot be correct for temperatures $T < T_c$. The origin of the problem lies with the behavior of the three-dimensional density of states $g(\epsilon)$, which is proportional to $\epsilon^{1/2}$ (see (6.104)). Because of this dependence on ϵ, $g(\epsilon = 0) = 0$, and hence our calculation of $\overline{N}$ has ignored all the particles in the ground state. For the classical and Fermi noninteracting gas, this neglect is of no consequence. In the classical case the mean number of particles in any microstate is much less than one, and in the degenerate Fermi case there are only two electrons in the ground state. However, for the noninteracting Bose gas, the mean number of particles in the ground state is given by

$$\overline{N}_0 = \frac{1}{e^{-\beta\mu} - 1}, \tag{6.213}$$

(Remember that we have set the ground state energy $\epsilon_0 = 0$.) When T is sufficiently small, $\overline{N}_0$ will be very large. Hence, the denominator of (6.213) must be very small, which implies that $e^{-\beta\mu} \approx 1$ and $-\beta\mu$ must be very small. Therefore, we can approximate $e^{-\beta\mu}$ as $1 - \beta\mu$ and $\overline{N}_0$ becomes

$$\overline{N}_0 = -\frac{kT}{\mu} = \frac{kT}{|\mu|} \gg 1. \tag{6.214}$$

The chemical potential must be such that the number of particles in the ground state approaches its maximum value which is of order N. Hence, if we were to use the integral (6.205) to calculate $\overline{N}$ for $T < T_c$, we would have ignored the particles in the ground state. We have resolved the problem – the missing particles are in the ground state! The phenomena we have described, *macroscopic occupation of the ground state*, is called *Bose-Einstein condensation*. Macroscopic occupation means that for $T < T_c$, the ratio $\overline{N}_0/N$ is nonzero in the limit $N \to \infty$.

Now that we know where the missing particles are, we can calculate the thermodynamics of the ideal Bose gas. For $T < T_c$ the chemical potential is zero in the thermodynamic limit, and the mean number of particles *not* in the ground state is given by (6.205):

$$\overline{N}_\epsilon = \frac{V}{4\pi^2\hbar^3}(2m)^{3/2}\int_0^\infty \frac{\epsilon^{1/2}\,d\epsilon}{e^{\beta\epsilon}-1} = N\Big(\frac{T}{T_c}\Big)^{3/2}, \qquad (T < T_c) \tag{6.215}$$

where T_c is defined by (6.210). The remaining particles, which we denote as $\overline{N}_0$, are in the ground state. Another way of understanding (6.215) is that for $T < T_c$, μ must be zero because the number of particles not in the ground state is determined by the temperature. We write $\overline{N} = \overline{N}_0 + \overline{N}_\epsilon$, and

$$\overline{N}_0 = N - \overline{N}_\epsilon = \overline{N}\Big[1 - \Big(\frac{T}{T_c}\Big)^{3/2}\Big]. \qquad (T < T_c) \tag{6.216}$$

Because the energy of the gas is determined by the particles with $\epsilon > 0$, we have for $T < T_c$

$$E = \int_0^\infty \frac{\epsilon\, g(\epsilon)\,d\epsilon}{e^{\beta\epsilon}-1} = \frac{V(mkT)^{3/2}\,kT}{2^{1/2}\pi^2\hbar^3}\int_0^\infty \frac{x^{3/2}\,dx}{e^x-1}. \tag{6.217}$$

The definite integral in (6.217) is given in Appendix A:

$$\int_0^\infty \frac{x^{3/2}\,dx}{e^x-1} = 1.341\,\frac{3\pi^{1/2}}{4}. \tag{6.218}$$

If we substitute (6.218) into (6.217), we can write the mean energy as

$$\overline{E} = 3\frac{1.341}{2^{5/2}\pi^{3/2}}\frac{V(mkT)^{3/2}kT}{\hbar^3} = 0.1277\,V\frac{m^{3/2}(kT)^{5/2}}{\hbar^3}. \tag{6.219}$$

Note that $\overline{E} \propto T^{5/2}$ for $T < T_c$. The heat capacity at constant volume is

$$C_V = \frac{\partial\overline{E}}{\partial T} = 3.2V\frac{(mkT)^{3/2}k}{\hbar^3}, \tag{6.220a}$$

or

$$C_V = 1.9\overline{N}_\epsilon k, \tag{6.220b}$$

where we have used (6.215) for $\overline{N}_\epsilon$. Note that the heat capacity has a form similar to an ideal classical gas for which $C_V \propto Nk$.

The pressure of the Bose gas for $T < T_c$ can be obtained from the general relation $PV = 2E/3$ for a nonrelativistic ideal gas. From (6.219) we obtain

$$P = \frac{1.341}{2^{3/2}\pi^{3/2}} \frac{m^{3/2}(kT)^{5/2}}{\hbar^3} = 0.085 \frac{m^{3/2}(kT)^{5/2}}{\hbar^3}. \tag{6.221}$$

Note that the pressure is proportional to $T^{5/2}$ and is independent of the density. This independence is a consequence of the fact that the particles in the ground state do not contribute to the pressure. If additional particles are added to the system at $T < T_c$, the number of particles in the single particle state $\epsilon = 0$ increases, but the pressure does not.

What is remarkable about the phase transition in an ideal Bose gas is that it occurs at all. That is, unlike all other known phase transitions, its occurrence has nothing to do with the interactions between the particles and has everything to do with the nature of the statistics. Depending on which variables are being held constant, the transition in an ideal Bose gas is either first-order or continuous. We postpone a discussion of the nature of first-order and continuous phase transitions until Chapter 9 where we will discuss phase transitions in more detail. It is sufficient to mention here that the order parameter in the ideal Bose gas can be taken to be the fraction of particles in the ground state, and this fraction goes continuously to zero as $T \to T_c$ from below at fixed density.

Another interesting feature of the Bose condensate is that for $T < T_c$, a finite fraction of the atoms are described by the same quantum wavefunction, which gives the condensate many unusual properties. In particular, Bose condensates have been used to produce atomic lasers – laser-like beams in which photons are replaced by atoms – and to study fundamental processes such as superfluidity.

Problem 6.40. Temperature dependence of the pressure

(a) Start from the classical pressure equation of state, $PV = NkT$, replace N by Neff for an ideal Bose gas, and give a qualitative argument why $P \propto T^{5/2}$ at low temperatures.

(b) Show that the ground state contribution to the pressure is given by

$$P_0 = \frac{kT}{V} \ln(\overline{N}_0 + 1). \tag{6.222}$$

Explain why P_0 can be regarded as zero and why the pressure of an Bose gas for $T < T_c$ is independent of the volume. □

Problem 6.41. Estimate of Bose condensation temperature

(a) What is the approximate value of T_c for an ideal Bose gas at a density of $\rho \approx 125\,\mathrm{kg/m^3}$, the density of liquid ^{4}He? Take $m = 6.65 \times 10^{-27}$ kg.

(b) The value of T_c for a collection of ^{87}Rb (rubidium) atoms is about $280\,\mathrm{nK}$ ($2.8 \times 10^{-7}\,\mathrm{K}$). What is the mean separation between the atoms? □

6.11 Supplementary Notes

6.11.1 Fluctuations in the number of particles

It is convenient to express Z_G in terms of the canonical partition function Z_N for N particles. The sum over all microstates in (6.70) can first be done over all possible microstates s for a fixed number of particles and then over all values of N:

$$Z_G = \sum_{N=1}^{\infty} e^{\beta \mu N} \sum_s e^{-\beta E_s}, \tag{6.223}$$

where E_s is the energy of microstate s with N particles. The latter sum in (6.223) is the canonical partition function for N particles, and we have

$$Z_G = \sum_{N=1}^{\infty} e^{\beta \mu N} Z_N. \tag{6.224}$$

In the following we will derive a relation between the compressibility and the fluctuations of the number of particles. The number of particles fluctuates about the mean number $\overline{N}$ which is given by

$$\overline{N} = kT \frac{\partial \ln Z_G}{\partial \mu} = \frac{1}{Z_G} \sum_N N e^{\beta \mu N} Z_N. \tag{6.225}$$

Because N fluctuates, we need to reinterpret (6.72) as $\overline{N} = -\partial \Omega / \partial \mu$.

Recall from (4.88) that the fluctuations in the energy are related to the heat capacity. In the following we show that the fluctuations in the number of particles are related to the isothermal compressibility κ, which is defined as (see (2.172))

$$\kappa = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_{T,N}. \tag{6.226}$$

The first step in the derivation is given in Problem 6.42.

Problem 6.42. Number fluctuations
Use the Gibbs distribution P_s in (6.73) to show that $\overline{N}$ can be written as

$$\overline{N} = \frac{\sum_s N_s \, e^{-\beta(E_s - \mu N_s)}}{\sum_s e^{-\beta(E_s - \mu N_s)}} \tag{6.227}$$

Then use (6.227) to show that

$$\left(\frac{\partial \overline{N}}{\partial \mu} \right)_{T,V} = \frac{1}{kT} [\overline{N^2} - \overline{N}^2], \tag{6.228}$$

or

$$[\overline{N^2} - \overline{N}^2] = kT \left(\frac{\partial N}{\partial \mu} \right)_{T,V}, \tag{6.229}$$

where

$$\overline{N^2} = \frac{\sum\limits_{s} N_s^{\,2}\, e^{-\beta(E_s - \mu N_s)}}{\sum\limits_{s} e^{-\beta(E_s - \mu N_s)}}. \tag{6.230}$$

$\square$

In Problem 6.43 we relate the partial derivatives $(\partial\mu/\partial N)_{T,V}$ to $(\partial V/\partial P)_{T,N}$.

Problem 6.43. Another Maxwell relation

Because the Helmholtz free energy $F(T, V, N)$ is extensive, it may be expressed in the form

$$F(T, V, N) = N f(T, \rho), \tag{6.231}$$

where f is the free energy per particle and is a function of the intensive variables T and ρ.

(a) Show that

$$\mu = f + \rho\left(\frac{\partial f}{\partial \rho}\right)_T \tag{6.232}$$

$$\left(\frac{\partial \mu}{\partial \rho}\right)_T = 2\left(\frac{\partial f}{\partial \rho}\right)_T + \rho\left(\frac{\partial^2 f}{\partial \rho^2}\right)_T, \tag{6.233}$$

and

$$P = \rho^2\left(\frac{\partial f}{\partial \rho}\right)_T \tag{6.234}$$

$$\left(\frac{\partial P}{\partial \rho}\right)_T = 2\rho\left(\frac{\partial f}{\partial \rho}\right)_T + \rho^2\left(\frac{\partial^2 f}{\partial \rho^2}\right)_T = \rho\left(\frac{\partial \mu}{\partial \rho}\right)_T. \tag{6.235}$$

Note that (6.235) is an example of a Maxwell relation (see Section 2.22).

(b) Show that

$$\left(\frac{\partial P}{\partial \rho}\right)_T = -\frac{V^2}{N}\left(\frac{\partial P}{\partial V}\right)_{T,V} \tag{6.236a}$$

$$\left(\frac{\partial \mu}{\partial \rho}\right)_T = V\left(\frac{\partial \mu}{\partial N}\right)_{T,V} \tag{6.236b}$$

(c) Use (6.235) and (6.236) to show that

$$N\left(\frac{\partial \mu}{\partial N}\right)_{T,V} = \frac{1}{\rho\kappa} \tag{6.237}$$

Hence it follows from (6.228) that

$$\kappa = \frac{1}{\rho kT}\frac{(\overline{N^2} - \overline{N}^2)}{\overline{N}}. \tag{6.238}$$

$\square$

Equation (6.238) is another example of the relation of a response function, the compressibility κ, to the mean-square fluctuations of a thermodynamic variable.

From (6.229) we have that

$$\frac{\left[\overline{N^2} - \overline{N}^2\right]}{\overline{N}} = \frac{kT}{\overline{N}} \left(\frac{\partial \overline{N}}{\partial \mu}\right)_{T,V}. \tag{6.239}$$

Because μ is an intensive quantity, the right-hand side of (6.239) is intensive, that is, independent of $\overline{N}$. Hence the left-hand side of (6.239) must also be independent of $\overline{N}$. This independence implies that the standard deviation is given by $\Delta N = \left[\overline{N^2} - \overline{N}^2\right]^{1/2} \propto \overline{N}^{1/2}$, and therefore the relative fluctuations in the number of particles is

$$\frac{\Delta N}{\overline{N}} \propto \overline{N}^{-1/2} \to 0 \text{ as } \overline{N} \to \infty. \tag{6.240}$$

That is, in the thermodynamic limit, $\overline{N} \to \infty$, $V \to \infty$ with $\rho = \overline{N}/V$ a constant, we can identify the thermodynamic variable N with $\overline{N}$. As in our discussion of the canonical ensemble in Section 4.6, we see that the thermodynamic properties calculated in different ensembles become identical in the thermodynamic limit.

*__Problem 6.44.__ Number fluctuations in a noninteracting classical gas

(a) Show that the grand partition function of a noninteracting classical gas can be expressed as

$$Z_G = \sum_{N=0}^{\infty} \frac{(zZ_1)^N}{N!} = e^{zZ_1}, \tag{6.241}$$

where the activity $z = e^{\beta\mu}$.

(b) Show that the mean value of N is given by

$$\overline{N} = zZ_1, \tag{6.242}$$

and the probability that there are N particles in the system is given by a Poisson distribution:

$$P_N = \frac{z^N Z_N}{Z_G} = \frac{(zZ_1)^N}{N! Z_G} = \frac{\overline{N}^N}{N!} e^{-\overline{N}}. \tag{6.243}$$

(c) What is the N-dependence of the variance, $\overline{(N - \overline{N})^2}$? ☐

6.11.2 Low temperature expansion of an ideal Fermi gas

We derive the low temperature expansion of the thermodynamic properties of an ideal Fermi gas. For convenience, we first give the formal expressions for the thermodynamic properties of a ideal Fermi gas at temperature T. The mean number of particles is given by

$$\overline{N} = \frac{2^{1/2} V m^{3/2}}{\pi^2 \hbar^3} \int_0^{\infty} \frac{\epsilon^{1/2} \, d\epsilon}{e^{\beta(\epsilon - \mu)} + 1}, \tag{6.244}$$

and the Landau potential Ω is given by (see (6.109))

$$\Omega = -\frac{2}{3}\frac{2^{1/2}Vm^{3/2}}{\pi^2\hbar^3}\int_0^\infty \frac{\epsilon^{3/2}\,d\epsilon}{e^{\beta(\epsilon-\mu)}+1}. \tag{6.245}$$

The integrals in (6.244) and (6.245) cannot be expressed in terms of familiar functions for all T. However, in the limit $T \ll T_F$ (as is the case for almost all metals), it is sufficient to approximate the integrals. To understand the approximations, we express the integrals (6.244) and (6.245) in the form

$$I = \int_0^\infty \frac{f(\epsilon)\,d\epsilon}{e^{\beta(\epsilon-\mu)}+1}, \tag{6.246}$$

where $f(\epsilon) = \epsilon^{1/2}$ and $e^{3/2}$, respectively.

The expansion procedure is based on the fact that the Fermi-Dirac distribution function $\overline{n}(\epsilon)$ differs from its $T = 0$ form only in a small range of width kT about μ. We let $\epsilon - \mu = kTx$ and write I as

$$I = kT\int_{-\beta\mu}^\infty \frac{f(\mu+kTx)}{e^x+1}\,dx \tag{6.247a}$$

$$= kT\int_{-\beta\mu}^0 \frac{f(\mu+kTx)}{e^x+1}\,dx + kT\int_0^\infty \frac{f(\mu+kTx)}{e^x+1}\,dx. \tag{6.247b}$$

In the first integrand in (6.247b) we let $x \to -x$ so that

$$I = kT\int_0^{\beta\mu} \frac{f(\mu-kTx)}{e^{-x}+1}\,dx + kT\int_0^\infty \frac{f(\mu+kTx)}{e^x+1}\,dx. \tag{6.247c}$$

We next write $1/(e^{-x}+1) = 1 - 1/(e^x+1)$ in the first integrand in (6.247c) and obtain

$$I = kT\int_0^{\beta\mu} f(\mu-kTx)\,dx - kT\int_0^{\beta\mu}\frac{f(\mu-kTx)}{e^x+1}\,dx + kT\int_0^\infty \frac{f(\mu+kTx)}{e^x+1}\,dx. \tag{6.248}$$

Equation (6.248) is still exact.

Because we are interested in the limit $T \ll T_F$ or $\beta\mu \gg 1$, we can replace the upper limit in the second integral by infinity. Then after making the change of variables, $w = \mu - kTx$, in the first integrand, we find

$$I = \int_0^\mu f(w)\,dw + kT\int_0^\infty \frac{f(\mu+kTx)-f(\mu-kTx)}{e^x+1}\,dx. \tag{6.249}$$

The values of x that contribute to the integrand in the second term in (6.249) are order one, and hence it is reasonable to expand $f(\mu \pm kTx)$ in a power series in kTx and integrate term by term. The result is

$$I = \int_0^\mu f(\epsilon)\,d\epsilon + 2(kT)^2 f'(\mu)\int_0^\infty \frac{xdx}{e^x+1}\,dx + \frac{1}{3}(kT)^4 f'''(\mu)\int_0^\infty \frac{x^3dx}{e^x+1}\,dx + \ldots \tag{6.250}$$

The definite integrals in (6.250) can be evaluated using analytical methods (see Appendix A). The results are

$$\int_0^\infty \frac{x\,dx}{e^x + 1} = \frac{\pi^2}{12} \tag{6.251}$$

$$\int_0^\infty \frac{x^3\,dx}{e^x + 1} = \frac{7\pi^4}{120} \tag{6.252}$$

If we substitute (6.251) and (6.252) into (6.250), we obtain the desired result

$$I = \int_0^\mu f(\epsilon)\,d\epsilon + \frac{\pi^2}{6}(kT)^2 f'(\mu) + \frac{7\pi^4}{360}(kT)^4 f''' + \dots \tag{6.253}$$

Note that although we expanded $f(\mu - kTx)$ in a power series in kTx, the expansion of I in (6.253) is not a power series expansion in $(kT)^2$. Instead (6.253) represents an asymptotic series that is a good approximation to I if only the first several terms are retained.

To find Ω in the limit of low temperatures, we let $f(\epsilon) = \epsilon^{3/2}$ in (6.253). From (6.245) and (6.253) we find that in the limit of low temperatures

$$\Omega = -\frac{2}{3}\frac{2^{1/2}Vm^{3/2}}{\pi^2 \hbar^3}\left[\frac{2}{5}\mu^{5/2} + \frac{\pi^2}{4}(kT)^2\mu^{1/2}\right]. \tag{6.254}$$

$$\overline{N} = -\frac{\partial\Omega}{\partial\mu} = \frac{V(2m)^{3/2}}{3\pi^2\hbar^3}\left[\mu^{3/2} + \frac{\pi^2}{8}(kT)^2\mu^{-1/2}\right]. \tag{6.255}$$

A more careful derivation of the low temperature behavior of an ideal Fermi gas has been given by Weinstock.

Vocabulary

thermal de Broglie wavelength, λ

semiclassical limit

equipartition theorem

Maxwell velocity and speed distributions

occupation numbers, spin and statistics, bosons and fermions

Bose-Einstein distribution, Fermi-Dirac distribution, Maxwell-Boltzmann distribution

single particle density of states, $g(\epsilon)$

Fermi energy ϵ_F, Fermi temperature T_F, and Fermi momentum p_F

macroscopic occupation, Bose-Einstein condensation

law of Dulong and Petit, Einstein and Debye theories of a crystalline solid

Additional Problems

Problem 6.45. Explain in simple terms why the mean kinetic energy of a classical particle in equilibrium with a heat bath at temperature T is $\frac{1}{2}kT$ per quadratic contribution to the kinetic
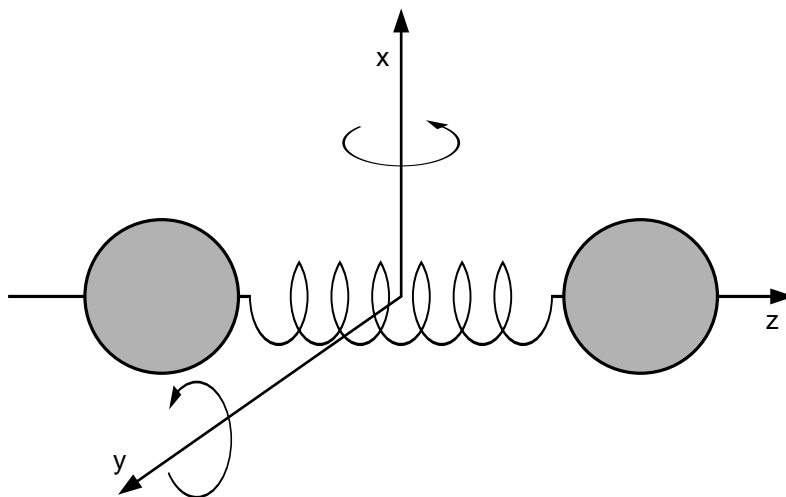
Figure 6.5: A schematic representation of a diatomic molecule.

energy, independent of the mass of the particle. □

Problem 6.46. Heat capacity of a linear rigid rotator

So far we have considered the thermal properties of an ideal monatomic gas consisting of spherically symmetrical, rigid molecules undergoing translational motion, that is, their internal motion was ignored. Real molecules are neither spherical nor rigid, and rotate about two or three axes and vibrate with many different frequencies. For simplicity, consider a linear rigid rotator consisting of two point masses m_1 and m_2 located a fixed distance r from each other. We will first assume that r is fixed and ignore vibrational motion, which is discussed in Problem 6.47. The rotational energy levels are given by

$$\epsilon(j) = j(j+1)\frac{\hbar^2}{2I}, \tag{6.256}$$

where I is the moment of inertia and $j = 0, 1, 2, \ldots$ is the angular momentum quantum number. The degeneracy of each rotational energy level is $(2j + 1)$.

(a) Express the partition function $Z_{\rm rot}$ for one molecule as a sum over energy levels.

(b) The sum that you found in part (a) cannot be evaluated exactly in terms of well known functions. However, for $T \gg T_{\rm rot} = \hbar^2/(2kI)$, the energy spectrum of the rotational states may be approximated by a continuum and the sum over j can be replaced by an integral. Show that the rotational heat capacity (at constant volume) of an ideal gas of linear rigid rotators is given by $C_{\rm rot} = Nk$ in the high temperature limit $T \gg T_{\rm rot}$. Compare this limiting behavior with the prediction of the equipartition theorem. In this case we say that the linear rigid rotator has two quadratic contributions to the energy. Explain.

(c) The magnitude of $T_{\rm rot}$ for a typical diatomic molecule such as HCl is $T_r \approx 15\,{\rm K}$. Sketch the temperature dependence of $C_{\rm rot}$, including its behavior for $T \ll T_{\rm rot}$ and $T \gg T_{\rm rot}$. □

Problem 6.47. Heat capacity of an ideal diatomic gas

In addition to translational and rotational motion, a diatomic molecule can exhibit vibrational motion (see Figure 6.5). It is a good approximation to take the rotational and vibrational motion to be independent and to express the total energy of an ideal diatomic gas as a sum of the translational, rotational, and vibrational contributions. Hence the total heat capacity (at constant volume) of the gas can be written as

$$C = C_{\text{tran}} + C_{\text{rot}} + C_{\text{vib}}. \tag{6.257}$$

The last two terms in (6.257) arise from the internal motion of the molecule. The rotational contribution C_{rot} was discussed in Problem 6.46.

(a) The vibrational motion of a diatomic molecule can be modeled by harmonic oscillations about the minimum of the potential energy of interaction between the two molecules. What is the high temperature limit of C_{vib}?

(b) Let us define a temperature $T_{\text{vib}} = \hbar\omega/k$. The magnitude of T_{vib} for HCl is $T_{\text{vib}} \approx 4227\,\text{K}$, where ω is the vibrational frequency and $\hbar\omega$ is the energy difference between neighboring vibrational energy levels. What do you expect the value of C_{vib} to be at room temperature?

(c) Use the value of T_{rot} given in Problem 6.46 and the value of T_{vib} given in part (b) for HCl to sketch the T-dependence of the total heat capacity C in the range $10\,\text{K} \leq T \leq 10000\,\text{K}$. $\quad\square$

Problem 6.48. Law of atmospheres

Consider an ideal classical gas in equilibrium at temperature T in the presence of an uniform gravitational field. Find the probability $P(z)dz$ that an atom is at a height between z and $z + dz$ above the earth's surface. How do the density and the pressure depend on z? $\quad\square$

Problem 6.49. Alternative derivation of the Maxwell velocity distribution

The Maxwell velocity distribution can also be derived by making some plausible assumptions. We first assume that the probability density $f(\mathbf{v})$ for one particle is a function only of its speed $|\mathbf{v}|$ or equivalently v^2. We also assume that the velocity distributions of the components v_x, v_y, v_z are independent of each other.

(a) Given these assumptions, explain why we can write

$$f(v_x^2 + v_y^2 + v_z^2) = Cf(v_x^2)f(v_y^2)f(v_z^2), \tag{6.258}$$

where C is a constant independent of v_x, v_y, and v_z.

(b) Show that a mathematical function that satisfies the condition (6.258) is the exponential function

$$f(v^2) = c\,e^{-\alpha v^2}, \tag{6.259}$$

where c and α are independent of $\mathbf{v}$.

(c) Determine c in terms of α using the normalization condition $1 = \int_{-\infty}^{\infty} f(u)du$ for each component. Why must α be positive?

(d) Use the fact that $\frac{1}{2}kT = \frac{1}{2}m\overline{v_x^2}$ to find the result Maxwell velocity distribution in (6.59).

(e) *Show that $f(v^2)$ in part (b) is the only function that satisfies the condition (6.258). ☐

Problem 6.50. Consequences of the Maxwell velocity distribution

(a) What is the probability that the kinetic energy of a classical nonrelativistic particle is in the range ϵ to $\epsilon + d\epsilon$? What is the most probable kinetic energy? Is it equal to $\frac{1}{2}m\tilde{v}^2$, where $\tilde{v}$ is the most probable speed?

(b) Find the values of $\overline{v}_x, \overline{v_x^2}, \overline{v_x^2 v_y^2}$, and $\overline{v_x v_y^2}$ for a classical system of particles at temperature T. No calculations are necessary. ☐

Problem 6.51. Mean energy of a nonlinear oscillator

Consider a classical one-dimensional nonlinear oscillator whose energy is given by

$$\epsilon = \frac{p^2}{2m} + ax^4, \tag{6.260}$$

where x, p, and m have their usual meanings; the parameter a is a constant.

(a) If the oscillator is in equilibrium with a heat bath at temperature T, calculate its mean kinetic energy, mean potential energy, and the mean total energy. (It is not necessary to evaluate any integrals explicitly.)

(b) Consider a classical one-dimensional oscillator whose energy is given by

$$\epsilon = \frac{p^2}{2m} + \frac{1}{2}kx^2 + ax^4. \tag{6.261}$$

In this case the anharmonic contribution ax^4 is very small. What is the leading contribution of this term to the mean potential energy? (Recall that for small u, $e^u \approx 1 + u$.) ☐

Problem 6.52. Granular systems

A system of glass beads or steel balls is an example of a *granular* system. In such a system the beads are macroscopic objects and the collisions between the beads are inelastic. Because the collisions in such a system are inelastic, a gas-like steady state is achieved only by inputting energy, usually by shaking or vibrating the walls of the container. Suppose that the velocities of the particles are measured in a direction perpendicular to the direction of shaking. Do the assumptions we used to derive the Maxwell-Boltzmann velocity distribution apply here? See for example, the experiments by Daniel L. Blair and Arshad Kudrolli, "Velocity correlations in dense granular gases," Phys. Rev. E **64**, 050301(R) (2001) and the theoretical arguments by J. S. van Zon and F. C. MacKintosh, "Velocity distributions in dissipative granular gases," Phys. Rev. Lett. **93**, 038001 (2004). ☐

Problem 6.53. A toy system of two particles

Consider a system consisting of two noninteracting particles in equilibrium with a heat bath at temperature T. Each particle can be in one of three states with energies 0, ϵ_1, and ϵ_2. Find the partition function for the cases described in parts (a)–(c) and then answer parts (d)–(f):

(a) The particles obey Maxwell-Boltzmann statistics and can be considered distinguishable.

(b) The particles obey Fermi-Dirac statistics.

(c) The particles obey Bose-Einstein statistics.

(d) Find the probability in each case that the ground state is occupied by one particle.

(e) What is the probability that the ground state is occupied by two particles?

(f) Estimate the probabilities in (d) and (e) for $kT = \epsilon_2 = 2\epsilon_1$. ☐

*Problem 6.54.** Consider a single particle of mass m in a one-dimensional harmonic oscillator potential given by $V(x) = \frac{1}{2}kx^2$. As we found in Example 4.3, the partition function is given by $Z_1 = e^{-x/2}/(1 - e^{-x})$, where $x = \beta\hbar\omega$.

(a) What is the partition function for two noninteracting distinguishable particles in the same potential?

(b) What is the partition function for two noninteracting fermions in the same potential assuming the fermions have no spin?

(c) What is the partition function for two noninteracting bosons in the same potential? Assume the bosons have spin zero.

(d) Calculate the mean energy and entropy in the three cases considered in parts (a)–(c). Plot E and S as a function of T and compare the behavior of E and S in the limiting cases of $T \to 0$ and $T \to \infty$. ☐

Problem 6.55. Neutron stars

A neutron star can be considered to be a collection of non-interacting neutrons, which are spin $1/2$ fermions. A typical neutron star has a mass M close to one solar mass $M_\odot \approx 2 \times 10^{30}$ kg. The mass of a neutron is about $m = 1.67 \times 10^{-27}$ kg. In the following we will estimate the radius R of the neutron star.

(a) Find the energy of a neutron star at $T = 0$ as a function of R, M, and m assuming that the star can be treated as an ideal non-relativistic Fermi gas.

(b) Assume that the density of the star is uniform and show that its gravitational energy is given by $E_G = -3GM^2/5R$, where the gravitational constant $G = 6.67 \times 10^{-11}$ Nm^2/kg^2. (Hint: from classical mechanics find the gravitational potential energy between an existing sphere of radius r and a shell of volume $4\pi r^2 dr$ coming from infinity to radius r. Then integrate from $r = 0$ to R.)

(c) Assume that gravitational equilibrium occurs when the total energy is minimized and find an expression for the radius R.

(d) Estimate the actual value of R in kilometers. Estimate the mass density and compare it with the density of material on the surface of the earth such as water.

(e) Determine the Fermi energy and Fermi temperature. A typical internal temperature for a neutron star is $T = 10^8$ K. Compare this value with the Fermi temperature and determine if the zero temperature approximation that we have used is applicable.

(f) Compare the rest energy mc^2 of a neutron with the Fermi energy of a neutron star. Is the non-relativistic approximation valid? □

Problem 6.56. White dwarfs

A white dwarf is a very dense star and can be considered to be a degenerate gas of electrons and an equal number of protons to make it charge neutral. We will also assume that there is one neutron per electron and that the mass of the star is about the same as our Sun. Many of the results of Problem 6.55 can be used here with slight modifications.

(a) Find the mean energy at $T = 0$ as a function of R, M, and m_e, where M is the total mass of the star and m_e is the electron mass.

(b) Assume that the star has a uniform density and show that the gravitational energy of the star is given by $E_G = -3GM^2/5R$.

(c) Assume that gravitational equilibrium occurs when the total energy is minimized and find an expression for the radius R.

(d) Estimate the actual value of R in kilometers. Estimate the mass density and compare it with the density of water on the surface of Earth.

(e) For extremely relativistic electrons the relation between the energy ϵ and momentum p of an electron is given by $\epsilon = cp$, where c is the speed of light. Find the Fermi energy and temperature.

(f) Find the mean energy at $T = 0$ for relativistic electrons in a white dwarf. Add this energy to the gravitational energy. Is there a minimum at a finite value of R? If not, what does this result mean about stability?

(g) Compare the rest energy $m_e c^2$ with the non-relativistic Fermi energy. Is the non-relativistic approximation valid? When the rest energy equals the non-relativistic Fermi energy, we know that the non-relativistic approximation is not valid. At what value of the total mass does this equality occur? Chandrasekhar obtained a limiting mass of $1.4M_\odot$ by taking into account the more accurate relation $\epsilon = (m_e^2 c^4 + c^2 p^2)^{1/2}$ and the variation of density within the star. How does your crude estimate compare? □

Problem 6.57. Toy systems of fermions

(a) Consider a system of noninteracting (spinless) fermions such that each particle can be a single particle state with energy 0, Δ, and 2Δ. Find an expression for Z_G using (6.224). Determine how the mean number of particles depends on μ for $T = 0$, $kT = \Delta/2$, and $kT = \Delta$.

(b) *A system contains N identical noninteracting fermions with $2N$ distinct single particle states. Suppose that $2N/3$ of these states have energy zero, $2N/3$ have energy Δ, and $2N/3$ have energy 2Δ. Show that μ is independent of T. Calculate and sketch the T-dependence of the energy and heat capacity. $\square$

*Problem 6.58. Periodic boundary conditions

Assume periodic boundary conditions so that the wave function ψ satisfies the condition (in one dimension)

$$\psi(x) = \psi(x + L). \tag{6.262}$$

The form of the one particle eigenfunction consistent with (6.262) is given by

$$\psi(x) \propto e^{ik_x x}. \tag{6.263}$$

What are the allowed values of k_x? How do they compare with the allowed values of k_x for a particle in a one-dimensional box? Generalize the form (6.263) to a cube and determine the allowed values of $\mathbf{k}$. Find the form of the density of states and show that the same result (6.96) is obtained. $\square$

Problem 6.59. Chemical potential of a one-dimensional ideal Fermi gas

Calculate the chemical potential $\mu(T)$ of an one-dimensional ideal Fermi gas at low temperatures $T \ll T_F$. Use the result for $\mu(T)$ found for the two-dimensional case in Problem 6.33 and compare the qualitative behavior of $\mu(T)$ in one, two, and three dimensions. $\square$

Problem 6.60. High temperature limit of the ideal Fermi gas

If $T \gg T_F$ at fixed density, quantum effects can be neglected and the thermal properties of an ideal Fermi gas reduce to the ideal classical gas. In the following we will find the first correction to the classical pressure equation of state.

(a) Does the pressure increase or decrease when the temperature is lowered (at constant density)? That is, what is the sign of the first quantum correction to the classical pressure equation of state? The pressure is given by (see (6.109))

$$P = \frac{(2m)^{3/2}}{3\pi^2 \hbar^3} \int_0^\infty \frac{\epsilon^{3/2}\, d\epsilon}{e^{\beta(x-\mu)} + 1}. \tag{6.264}$$

In the high temperature limit, $e^{\beta\mu} \ll 1$, we can make the expansion

$$\frac{1}{e^{\beta(\epsilon-\mu)} + 1} = e^{\beta(\mu-\epsilon)} \frac{1}{1 + e^{-\beta(\epsilon-\mu)}} \tag{6.265a}$$

$$\approx e^{\beta(\mu-\epsilon)}[1 - e^{-\beta(\epsilon-\mu)}]. \tag{6.265b}$$

If we use (6.265b), we obtain

$$e^{\beta\mu} \int_0^\infty x^{3/2} e^{-x} (1 - e^{\beta\mu} e^{-x})\, dx = \frac{3}{4}\pi^{1/2} e^{\beta\mu}\left[1 - \frac{1}{2^{5/2}}e^{\beta\mu}\right]. \tag{6.266}$$

Use (6.266) to show that P is given by

$$P = \frac{m^{3/2}(kT)^{5/2}}{2^{1/2}\,\pi^{3/2}\hbar^3}\, e^{\beta\mu}\left[1 - \frac{1}{2^{5/2}}e^{\beta\mu}\right]. \tag{6.267}$$

(b) Derive an expression for N similar to (6.267). Eliminate μ and show that the leading order correction to the equation of state is given by

$$PV = NkT\Big[1 + \frac{\pi^{3/2}}{4}\frac{\rho\hbar^3}{(mkT)^{3/2}}\Big], \tag{6.268a}$$

$$= NkT\Big[1 + \frac{1}{2^{7/2}}\rho\lambda^3\Big]. \tag{6.268b}$$

(c) What is the condition for the correction term in (6.268b) to be small? Note that as the temperature is lowered at constant density, the pressure increases. What do you think would be the effect of Bose statistics in this context (see Problem 6.61)? Mullin and Blaylock have emphasized that it is misleading to interpret the sign of the correction term in (6.268b) in terms of an effective repulsive exchange "force," and stress that the positive sign is a consequence of the symmetrization requirement for same spin fermions. □

Problem 6.61. High temperature limit of ideal Bose gas

If $T \gg T_c$ at fixed density, quantum effects can be neglected and the thermal properties of an ideal Bose gas reduces to the ideal classical gas. Does the pressure increase or decrease when the temperature is lowered (at constant density)? That is, what is the first quantum correction to the classical equation of state? The pressure is given by (see (6.109))

$$P = \frac{2^{1/2}m^{3/2}(kT)^{5/2}}{3\pi^2\hbar^3}\int_0^\infty \frac{x^{3/2}\,dx}{e^{x-\beta\mu}-1}. \tag{6.269}$$

Follow the same procedure as in Problem 6.60 and show that

$$PV = NkT\Big[1 - \frac{\pi^{3/2}}{2}\frac{\rho\hbar^3}{(mkT)^{3/2}}\Big]. \tag{6.270}$$

We see that as the temperature is lowered at constant density, the pressure becomes less than its classical value. □

Problem 6.62. Bose condensation in one and two dimensions?

Does Bose condensation occur for a one and two-dimensional ideal Bose gas? If so, find the transition temperature. If not, explain. □

***Problem 6.63.** Graphene

Graphene is a two-dimensional sheet of carbon, which was first made in the laboratory in 2004 with the help of everyday clear adhesive (Scotch) tape. Graphite, the material used in pencils, consists of many layers of graphene. The gentle stickiness of the tape was used to break apart the many layers of graphite. Among graphene's many interesting properties is that its low temperature behavior can be understood by treating it as a collection of noninteracting excitations which behave as relativistic Dirac fermions and obey the dispersion relation

$$\epsilon_\pm(k) = \pm hvk. \tag{6.271}$$

The spin degeneracy is $g = 2$ and $v \approx 10^6\,\text{m/s}$.

(a) Find the chemical potential at $T = 0$, assuming that all negative energy states are occupied and all positive energy states are empty.

(b) Show that the mean energy is given by

$$E(T) - E(0) = 4A \int \frac{\epsilon_+(k)}{e^{\beta \epsilon_+(k)} + 1} d^2 k, \qquad (6.272)$$

where A is the area of the system.

(c) Calculate the temperature dependence of the heat capacity at low temperatures due to these massless Dirac particles.

(d) Besides the contribution to the heat capacity calculated in part (c), there is the usual contribution of the lattice vibrations (phonons) to the heat capacity. Given that the sound speed in graphite is $\approx 2 \times 10^4$ m/s, determine whether the low temperature heat capacity is controlled by phonon or electron contributions. □

Problem 6.64. Discuss why Bose condensation does not occur in a system of photons corresponding to blackbody radiation. □

Problem 6.65. More on the Debye model

(a) Show that if the volume of the crystal is Na^3, where a is the equilibrium distance between atoms, then the Debye wave number, $k_D = \omega_D/\overline{c}$, is about π/a.

(b) Evaluate the integral in (6.202) numerically and plot the heat capacity versus T/T_D over the entire temperature range. □

Problem 6.66. Bose-Einstein condensation in low-dimensional traps

As you found in Problem 6.62, Bose-Einstein condensation does not occur in ideal one and two-dimensional systems. However, this result holds only if the system is confined by rigid walls. In the following, we will show that Bose-Einstein condensation can occur if a system is confined by a spatially varying potential. For simplicity, we will treat the system semiclassically

Let us assume that the confining potential has the form

$$V(r) \sim r^n. \qquad (6.273)$$

In this case the region accessible to a particle with energy ϵ has a radius $\ell \sim \epsilon^{1/n}$. Show that the corresponding density of states behaves as

$$g(\epsilon) \sim \ell^d \epsilon^{\frac{1}{2}d-1} \sim \epsilon^{d/n} \epsilon^{\frac{1}{2}d-1} \sim \epsilon^\alpha, \qquad (6.274)$$

where

$$\alpha = \frac{d}{n} + \frac{d}{2} - 1 \qquad (6.275)$$

What is the range of values of n for which $T_c > 0$ for $d = 1$ and 2? More information about experiments on Bose-Einstein condensation can be found in the references. □

***Problem 6.67.** Number fluctuations in a degenerate ideal Fermi gas

Use the relation (6.228)

$$\overline{(N - \overline{N})^2} = kT\frac{\partial N}{\partial \mu} \tag{6.276}$$

to find the number fluctuations in the ideal Fermi gas for fixed T, V, and μ. Show that

$$\overline{(N - \overline{N})^2} = \frac{kT}{2}\frac{V(2m)^{3/2}}{2\pi^2\hbar^3}\int_0^\infty \frac{\epsilon^{-1/2}\,d\epsilon}{e^{\beta(\epsilon-\mu)} + 1}, \tag{6.277a}$$

$$\longrightarrow \frac{3\overline{N}T}{2T_F} \qquad (T \ll T_F). \tag{6.277b}$$

Explain why the fluctuations in a degenerate Fermi system are much less than in the corresponding classical system. □

Suggestions for further reading

More information about Bose-Einstein condensation can be found at `<jilawww.colorado.edu/bec/>`, `<bec.nist.gov/>`, and `<www.rle.mit.edu/cua_pub/ketterle_group/>`.

Vanderlei Bagnato and Daniel Kleppner, "Bose-Einstein condensation in low-dimensional traps," Phys. Rev. A **44**, 7439–7441 (1991).

Ralph Baierlein, "The elusive chemical potential," Am. J. Phys. **69**, 428–434 (2001).

Roger Balian and Jean-Paul Blaizot, "Stars and statistical physics: A teaching experience," Am. J. Phys. **67**, 1189–1206 (1999). The article, which is part of a theme issue on thermal and statistical mechanics, contains an excellent introduction to the use of statistical physics in studying stars.

See John J. Brehm and William J. Mullin, *Introduction to the Structure of Matter*, John Wiley & Sons (1989) or Robert Eisberg and Robert Resnick, *Quantum Physics of Atoms, Molecules, Solids, Nuclei, and Particles*, second edition, John Wiley & Sons (1985) for a more complete discussion of blackbody radiation.

Ian Duck and E. C. G. Sudarshan, *Pauli and the Spin-Statistics Theorem*, World Scientific (1998). This graduate level text simplifies and clarifies the formal statements of the spin-statistics theorem, and corrects the flawed intuitive explanations that are frequently given.

David L. Goodstein, *States of Matter*, Prentice Hall (1975). An excellent text whose emphasis is on the applications of statistical mechanics to gases, liquids and solids. Chapter 3 on solids is particularly relevant to this chapter.

J. D. Gunton and M. J. Buckingham, "Condensation of ideal Bose gas as cooperative transition," Phys. Rev. **166**, 152–158 (1968).

F. Herrmann and P. Würfel, "Light with nonzero chemical potential," Am. J. Phys. **73**, 717–721 (2005). The authors discuss thermodynamic states and processes involving light in which the chemical potential of light is nonzero.

Charles Kittel, *Introduction to Solid State Physics*, seventh edition, John Wiley & Sons (1996). See Chapters 5 and 6 for a discussion of the Debye model and the free electron gas.

W. J. Mullin and G. Blaylock, "Quantum statistics: Is there an effective fermion repulsion or boson attraction?," Am. J. Phys. **71**, 1223–1231 (2003).

A. Pais, "Einstein and the quantum theory," Rev. Mod. Phys. **51**, 863–914 (1979). This review article has a fascinating account of how Planck arrived at his famous blackbody radiation formula.

Donald Rogers, *Einstein's Other Theory: The Planck-Bose-Einstein Theory of Heat Capacity*, Princeton University Press (2005).

Robert H. Swendsen, "Statistical mechanics of colloids and Boltzmann's definition of the entropy," Am. J. Phys. **74**, 187–190 (2006). The author argues that the usual definition of the entropy for a classical system of particles in terms of the logarithm of a volume in phase space is not fundamental and not the definition orginally given by Boltzmann. Swendsen's treatment resolves the Gibbs' paradox in a novel way.

Robert Weinstock, "Heat capacity of an ideal free electron gas: A rigorous derivation," Am. J. Phys. **37**, 1273–1279 (1969).