

Chapter 7

Quantum Gases

7.1 THE GRAND CANONICAL ENSEMBLE

The calculations done in Chapter 4 should make it clear that the canonical ensemble, in which the energy of the system is not fixed exactly, is much more convenient to use than the microcanonical ensemble. The canonical ensemble describes a system that is in thermal contact with a reservoir and can therefore exchange energy with it. The average energy of the system is determined by the reservoir temperature. Although the system described by the canonical ensemble does not have an exactly predictable energy, it does have an exact and definite number of particles. We will now introduce another ensemble that is designed to describe a system that can exchange both energy and particles with a much larger reservoir. It is called the *grand canonical ensemble*. In the grand canonical ensemble, both the number of particles and the energy are allowed to fluctuate, their average values being determined by the given values of the affinity and temperature.

In order to derive the probability distribution appropriate for such a situation, we will consider a system, like that shown in Fig. 7.1, composed of a small but macroscopic sample volume and a much larger particle reservoir. Both can exchange energy with a still larger heat reservoir at inverse temperature β . The system, composed of the sample and the particle reservoir (but not the heat reservoir),

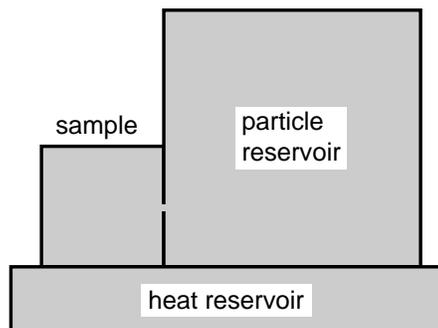


Fig. 7.1 A sample and a much larger reservoir that can exchange energy and particles. The two parts of ‘the system’ can exchange energy (but not particles) with a heat reservoir.

can be described by a canonical ensemble. It contains a total of N_T particles. We introduce a more compact symbol, z_i , for the six-dimensional phase-space coordinates $(\mathbf{r}_i, \mathbf{p}_i)$ of the i th particle. We assume that the particles in the sample volume do not interact with the particles in the reservoir volume. Thus, if particles 1 through N are in the sample volume while particles $N + 1$ through N_T are in the reservoir volume, then

the energy can be written as

$$E = H_S(z_1, \dots, z_N) + H_R(z_{N+1}, \dots, z_{N_T}) \quad (7.1)$$

where H_S is the Hamiltonian function for the sample particles and H_R is that for the reservoir. Now, using a canonical probability density for the system, we can easily calculate the probability of finding particles numbered 1 through N in the sample volume at phase-space points, (z_1, \dots, z_N) , with the other $N_T - N$ particles being somewhere in the reservoir. It is [see Eq. (4.56)]

$$\tilde{P}_N(z_1, \dots, z_N) = e^{-\beta H_S(z_1 \dots z_N)} \int_R e^{-\beta H_R} d^6 z_{N+1} \dots d^6 z_{N_T} / h^{3N_T} N_T! Z_T \quad (7.2)$$

where Z_T is the partition function of the system. The probability of finding *any* N particles at phase space points z_1 to z_N within the sample and all other particles in the particle reservoir is obtained by multiplying this by the number of ways of choosing N particles from N_T particles, that is, by the binomial coefficient.

$$\begin{aligned} P_N(z_1, \dots, z_N) &= \binom{N_T}{N} e^{-\beta H_S(z_1 \dots z_N)} \int_R e^{-\beta H_R} d^6 z_{N+1} \dots d^6 z_{N_T} / h^{3N_T} N_T! Z_T \\ &= e^{-\beta H_S(z_1 \dots z_N)} \int_R e^{-\beta H_R} d^6 z_{N+1} \dots d^6 z_{N_T} / h^{3N_T} N!(N_T - N)! Z_T \end{aligned} \quad (7.3)$$

The integral over the reservoir phase space can be written in terms of the canonical potential of the reservoir with $N_T - N$ particles, which can then be expanded to first order in N . According to Eq. (4.55),

$$\begin{aligned} \int_R e^{-\beta H_R} d^{6(N_T - N)} z &= h^{3(N_T - N)} (N_T - N)! \exp[\phi_R(N_T - N, \beta, V_R)] \\ &\approx h^{3(N_T - N)} (N_T - N)! \exp[\phi_R(N_T, \beta, V_R)] \exp(-\alpha N) \end{aligned} \quad (7.4)$$

Using this in the equation for $P_N(z_1, \dots, z_N)$, and lumping together all factors that are independent of N into one normalization constant that we will call Λ^{-1} , we get the desired *grand canonical probability distribution*

$$P_N(z_1, \dots, z_N) = \frac{e^{-\alpha N - \beta H_S(z_1, \dots, z_N)}}{\Lambda h^{3N} N!} \quad (7.5)$$

Thus, if a system can exchange particles and energy with a reservoir at affinity α and coldness β , then, at equilibrium, the probability of finding the system to contain exactly N particles with positions $(\mathbf{r}_1, \dots, \mathbf{r}_N)$ and momenta $(\mathbf{p}_1, \dots, \mathbf{p}_N)$ is given by

$$P_N(\mathbf{r}_1, \mathbf{p}_1, \dots, \mathbf{r}_N, \mathbf{p}_N) = \frac{e^{-\alpha N - \beta H(\mathbf{r}_1, \mathbf{p}_1, \dots, \mathbf{r}_N, \mathbf{p}_N)}}{\Lambda h^{3N} N!} \quad (7.6)$$

The normalization constant Λ , called the *grand partition function*, must be chosen so that the integration and sum of P_N over all possible states of the system is one. This gives

$$\Lambda(\alpha, \beta, V) = \sum_{N=0}^{\infty} \frac{e^{-\alpha N}}{h^{3N} N!} \int e^{-\beta H(1, \dots, N)} d^{3N} x d^{3N} p \quad (7.7)$$

The sum on N has been extended from what would be its natural limit, N_T , to infinity by using the fact that, for very large N , the $N!$ in the denominator makes the terms diminish very rapidly. We will see that the probability of obtaining a value of N that is much larger than the average value of N is negligibly small.

An equivalent calculation for a quantum mechanical system shows that the probability of finding the system with exactly N particles and in the N -particle quantum state $\psi_K(\mathbf{r}_1, \dots, \mathbf{r}_N)$ of energy E_{NK} is

$$P_{NK} = \Lambda^{-1} e^{-\alpha N - \beta E_{NK}} \quad (7.8)$$

The normalization constant Λ must then be chosen so that the sum of P_{NK} over all N and K is unity.

$$\Lambda = \sum_N \sum_K e^{-\alpha N - \beta E_{NK}} \quad (7.9)$$

It can be shown that, as $\hbar \rightarrow 0$, the quantum mechanical expression for Λ reduces to the classical formula given in Eq. (7.7).

As expected (see Problem 7.7), the logarithm of the grand partition function gives the grand potential in rational units.

$$\log \Lambda(\alpha, \beta, V) = \psi(\alpha, \beta, V) = S^o - \alpha N - \beta E \quad (7.10)$$

Using the thermodynamic identity $S^o = \alpha N + \beta E + \gamma V$, ψ can be written in the simpler form

$$\log \Lambda = \psi(\alpha, \beta, V) = \beta p V \quad (7.11)$$

The probability of finding the system with exactly N particles, irrespective of the quantum state, is

$$P_N = \sum_K e^{-\alpha N - \beta E_{NK}} / \Lambda \quad (7.12)$$

This shows that the average number of particles is given by the expected thermodynamic relation.

$$\begin{aligned} \langle N \rangle &= \Lambda^{-1} \sum_N \sum_K N e^{-\alpha N - \beta E_{NK}} \\ &= -\Lambda^{-1} \frac{\partial}{\partial \alpha} \sum_N \sum_K e^{-\alpha N - \beta E_{NK}} \\ &= -\frac{\partial \Lambda / \partial \alpha}{\Lambda} \\ &= -\frac{\partial \log \Lambda}{\partial \alpha} \\ &= -\frac{\partial \psi}{\partial \alpha} \end{aligned} \quad (7.13)$$

In an almost identical way, one can show that

$$\langle E \rangle = -\frac{\partial \psi}{\partial \beta} \quad (7.14)$$

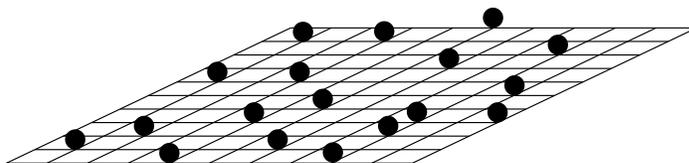


Fig. 7.2 A surface containing adsorption sites that can each accept a single particle.

7.2 SURFACE ADSORPTION

The surfaces of real vessels containing gases do not have the convenient but artificial properties of the hard-wall or periodic boxes we have been using in our calculations. Even when cleaned and polished, they are usually covered with adsorption sites, at which particles of the gas may temporarily attach themselves, due to interatomic forces between the gas molecules and the surface atoms (see Fig. 7.2). The disappearance of particles onto the surface or their reappearance in the gas as the temperature is raised causes a change in the

apparent properties of the gas, which must be corrected for in order to interpret experimental measurements in terms of the true properties of the gas alone.

When investigating the phenomenon of adsorption, it is convenient to use a grand canonical ensemble, since the number of adsorbed particles is not fixed. The model that will be used is a surface containing K independent adsorption sites. Each site may be unoccupied or it may be occupied by a single gas particle, which may be in any of a finite number of discrete quantum states of energies $\varepsilon_1, \varepsilon_2, \dots$. In this calculation, the system is only the set of adsorbed particles. The particles in the gas act as the reservoir and do not enter explicitly into the calculation. In summing over all states of the surface, we need only sum over the occupation number (0 or 1) at each site, and, for the occupied sites, over the set of energy states.

As usual, the most efficient procedure is to calculate the normalization constant Λ , which will then yield the thermodynamic potential ψ , from which other physical properties can be calculated. The easiest way of deriving the correct expression for Λ is to consider first the trivial cases of a single adsorption site and two adsorption sites. If $K = 1$, then N can be either 0 or 1, and the sum over quantum states only appears if $N = 1$.

$$\Lambda = \sum_{N=0}^1 e^{-\alpha N} \sum_k e^{-\beta \varepsilon_k} = 1 + e^{-\alpha} \sum_k e^{-\beta \varepsilon_k} \quad (7.15)$$

For $K = 2$ there are two adsorption sites and therefore two occupation numbers, N_1 and N_2 . Again, the sum over quantum states at a particular site only occurs when that occupation number is not zero.

$$\begin{aligned} \Lambda &= \sum_{N_1=0}^1 \sum_{N_2=0}^1 e^{-\alpha N_1 - \alpha N_2} \sum_{k_1} \sum_{k_2} e^{-\beta \varepsilon_{k_1} - \beta \varepsilon_{k_2}} \\ &= \left(\sum_{N_1=0}^1 e^{-\alpha N_1} \sum_{k_1} e^{-\beta \varepsilon_{k_1}} \right) \left(\sum_{N_2=0}^1 e^{-\alpha N_2} \sum_{k_2} e^{-\beta \varepsilon_{k_2}} \right) \\ &= \left(1 + e^{-\alpha} \sum_k e^{-\beta \varepsilon_k} \right)^2 \end{aligned} \quad (7.16)$$

For general K ,

$$\Lambda = \left(1 + e^{-\alpha} \sum_k e^{-\beta \varepsilon_k} \right)^K \quad (7.17)$$

The sum $z_a = \sum \exp(-\beta \varepsilon_k)$ is just the canonical partition function for a single occupied adsorption site. Using the grand potential,

$$\psi(\alpha, \beta) = K \log(1 + e^{-\alpha} z_a) \quad (7.18)$$

it is easy to calculate the fraction of occupied adsorption sites, $f_a = N_a/K$.

$$f_a = -\frac{\partial}{\partial \alpha} \log(1 + e^{-\alpha} z_a) = \frac{e^{-\alpha} z_a}{1 + e^{-\alpha} z_a} \quad (7.19)$$

This can be solved for α as a function of f_a .

$$\alpha = \log\left(\frac{1-f_a}{f_a}\right) + \log z_a \quad (7.20)$$

It will be assumed that the adsorbing surface is in equilibrium with an ideal gas at pressure p . For any ideal gas, not necessarily monatomic, Eq. 5.46 says that

$$\frac{\partial \alpha(p, T)}{\partial p} = -\frac{1}{p} \quad (7.21)$$

which can be integrated to give

$$\alpha = -\log p + \log g(T) \quad (7.22)$$

where the function $g(T)$ cannot be determined by the ideal gas equation alone and is different for different ideal gases. Eliminating α between Eqs. (7.20) and (7.22) gives a relation between the gas pressure and the adsorption fraction.

$$\log\left(\frac{g}{p}\right) = \log\left(\frac{1-f_a}{f_a}\right) + \log z_a \quad (7.23)$$

which can easily be solved for f_a as a function of p and T .

$$f_a = \frac{p}{p + g/z_a} \quad (7.24)$$

It is clear that, for fixed T , the adsorption site occupation probability goes from 0 to 1 as the pressure goes from 0 to infinity.

In order to proceed further, one must determine the functions $z_a(T)$ and $g(T)$. Let us consider the simplest case by assuming that the gas is a monatomic gas and that there is only one possible quantum state at each adsorption site. We assume that the state has a negative energy, $\varepsilon = -kT_o$, indicating a bound state. Then

$$z_a(T) = e^{T_o/T} \quad (7.25)$$

The affinity of the gas can be calculated as a function of the pressure and temperature by first computing the partition function.

$$\begin{aligned} Z &= \frac{1}{N!h^{3N}} \int e^{-\beta \sum p_n^2/2m} d^{3N} \mathbf{r} d^{3N} \mathbf{p} \\ &= \frac{1}{N!} \left(\frac{V}{\lambda^3}\right)^N \end{aligned} \quad (7.26)$$

where λ is the thermal de Broglie wavelength. The canonical potential of the gas is

$$\phi = N(\log V - \log N + 1 - \log \lambda^3) \quad (7.27)$$

and the affinity is equal to $\partial\phi/\partial N$.

$$\begin{aligned} \alpha &= \log(V/N) - \log \lambda^3 \\ &= -\log p + \log[(kT)^{5/2}(2\pi m)^{3/2}/h^3] \end{aligned} \quad (7.28)$$

This gives

$$g(T) = (kT)^{5/2}(2\pi m)^{3/2}/h^3 \equiv \gamma T^{5/2} \quad (7.29)$$

and

$$f_a = \frac{p}{p + \gamma T^{5/2} e^{-T_o/T}} \quad (7.30)$$

For fixed p , f_a goes from 1 to 0 as T goes from 0 to infinity.

7.3 QUANTUM IDEAL GASES

The distribution functions for Bose–Einstein and Fermi–Dirac ideal gases were derived in Chapter 2 by the method of determining the most probable macrostate. It will be instructive to apply the grand canonical ensemble to a study of the same systems. For both bosons and fermions, the many-particle quantum states are defined by a sequence of occupation numbers N_1, N_2, \dots , where N_k is the number of particles in the k th single-particle quantum state. The total number of particles and the total energy of the state are given by

$$N = \sum_k N_k \quad (7.31)$$

and

$$E = \sum_k \varepsilon_k N_k \quad (7.32)$$

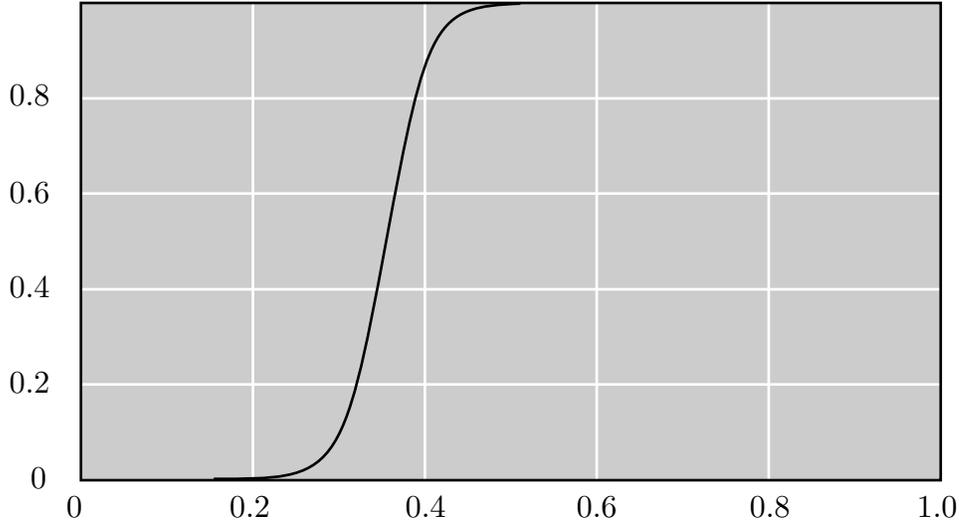


Fig. 7.3 The fraction of occupied adsorption sites as a function of the binding energy (in K), T_o , for the case of argon at STP. The vertical axis gives f_a and the horizontal axis is T_o/T_{STP} .

In using the grand canonical ensemble, the first thing one should do is calculate the grand partition function Λ . From Λ , the grand potential, $\psi = \log \Lambda$, can be easily calculated. Then the thermodynamic relations $N = -\partial\psi/\partial\alpha$, $E = -\partial\psi/\partial\beta$, and $\beta p = \partial\psi/\partial V$ will give the equations of state of the system. According to Eq. (7.9), Λ is equal to the sum of $\exp(-\alpha N - \beta E)$ over all values of N and, for each value of N , over all N -particle quantum states of the system. Expressing N and E by means of Eqs. (7.31) and (7.32), we can write Λ as

$$\begin{aligned} \Lambda &= \sum_{N=0}^{\infty} \sum_{\{N_k\}_N} \exp\left(-\alpha \sum_k N_k - \beta \sum_k \varepsilon_k N_k\right) \\ &= \sum_{N=0}^{\infty} \sum_{\{N_k\}_N} \exp\left(-\sum_k (\alpha + \beta \varepsilon_k) N_k\right) \end{aligned} \tag{7.33}$$

where $\{N_k\}_N$ indicates a sum over all combinations of occupation numbers that add up to N . But summing over all values of N and, for each value of N , summing over all N -particle quantum states is equivalent to summing independently over all single-particle occupation numbers. Therefore, writing $\{N_k\}$ for the infinite sequence of occupation numbers $\{N_1, N_2, \dots\}$, we get

$$\begin{aligned} \Lambda &= \sum_{\{N_k\}} \exp\left(-\sum_k (\alpha + \beta \varepsilon_k) N_k\right) \\ &= \sum_{N_1} e^{-(\alpha + \beta \varepsilon_1) N_1} \sum_{N_2} e^{-(\alpha + \beta \varepsilon_2) N_2} \sum_{N_3} e^{-(\alpha + \beta \varepsilon_3) N_3} \dots \end{aligned} \tag{7.34}$$

and, because the logarithm of a product is equal to the sum of the logarithms of its factors

$$\psi(\alpha, \beta, V) = \log \Lambda = \sum_k \log\left(\sum_{N_k} e^{-(\alpha + \beta \varepsilon_k) N_k}\right) \tag{7.35}$$

For bosons, $N_k = 0, 1, 2, \dots$, which means that the sum over N_k in Eq. (7.35) is of the form

$$\sum_{N_k} x^{N_k} = \frac{1}{1-x}$$

with $x = \exp[-(\alpha + \beta \varepsilon_k)]$. That is

$$\sum_{N_k=0}^{\infty} e^{-(\alpha + \beta \varepsilon_k) N_k} = \frac{1}{1 - e^{-(\alpha + \beta \varepsilon_k)}} \tag{7.36}$$

and therefore

$$\psi(\alpha, \beta, V) = - \sum_k \log[1 - e^{-(\alpha + \beta \varepsilon_k)}] \quad (7.37)$$

For fermions, the sum has only two terms, giving

$$\sum_{N_k=0}^1 e^{-(\alpha + \beta \varepsilon_k) N_k} = 1 + e^{-(\alpha + \beta \varepsilon_k)} \quad (7.38)$$

and

$$\psi(\alpha, \beta, V) = \sum_k \log[1 + e^{-(\alpha + \beta \varepsilon_k)}] \quad (7.39)$$

Both cases can be treated simultaneously by the formula

$$\psi = \zeta \sum_k \log[1 + \zeta e^{-(\alpha + \beta \varepsilon_k)}] \quad (7.40)$$

where

$$\zeta = \begin{cases} +1, & \text{for FD} \\ -1, & \text{for BE} \end{cases} \quad (7.41)$$

N and E are then given, in terms of α and β , by the thermodynamic relations

$$N = - \frac{\partial \psi}{\partial \alpha} = \sum_k \frac{e^{-(\alpha + \beta \varepsilon_k)}}{1 + \zeta e^{-(\alpha + \beta \varepsilon_k)}} = \sum_k \frac{1}{e^{\alpha + \beta \varepsilon_k} + \zeta} \quad (7.42)$$

and

$$E = - \frac{\partial \psi}{\partial \beta} = \sum_k \frac{\varepsilon_k e^{-(\alpha + \beta \varepsilon_k)}}{1 + \zeta e^{-(\alpha + \beta \varepsilon_k)}} = \sum_k \frac{\varepsilon_k}{e^{\alpha + \beta \varepsilon_k} + \zeta} \quad (7.43)$$

These equations are in agreement with the Fermi–Dirac and Bose–Einstein distribution functions obtained in Chapter 2. The average number of particles that occupy any single-particle quantum state of energy ε is

$$f_{\text{BE}}(\varepsilon) = \frac{1}{e^{\alpha + \beta \varepsilon} - 1} \quad \text{or} \quad f_{\text{FD}}(\varepsilon) = \frac{1}{e^{\alpha + \beta \varepsilon} + 1} \quad (7.44)$$

for bosons and fermions, respectively.

7.4 BOLTZMANN STATISTICS

If the average occupation number of each single-particle quantum state is much less than one, then $e^{\alpha + \beta \varepsilon} \gg 1$, and both the Bose–Einstein and the Fermi–Dirac density formulas can be approximated by the Maxwell–Boltzmann formula

$$f_{\text{MB}}(\varepsilon) = e^{-\alpha - \beta \varepsilon} \quad (7.45)$$

When this is done, one says that one is using *Boltzmann statistics*. Because $f_{\text{FD}} < f_{\text{MB}} < f_{\text{BE}}$, quantities calculated using this approximation usually are intermediate between those for bosons and fermions at the same values of α and β .

7.5 THE IDEAL FERMI GAS AT LOW TEMPERATURE

In Chapter 2 it was shown that the quantum mechanical distribution functions reduced to their classical equivalents at sufficiently high temperatures. Therefore, the specifically quantum mechanical aspects of quantum gases are revealed by studying their low-temperature behavior. This must be done separately for Fermi–Dirac and Bose–Einstein systems, because their low-temperature properties are very different. In the next two sections the low-temperature properties of a system of nonrelativistic spin- $\frac{1}{2}$ fermions will be analyzed. Following this, we will consider an equivalent system of bosons.

It is assumed that the particles are in a cubic periodic box of side L . It was shown in Section 2.15 that the single-particle energy eigenstates are then plane waves with allowed momentum values that form a cubic lattice of spacing h/L in momentum space, where $h = 2\pi\hbar$. The energy of a particle with momentum \mathbf{p} is $\varepsilon_p = p^2/2m$. Each allowed momentum eigenstate can be occupied by two particles of opposite spin. Therefore, the sum in Eq. (7.39) for the grand potential ψ can be converted to an integral of the form

$$\psi = 2(L/h)^3 \int \log[1 + e^{-(\alpha + \beta p^2/2m)}] d^3\mathbf{p} \quad (7.46)$$

By converting to an energy variable, $\varepsilon = p^2/2m$, and using the facts that $p = \sqrt{2m\varepsilon}$, $dp = d\varepsilon\sqrt{2m/\varepsilon}/2$, and $L^3 = V$, this integral can be transformed as follows.

$$\begin{aligned} \psi &= \frac{8\pi V}{h^3} \int_0^\infty \log[1 + e^{-(\alpha + \beta p^2/2m)}] p^2 dp \\ &= 2\gamma V \int_0^\infty \log[1 + e^{-(\alpha + \beta\varepsilon)}] \varepsilon^{1/2} d\varepsilon \end{aligned} \quad (7.47)$$

where the constant $\gamma = 2\pi(2m/h^2)^{3/2}$. The same transformation of Eqs. (7.42) and (7.43) gives

$$N = 2\gamma V \int_0^\infty \frac{\varepsilon^{1/2} d\varepsilon}{e^{\alpha + \beta\varepsilon} + 1} \quad (7.48)$$

and

$$E = 2\gamma V \int_0^\infty \frac{\varepsilon^{3/2} d\varepsilon}{e^{\alpha + \beta\varepsilon} + 1} \quad (7.49)$$

The logarithmic function in Eq. (7.47) can be eliminated by a partial integration. If that is done, and the thermodynamic relation $\psi = \beta pV$ is used, one finds that the classical relationship between pressure and energy density, $p = \frac{2}{3}(E/V)$, is also valid for a quantum mechanical ideal gas (see Problem 7.8).

In analyzing the low-temperature properties of the Fermi–Dirac gas, it is best to change variables from the affinity α to the chemical potential $\mu = -\alpha\tau$, where $\tau = kT$. The integrals for N and E , in terms of μ and τ , are

$$\frac{N}{V} = 2\gamma \int_0^\infty \frac{\varepsilon^{1/2} d\varepsilon}{e^{(\varepsilon - \mu)/\tau} + 1} \quad (7.50)$$

and

$$\frac{E}{V} = 2\gamma \int_0^\infty \frac{\varepsilon^{3/2} d\varepsilon}{e^{(\varepsilon - \mu)/\tau} + 1} \quad (7.51)$$

These integrals are both of the general form

$$I = \int_0^\infty \frac{g(\varepsilon) d\varepsilon}{e^{(\varepsilon - \mu)/\tau} + 1} \quad (7.52)$$

where $g(\varepsilon)$ is a smooth function that is independent of τ . Therefore, we will present a general method of evaluating integrals of this type as a power series expansion in the temperature. It is easy to verify the following limit formula for the Fermi–Dirac function $f_{\text{FD}}(\varepsilon)$.

$$\lim_{\tau \rightarrow 0} \left(\frac{1}{e^{(\varepsilon - \mu)/\tau} + 1} \right) = \begin{cases} 1, & \text{if } \varepsilon < \mu \\ 0, & \text{if } \varepsilon > \mu \end{cases} \quad (7.53)$$

This has a simple physical interpretation. The Fermi–Dirac function gives the probability that a single-particle state of energy ε is occupied. At zero temperature, the N -particle system goes to a state in which the N single-particle states of lowest energy are occupied while all higher states are unoccupied. Thus at zero temperature the chemical potential has a value equal to the cutoff energy separating the occupied states

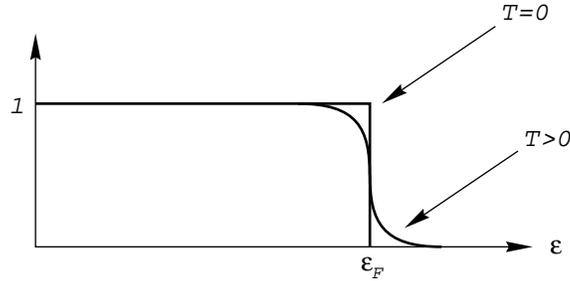


Fig. 7.4 The average occupation of a Fermi–Dirac single-particle state of energy ε at zero temperature and at some small but nonzero temperature.

from the unoccupied ones. This is called the *Fermi energy* and is written ε_F . The Fermi energy is defined by the relation [see Eq. (7.50)]

$$n = \frac{N}{V} = 2\gamma \int_0^{\varepsilon_F} \varepsilon^{1/2} d\varepsilon = \frac{4}{3}\gamma\varepsilon_F^{3/2} \quad (7.54)$$

which gives $\varepsilon_F = (3n/4\gamma)^{2/3}$. At finite temperature $f_{\text{FD}}(\varepsilon)$ deviates from its zero-temperature limit, as shown in Fig. 7.4.

In the Mathematical Appendix, the following low-temperature expansion is derived for the general Fermi–Dirac integral shown in Eq. (7.52).

$$\int_0^{\infty} \frac{g(\varepsilon) d\varepsilon}{e^{(\varepsilon-\mu)/\tau} + 1} = \int_0^{\mu} g(\varepsilon) d\varepsilon + \frac{\pi^2}{6} g'(\mu) \tau^2 + \frac{7\pi^4}{360} g'''(\mu) \tau^4 + \dots \quad (7.55)$$

where the primes indicate derivatives with respect to ε , evaluated at $\varepsilon = \mu$. Using this expansion to order τ^2 in Eq. (7.50) gives the following relation for the particle density, $n = N/V$.

$$\frac{3n}{4\gamma} \approx \mu^{3/2} + \frac{\pi^2 \tau^2}{8\mu^{1/2}} \quad (7.56)$$

We can determine the dependence of the chemical potential μ on the temperature τ for small τ as follows. In the second term, which is of order τ^2 , we will make a negligible error in replacing μ by ε_F . The left-hand side is equal to $\varepsilon_F^{3/2}$. Therefore

$$\varepsilon_F^{3/2} \approx \mu^{3/2} + \frac{\pi^2 \tau^2}{8\varepsilon_F^{1/2}} \quad (7.57)$$

Dividing through by $\varepsilon_F^{3/2}$, solving for μ/ε_F , and expanding the solution as a power series in τ^2 gives

$$\frac{\mu}{\varepsilon_F} \approx \left(1 - \frac{\pi^2 \tau^2}{8\varepsilon_F^2}\right)^{2/3} \approx 1 - \frac{\pi^2 \tau^2}{12\varepsilon_F^2} \quad (7.58)$$

or

$$\mu \approx \varepsilon_F - \frac{\pi^2 \tau^2}{12\varepsilon_F} \quad (7.59)$$

which shows that, to first order in τ , the chemical potential is independent of temperature for fixed density. The reason is that, in going from zero temperature to some low temperature, the *change* in the Fermi–Dirac distribution function is an odd function of $\varepsilon - \mu$. Thus for fixed μ the same number of particles are added to the region $\varepsilon > \mu$ as are removed from the region $\varepsilon < \mu$ (see Fig. 7.4).

The expansion of the energy equation to second order in τ is

$$\frac{E}{2\gamma V} = \frac{2}{5}\mu^{5/2} + \frac{\pi^2}{4}\mu^{1/2}\tau^2 \quad (7.60)$$

The energy to order τ^2 at fixed n is obtained by using $\mu = \varepsilon_F - \pi^2\tau^2/12\varepsilon_F$ in this equation and retaining terms of order τ^2 . Using the definition of ε_F , the result can be expressed in the form

$$\frac{E}{N} = \frac{3}{5}\varepsilon_F + \frac{\pi^2\tau^2}{4\varepsilon_F} \quad (7.61)$$

The pressure as a function of temperature and density is then given by the relation $p = \frac{2}{3}(E/V)$.

The dimensionless expansion parameter in these expressions is clearly τ/ε_F . If $\tau/\varepsilon_F \gg 1$, then the ideal Fermi gas behaves as a classical ideal gas. In that case it is said to be *nondegenerate*. For $\tau/\varepsilon_F \ll 1$ the gas is called a *degenerate* Fermi gas, and the exclusion principle is the most important factor determining the properties of the system.

7.6 THE ELECTRON GAS

A metallic crystal is distinguished from other types of crystals by the existence of a large system of *conduction electrons* within it. The number of conduction electrons is equal to the number of atoms in the sample times the valence of the atomic species (1 for sodium, potassium, and copper, 2 for zinc, etc.). The conduction electrons occupy single-particle quantum states in what is called the *conduction band*. Semiconductors also contain conduction electrons, but these are either electrons that have been thermally excited from the valence band to the conduction band (in which case the material is called an *intrinsic semiconductor*) or they are electrons that are associated with donor impurities (in a *doped semiconductor*). In either case, the number of conduction electrons is much smaller than it is for a typical metal. At zero temperature the states in the conduction band are filled (two electrons per state, with opposite spins) up to the Fermi energy, ε_F . Each state in the conduction band is also an eigenstate of crystal momentum with eigenvalue $\mathbf{p} = \hbar\mathbf{k}$, where \mathbf{k} is the wave vector of the state. For some metals the relationship between the energy and momentum of a state in the conduction band can be approximated by that for a free particle.

$$\varepsilon_{\mathbf{k}} = \frac{\hbar^2 k^2}{2m^*} \quad (7.62)$$

where the *effective mass* m^* is a parameter that is of the order of an electron mass but is not equal to m_e .

We can get an estimate of the contribution made by the conduction electrons to the specific heat of a typical metal by taking $m^* = m_e$ and $V/N = a^3$, where $a = 4 \text{ \AA}$ is the diameter of a sodium atom. Using these values to calculate γ and ε_F , we find that $\varepsilon_F \approx 1 \text{ eV}$. This energy corresponds to a temperature of about 10,000 K. Therefore, at room temperature, the expansion parameter $\tau/\varepsilon_F \approx 0.03$, which justifies neglecting all but the first nonvanishing term in the expansion for E/N . The specific heat per particle at room temperature is then given by

$$C_{\text{el}} = \frac{\partial(E/N)}{\partial T} = \frac{\pi^2 k^2 T}{2\varepsilon_F} \approx 0.15 k \quad (7.63)$$

where k is Boltzmann's constant. The Debye temperature of sodium is about 158 K and, therefore, at room temperature we can use the Dulong–Petit law, which states that the vibrational specific heat per particle is equal to $3k$.

$$C_{\text{vib}} = 3k \quad (7.64)$$

Comparing these equations shows that at room temperature the electronic motion makes only a slight contribution to the specific heat of a metal. However, at temperatures lower than the Debye temperature of the metal, the vibrational specific heat goes to zero as T^3 while the electronic specific heat is proportional to T . Thus at sufficiently low temperature the electronic specific heat dominates.

7.7 THE IDEAL BOSE GAS AT LOW TEMPERATURE

As $T \rightarrow 0$ the Pauli exclusion principle becomes the most important factor determining the properties of a system of fermions. Since bosons do not satisfy an exclusion principle, their physical characteristics at low temperature will obviously be very different from those of fermions. In this section we will analyze the low-temperature properties of a gas of noninteracting spinless bosons. The basic equations for N and E in

terms of α and β can be taken from the fermion case by dropping the factor of 2 that is due to the spin degeneracy, and making a change of sign in the Fermi–Dirac distribution function. When this is done, the equation for N [Eq. (7.50)] becomes

$$n = \frac{N}{V} = \gamma \int_0^\infty \frac{\varepsilon^{1/2} d\varepsilon}{e^{\alpha+\beta\varepsilon} - 1} \quad (7.65)$$

The temperature dependence of this equation can be made explicit by transforming the variable of integration to $x = \beta\varepsilon$.

$$n = \gamma\tau^{3/2} \int_0^\infty \frac{x^{1/2} dx}{e^{\alpha+x} - 1} \quad (7.66)$$

The affinity is limited to the range $0 \leq \alpha < \infty$. If α is chosen to be negative, then $f_{\text{BE}}(\varepsilon)$ would be negative at small ε , which is physically meaningless, because it is the average occupation of a single-particle state. It is easy to see that $n(\alpha, \tau)$ is a monotonically decreasing function of α (at each value of x , the integrand decreases if α is increased). The maximum value, which occurs at $\alpha = 0$, is

$$n_c(\tau) = \gamma\tau^{3/2} \int_0^\infty \frac{x^{1/2} dx}{e^x - 1} \quad (7.67)$$

n_c is called the critical density. This integral is of a type that can be evaluated in terms of the gamma function $\Gamma(x)$ and the Riemann zeta function $\zeta(x)$. The general formula is

$$\int_0^\infty \frac{x^\nu dx}{e^x - 1} = \Gamma(\nu + 1)\zeta(\nu + 1) \quad (7.68)$$

The maximum particle density is therefore given by

$$n_c(\tau) = \Gamma\left(\frac{3}{2}\right)\zeta\left(\frac{3}{2}\right)\gamma\tau^{3/2} \quad (7.69)$$

But this result is clearly absurd! Since the particles do not interact, there is no physical mechanism preventing one from constructing a system with a density greater than n_c . A mistake has been made somewhere. The mistake is not hard to find. The lowest-energy single-particle state is the zero-momentum state (which has zero energy). According to the Bose–Einstein distribution, the number of particles in that state at affinity α is

$$N_{\mathbf{p}=0} = \frac{1}{e^\alpha - 1} \rightarrow \infty \quad \text{as } \alpha \rightarrow 0 \quad (7.70)$$

Thus, in making the transformation from a sum over discrete momentum states to an integral, the zero-momentum state must be singled out for special treatment. In Problem 7.22, the reader is asked to show that this is sufficient to fix the difficulty; it is not necessary to take into account, individually, the other very low-energy states neighboring the zero-momentum state. Therefore, Eq. (7.66) must be modified to read

$$n = \frac{1}{V(e^\alpha - 1)} + \gamma\tau^{3/2} \int_0^\infty \frac{x^{1/2} dx}{e^{\alpha+x} - 1} \quad (7.71)$$

With this modification, for any value of the density n , there is a corresponding value of the affinity α that satisfies this equation. When n is larger than the critical density, then α is of order $1/N$ and, in the integral part of Eq. (7.71), α may be set equal to zero. In this case, a finite fraction of all of the particles in the system occupy the discrete zero-momentum quantum state.

The collection of particles in the zero momentum state is called the Bose–Einstein *condensate*. It exists whenever $n > n_c(\tau)$. The number of particles in the condensate is just the difference between the total number of particles and $n_c V$. Since the condensate, when it exists, accounts for a finite fraction of the particles in the system, the gas with the condensate has macroscopically different properties than the gas without it. The change from one state to the other is a thermodynamic phase transition, called *Bose condensation*. The phase diagram is shown in Fig. 7.5. The phase without the condensate (that is, $n < n_c$) is called phase I, while the phase that contains a condensate ($n > n_c$) is called phase II.

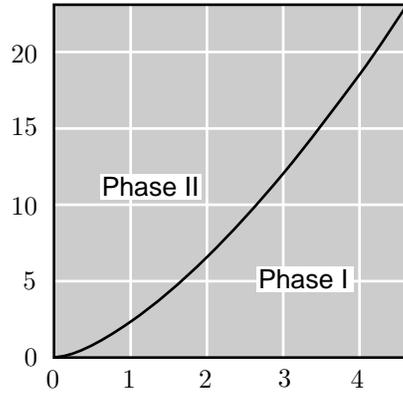


Fig. 7.5 The phase diagram for the ideal Bose gas. The vertical axis gives n/γ and the horizontal axis is $\tau = kT$. Recall that $\gamma = 2\pi(2m/h^2)^{3/2}$.

In phase I the function $\alpha(n, \tau)$ must be determined by numerically solving the Eq. (7.71) in the form

$$\int_0^\infty \frac{x^{1/2} dx}{e^{\alpha+x} - 1} = \frac{n}{\gamma\tau^{3/2}} \quad (7.72)$$

In phase II the function $\alpha(n, \tau)$ has the simple form (see Problem 7.24)

$$\alpha(n, \tau) = \frac{1}{V[n - n_c(\tau)]} \quad \text{Phase II} \quad (7.73)$$

For phase II, in any integral, the value of α may be replaced by zero, since it is of order $1/N$. The condensate particles all have zero energy; therefore, the condensate makes no contribution to the energy and so the integral expression for E can be used in both phases.

$$E(n, \tau, V) = \gamma V \int_0^\infty \frac{\varepsilon^{3/2} d\varepsilon}{e^{\alpha+\beta\varepsilon} - 1} = \gamma V \tau^{5/2} \int_0^\infty \frac{x^{3/2} dx}{e^{\alpha+x} - 1} \quad (7.74)$$

where α is understood to mean $\alpha(n, \tau)$. In the condensed phase, $\alpha \approx 0$, and thus, the energy becomes independent of n .

$$E = \gamma V \tau^{5/2} \int_0^\infty \frac{x^{3/2} dx}{e^x - 1} = \Gamma\left(\frac{5}{2}\right)\zeta\left(\frac{5}{2}\right)\gamma V \tau^{5/2} \quad \text{Phase II} \quad (7.75)$$

The constant volume specific heat (in rational units) in Phase II is

$$C_V = \frac{dE}{d\tau} = \frac{5}{2}\Gamma\left(\frac{5}{2}\right)\zeta\left(\frac{5}{2}\right)\gamma V \tau^{3/2} \quad \text{Phase II} \quad (7.76)$$

The entropy is the integral of dQ/τ .

$$S^o = \int_0^\tau \frac{C_V d\tau}{\tau} = \frac{5}{3}\Gamma\left(\frac{5}{2}\right)\zeta\left(\frac{5}{2}\right)\gamma V \tau^{3/2} \quad \text{Phase II} \quad (7.77)$$

For a given density, the transition from one phase to the other occurs at a *critical temperature* τ_c that is given by solving Eq. 7.69 for τ .

$$\tau_c = [n/\Gamma\left(\frac{3}{2}\right)\zeta\left(\frac{3}{2}\right)\gamma]^{2/3} \quad (7.78)$$

In terms of τ_c , the specific heat per particle can be written in the simple form

$$\frac{C_V}{N} = \frac{15}{4} \frac{\zeta\left(\frac{5}{2}\right)}{\zeta\left(\frac{3}{2}\right)} \left(\frac{\tau}{\tau_c}\right)^{3/2} \quad \text{Phase II} \quad (7.79)$$

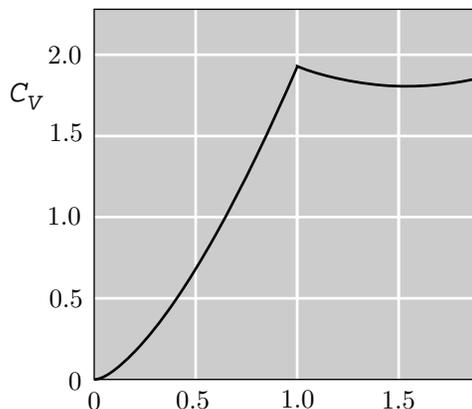


Fig. 7.6 The constant volume specific heat per particle as a function of τ/τ_c . In rational units the specific heat is dimensionless.

In Phase I, $E(n, \tau)$ and $C_V(n, \tau)$ must be calculated from Eq. (7.74) using the function $\alpha(n, \tau)$. A graph of C_V/N as a function of τ/τ_c is given in Fig. 7.6. Notice that Bose condensation is a very subtle phase transition. Across the phase transition line the density and the energy per particle are continuous. Even the specific heat is continuous. One must go to $dC_V/d\tau$ in order to find a quantity that jumps discontinuously at the phase transition.

7.8 FLUCTUATIONS IN THE IDEAL BOSE GAS*

A study of fluctuations in the ideal Bose gas below the critical temperature yields some surprising results. In phase II, $\alpha = 0$, and therefore, the fundamental relation for S° becomes

$$S^\circ = \beta E + \beta pV = \frac{E + pV}{\tau} \tag{7.80}$$

Noninteracting bosons also satisfy the ideal gas relation $pV = \frac{2}{3}E$ (see Problem 7.8), which gives

$$S^\circ = \frac{5}{3}E/\tau \tag{7.81}$$

Equation (7.75) gives τ as a function of the energy density E/V , which can be used in Eq. (7.81) to write S° in terms of E and V .

$$S^\circ = \frac{5}{3} \left(\Gamma\left(\frac{5}{2}\right) \zeta\left(\frac{5}{2}\right) \gamma \right)^{2/5} V^{2/5} E^{3/5} \tag{7.82}$$

We notice that this entropy function does not contain the variable N . This is reasonable, because $\alpha = (\partial S^\circ / \partial N)_E = 0$ in phase II. If more particles are added to the system, they all go into the condensate, leaving E and S° unchanged. We will now see that this has disastrous consequences for the thermodynamic properties of the system. Letting s° , n , and ε be the entropy, number of particles, and energy per unit volume, Eq. (7.82) can be written

$$s^\circ(n, \varepsilon) = \frac{5}{3} A \varepsilon^{3/5} \tag{7.83}$$

where $A = \left[\Gamma\left(\frac{5}{2}\right) \zeta\left(\frac{5}{2}\right) \gamma \right]^{2/5}$. The fact that s° is not a function of n means that, in the situation depicted in Fig. 7.7, the condition of maximum entropy would not determine the equilibrium density in the two halves.

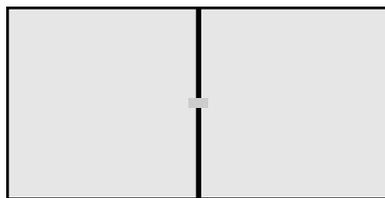


Fig. 7.7 Two volumes containing an ideal Bose gas are connected by a pinhole.

This peculiar phenomenon is easy to understand. Because the condensate particles all have zero momentum, they make no contribution to the pressure in a container. Thus, if the condensate densities in the left and right sides were unequal, this would not create a pressure difference that would bring the system back to equal densities. Because of this characteristic, the ideal Bose gas cannot be considered as an acceptable model of any physical system. An example of the bad features of the model is that, in the presence of a weak gravitational field in the z direction, if the temperature is below the critical temperature, all of the condensate, which contains a finite fraction of the particles in the system, becomes smeared against the bottom of the vessel in a single quantum state that has a scale height of $(\hbar^2/m^2g)^{1/3}$. For the earth's gravitational field, which is weak for thermodynamic purposes, this scale height is about one micrometer (see Problem 7.28). Also, if the periodic boundary conditions are replaced by hard-wall boundary conditions, then a macroscopic change would take place in the particle density throughout the container, not only near the walls (see Problem 7.29). This extreme sensitivity of the particle density to the boundary conditions is never exhibited by real systems.

7.9 THE MEAN-FIELD INTERACTION*

In order to obtain a reasonable model of a system of Bose–Einstein particles, some interaction between the particles must be introduced. Even a very weak interaction eliminates the bizarre properties of the model. In order to construct a model that has normal physical properties without seriously complicating the analysis, we will introduce an interaction potential, $v(r)$, with the following characteristics:

1. $v(r)$ is a steadily decreasing positive function. Therefore, it creates purely repulsive interparticle forces.
2. The range of $v(r)$ is much larger than the average distance between particles in the system but the volume integral of $v(r)$, $4\pi \int_0^\infty v(r)r^2 dr = \sigma$, is finite.

An interaction potential with these characteristics, called a *mean-field interaction*, can be constructed by starting with any positive, decreasing potential function $V(r)$ that has a finite volume integral σ and reducing its amplitude while increasing its range by scaling it according to the formula

$$v(r) = \epsilon^3 V(r/\epsilon) \quad (7.84)$$

where ϵ is a dimensionless adjustable parameter. The integral of $v(r)$ is then independent of ϵ , but its range gets larger and larger as ϵ is made smaller and smaller.

For very small values of ϵ the interaction between any two particles is negligible but a particle finds itself in a very smooth potential field due to the combined interactions of thousands of particles in its large “interaction volume.” If the density of particles is uniform, then that potential field will be constant. But adding a constant to the Hamiltonian will not change the energy eigenfunctions of the system. Thus the energy eigenstates for the uniform ideal Bose–Einstein gas are still energy eigenstates of the system, but their energies have been shifted by an amount that depends upon the particle density. Being careful not to double count the interaction energies, one can easily evaluate the total energy of a state with occupation numbers $N_{\mathbf{p}}$.

$$E = \sum_{\mathbf{p}} \frac{p^2}{2m} N_{\mathbf{p}} + \frac{1}{2} \sigma n N \equiv E_K + \frac{1}{2} \sigma n N \quad (7.85)$$

where the sum is over all the momentum eigenstates of the system, σ is the volume integral of $v(\mathbf{r})$, and $n = N/V$. With fixed N , a shift in all energy levels has no effect on their occupations. Therefore, E_K and S° , as functions of T , are unaffected by the shift. Thus we can use Eq. (7.83) for S° with E replaced by E_K .

$$S^\circ(N, E, V) = \frac{5}{3} A V^{2/5} (E - \frac{1}{2} \sigma n^2 V)^{3/5} \quad (7.86)$$

The entropy per unit volume is then

$$s^\circ(n, \epsilon) = \frac{5}{3} A (\epsilon - \frac{1}{2} \sigma n^2)^{3/5} \quad (7.87)$$

The reader will be asked to show (see Problem 7.30) that this entropy function is strictly convex and therefore leads to reasonable predictions for macroscopic properties. (Note that, because E_K is always positive, ϵ has the range $\frac{1}{2} \sigma n^2 < \epsilon < \infty$.)

7.10 THE STATISTICS OF COMPOSITE PARTICLES

The elementary particles of nature are either bosons or fermions. Those that contribute to the structure of atoms, namely protons, neutrons, and electrons, are all spin- $\frac{1}{2}$ Fermi–Dirac particles. The atom, when treated as a single particle, inherits its statistics from the elementary particles that compose it. If it contains an even number of elementary fermions, then it is itself a Bose–Einstein particle; if it contains an odd number, it is a Fermi–Dirac particle. The reasoning behind this rule is easily understood by considering a simple example. A hydrogen molecule can be treated either as a system composed of two hydrogen atoms or as a system of two protons and two electrons. In the first case, it has a wave function $\phi(Q_A, Q_B)$, where Q_A and Q_B are each a set of coordinates, sufficient to define the position and state of a hydrogen atom. In the second case it has a wave function $\psi(x_A, y_A, x_B, y_B)$, where x_A and x_B are coordinates appropriate to the two protons and y_A and y_B are each space and spin coordinates for an electron. The transformation

$$\psi(x_A, y_A, x_B, y_B) \longrightarrow \psi(x_B, y_B, x_A, y_A) \quad (7.88)$$

which describes an exchange in position of the protons and the electrons, is equivalent to the combination of the two separate transformations

$$\psi(x_A, y_A, x_B, y_B) \longrightarrow \psi(x_B, y_A, x_A, y_B) \longrightarrow \psi(x_B, y_B, x_A, y_A) \quad (7.89)$$

But, because protons and electrons are Fermi–Dirac particles, each of the separate transformations multiplies the wave function ψ by -1 . Thus, the combined transformation leaves ψ unchanged. When this fact is expressed in atomic coordinates it takes the form

$$\phi(Q_a, Q_B) = \phi(Q_B, Q_a) \quad (7.90)$$

This line of reasoning clearly leads to the conclusion that the exchange of the full sets of coordinates for two identical atoms multiplies the wave function by $+1$ or -1 depending upon whether the atoms contain an even or odd number of elementary fermions.

7.11 SUPERFLUIDITY AND LIQUID HELIUM

There is no real system that is well approximated by the ideal Bose gas. Photons are Bose–Einstein particles, and they are noninteracting to a very high degree, but the fact that the number of photons is not a conserved quantity has a strong effect on the properties of the photon gas. In particular, it eliminates the phase transition associated with Bose condensation, which is the most striking characteristic of the ideal Bose gas. The photon gas will be discussed in a later section.

Liquid helium is the system that is closest (although not very close) to the ideal Bose gas. Helium exists in two isotopic forms, ^3He and ^4He . The two isotopes, although they are chemically almost identical, have very different physical properties at low temperatures. The differences in their physical characteristics are not due to the difference in their masses, which are approximately in a ratio of 3 to 4. Their most fundamental difference is that the ^3He atom, composed of 5 fermions (2 protons, 1 neutron, and 2 electrons), is itself a Fermi–Dirac particle, while the ^4He atom is a Bose–Einstein particle. We will restrict our attention to the heavier isotope, which incidentally constitutes the bulk of naturally occurring helium, the lighter isotope contributing less than one part per million. The phase diagram of bulk ^4He is shown in Fig. 7.8. It differs substantially from that of other inert elements, such as neon and argon. It has no triple point, in the ordinary sense of having liquid, solid, and gas simultaneously in equilibrium, because the liquid phase extends down to zero temperature. The λ line separates two different liquid phases. (The isotopes of helium are the only pure substances that have more than one liquid phase.) The phase transition separating the two liquid phases, called the *lambda transition*, derives its name from the appearance of the specific heat singularity that occurs at the transition. As can be seen in Fig. 7.8, the specific heat curve resembles the Greek letter λ . The phase transition curve in the p - T plane is called the λ line and is written $T_\lambda(p)$. If no pressure is specified, then T_λ will always mean its lower endpoint, where the λ line meets the liquid–vapor phase transition curve. Extremely careful measurements have shown that, very close to $T_\lambda(p)$, along the whole length of the λ transition line, C_p can be accurately represented by a function of the form

$$C_p = B - At^{-\alpha}(1 + D\sqrt{t}) \quad \text{for } T > T_\lambda(p) \quad (7.91)$$

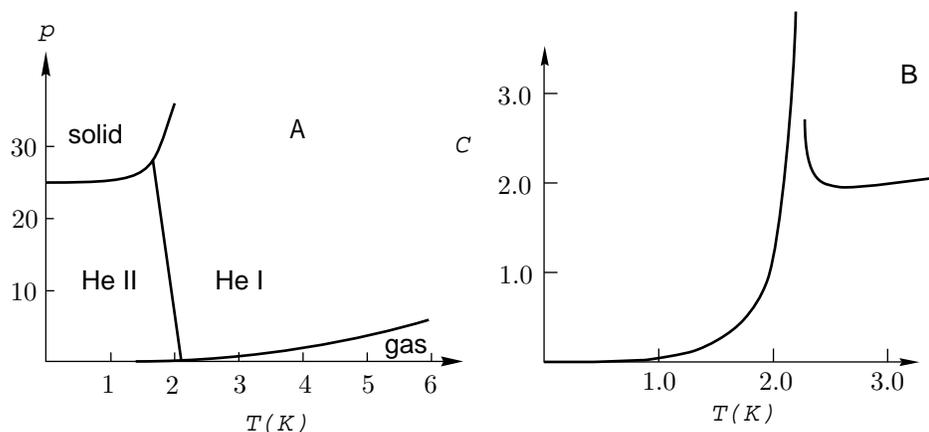


Fig. 7.8 (A) The phase diagram for ^4He . At zero temperature, it requires about 25 atmospheres of pressure to solidify helium. (B) The specific heat of liquid helium in equilibrium with its own vapor (in J/g-K).

and

$$C_p = B' - A't^{-\alpha}(1 + D'\sqrt{t}) \quad \text{for } T < T_\lambda(p) \quad (7.92)$$

where $t = |T - T_\lambda|/T_\lambda$ is a dimensionless temperature variable. The parameters A , A' , B , B' , D , and D' have values that vary substantially along the λ transition line, but their ratios, A/A' , B/B' , and D/D' , are independent of position on the λ line. The values of these *universal amplitude ratios* and the value of the *critical exponent* α (all given in Table 7.1) can be calculated using the renormalization group theory of critical phase transitions, which will be discussed in a later chapter. There is, at present, no way of calculating the individual amplitudes, $A(p)$, $B(p)$, and $D(p)$. They must be taken from experiment.

Table 7.1
Specific heat parameters for liquid He*

α	A/A'	B/B'	D/D'
-.016	1.07	1.00	1.03

* These values are “best estimates.” There is still substantial experimental and theoretical uncertainty in them.

Although liquid helium is a system of strongly interacting particles, and therefore has properties very different from the ideal Bose gas, it has one thing in common with the ideal Bose gas; it is clear that the λ transition is associated with a Bose–Einstein condensation of the helium atoms into a macroscopically occupied single-particle quantum state. Liquid helium has another striking property, namely superfluidity, that the ideal Bose gas, if it existed, would not have. The phenomenon of superfluidity, in which a fluid can flow through extremely narrow, crooked channels with absolutely no resistance or viscosity, seems to defy one’s physical intuition. In this section we will explore the basic mechanism that leads to superfluidity.

In trying to elucidate the mechanism of superfluidity, we will consider the properties of the substance near zero temperature, where the theoretical analysis is simpler than it is close to the λ line. The most essential aspect of the analysis is the form of the quantum mechanical excitations near the ground state. According to Eq. (7.85), the total energy and momentum of a Bose–Einstein gas with mean-field interactions can be written in terms of a set of occupation numbers as

$$E = E_g + \sum_{\mathbf{p}} N_{\mathbf{p}} \varepsilon_{\mathbf{p}} \quad (7.93)$$

and

$$\mathbf{P} = \sum_{\mathbf{p}} N_{\mathbf{p}} \mathbf{p} \quad (7.94)$$

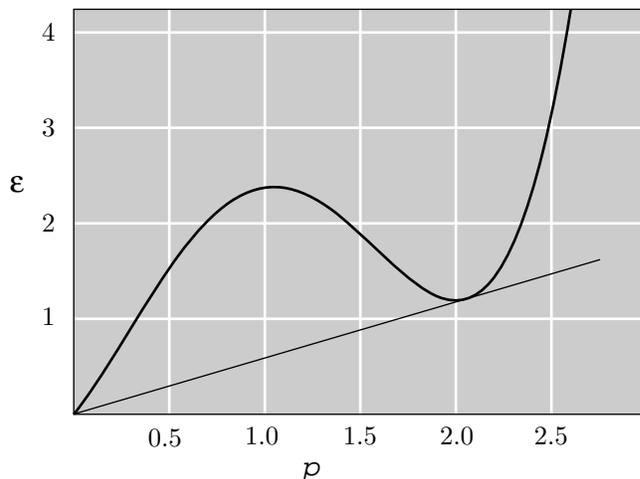


Fig. 7.9 The relation between energy and momentum for the elementary excitations in liquid helium near zero temperature. ϵ is given in units of 10^{-22} J and p in units of 10^{-24} kg-m/s. The slope of the straight line is defined as V_c .

where the ground-state energy, E_g , depends on the total density and $\epsilon_p = p^2/2m$. Each occupation number can take the values $0, 1, 2, \dots$. Any many-particle system whose total energy and momentum eigenvalues satisfy formulas of this general form is said to have a Bose–Einstein quasiparticle spectrum. For the ideal Bose gas the quasiparticles are simply the actual particles in the system, and the prefix “quasi” is therefore illogical. However, for liquid ^4He close to $T = 0$, it can be shown, both experimentally and theoretically, that the energy and momentum eigenstates are given by formulas like Eqs. (7.93) and (7.94) in which the quasiparticles are quantized sound waves or phonons. These excitations are similar to the phonon excitations that account for the vibrational specific heat of crystals at low temperatures, with the one difference that, for a liquid, there are only longitudinally polarized waves. The energy and momentum carried by a phonon are given in terms of its angular frequency and wave vector by $\epsilon = \hbar\omega$ and $\mathbf{p} = \hbar\mathbf{k}$. For very long wavelengths (very small k) the usual dispersion relation for sound waves, $\omega = ck$, where c is the speed of sound, gives rise to a linear energy function.

$$\epsilon_p = cp \tag{7.95}$$

As the wavelength decreases, becoming comparable to the average interparticle spacing in the liquid, the function ϵ_p begins to differ substantially from its long-wavelength linear form. The actual energy-momentum relation for quasiparticle excitations in liquid ^4He is shown in Fig. 7.9. The quasiparticle excitations in the linear part of the curve are called *phonons*; those near the local minimum are called *rotons*. There is no sharp borderline between phonons and rotons. In Fig. 7.9, a line is drawn whose slope defines what we will call the *critical velocity*, V_c . The critical velocity is the largest velocity that has the property that $V_c \leq \epsilon_p/p$ for all quasiparticle excitations.

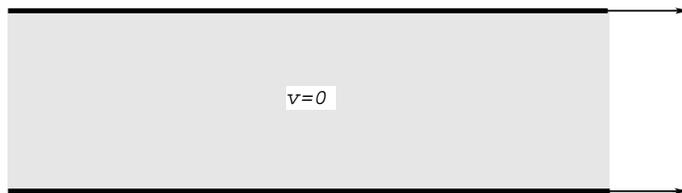


Fig. 7.10 A stationary sample of liquid helium at $T = 0$ fills an infinite pipe that is initially moving to the right.

To see how the details of the excitation spectrum are associated with the existence of superfluidity, we consider the system shown in Fig. 7.10. An infinite circular pipe, whose linear mass density is M , is filled with liquid ^4He in its ground state. The pipe, but not the fluid, is initially moving to the right at a speed v , less than V_c . We do not assume that the surface of the pipe is perfectly smooth. Rather, we assume

that it has microscopic irregularities that would, because of the relative motion of the pipe and the fluid, be expected to transfer energy and momentum from the pipe to the fluid until both are moving with the same velocity. This would mean that, at some later time, the fluid would no longer be in its ground state but would be in some excited state of energy E and momentum P . Naturally, the energy and momentum picked up by the fluid must have come from the pipe, since the total system is assumed to be isolated. The pipe is assumed to be a heavy, classical system. We will consider what happens within a unit length of the pipe. Initially, the pipe has an energy $Mv^2/2$ and the fluid has energy E_g . At the later time, the pipe velocity has decreased to $v - \Delta v$ and the fluid is in an excited state described by occupation numbers $\{N_{\mathbf{p}}\}$. The energy and momentum conservation laws demand that

$$\frac{1}{2}Mv^2 + E_g = \frac{1}{2}M(v - \Delta v)^2 + E_g + \sum_{\mathbf{p}} N_{\mathbf{p}}\varepsilon_p \quad (7.96)$$

and

$$Mv = M(v - \Delta v) + \sum_{\mathbf{p}} N_{\mathbf{p}}p_x \quad (7.97)$$

If we assume that $\Delta v \neq 0$, then

$$\sum_{\mathbf{p}} N_{\mathbf{p}}\varepsilon_p = Mv\Delta v - \frac{1}{2}M(\Delta v)^2 < Mv\Delta v \quad (7.98)$$

and

$$M\Delta v = \sum_{\mathbf{p}} N_{\mathbf{p}}p_x \leq \sum_{\mathbf{p}} N_{\mathbf{p}}p \quad (7.99)$$

Using the second inequality to eliminate $M\Delta v$ in the first, we get

$$\sum_{\mathbf{p}} N_{\mathbf{p}}\varepsilon_p < v \sum_{\mathbf{p}} N_{\mathbf{p}}p \quad (7.100)$$

or

$$\sum_{\mathbf{p}} N_{\mathbf{p}}(\varepsilon_p - vp) < 0 \quad (7.101)$$

But this is clearly impossible, since $\varepsilon_p - vp > 0$ for all \mathbf{p} and $N_{\mathbf{p}} \geq 0$. (Remember that we have assumed that v is less than V_c .) Thus, the only solution to the energy and momentum conservation laws is the trivial one, $\Delta v = 0$ and $N_{\mathbf{p}} = 0$ for all \mathbf{p} . In spite of its rough surface, there is no way that the pipe can transfer energy and momentum to the fluid without violating the fundamental conservation laws. Therefore, according to our argument, no energy and momentum will be transferred and the fluid will simply remain stationary, sitting there inside a rough, moving pipe! It would be very reasonable for the reader to react with extreme skepticism toward this bizarre conclusion. To overcome some of that skepticism, we describe the following real experiment.

A toroidal (doughnut-shaped) hollow tube is tightly packed with a fine powder, such as ground glass, saturated with liquid helium, and sealed (see Fig. 7.11). It is mounted on a fine wire so that it can oscillate about its axis of symmetry as a torsional pendulum within an evacuated, temperature-controlled chamber. The resonant frequency of the torsional pendulum is monitored as the temperature is gradually reduced. It remains constant until the temperature falls below T_λ . Then the oscillation frequency begins to increase and, near $T = 0$, reaches the value that it would have if there were no liquid helium present, that is, if only the container and the ground glass were contributing to the moment of inertia. The process is completely reversible. If the temperature is raised, the full moment of inertia returns. The only obvious explanation is that, below T_λ , only a part of the fluid (called the *normal fluid* component) is participating in the oscillatory motion, while the rest of it (the *superfluid* component) avoids moving along with the tube by winding its way, without resistance, through the narrow convoluted channels between the pieces of ground glass! One should not attempt to picture the superfluid motion as the ordinary motion of fluid particles. It is something closer to quantum tunneling on a massive scale. A way to appreciate just how “quantum mechanical” the superfluid motion is, is to remember that, if a helium atom is in a single-particle quantum state that extends

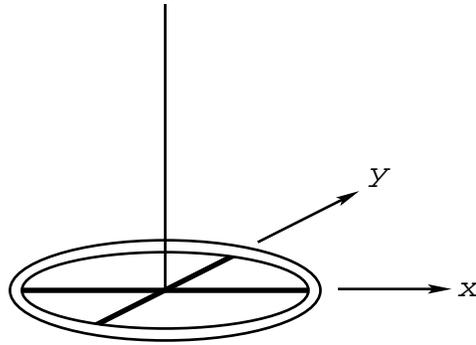


Fig. 7.11 A hollow toroid, filled with packed powder and liquid helium, hangs on a wire so that it can oscillate about its axis of symmetry as a torsional pendulum.

throughout the free volume within the torus, then that atom is not at any particular place in the torus at all—it is simultaneously everywhere in that macroscopic volume! But, with Bose–Einstein condensation, a substantial fraction of the particles are in just such a macroscopically extended state.

Another real experiment, using the same ground glass filled torus, illustrates the wonders of superfluid motion even more clearly. By rotating the wire, the torus is spun like a top about its symmetry axis. This is done at a temperature above T_λ . Keeping the rotation constant, the temperature is gradually reduced to near 0 K. Then a small amount of friction is applied to the wire so that the torus slows down and stops. Everything looks completely quiescent. Let us call the symmetry axis (the wire axis) the z axis and choose perpendicular x and y axes in the plane of the torus. Now a small amount of torque is applied about the x axis. Due to that torque the torus rotates *about the y axis*, like a spinning top! The torus clearly carries angular momentum. The fluid inside has never stopped moving and is now flowing freely through the narrow channels. Remember, the fluid was put into rotation while it was normal ($T > T_\lambda$), kept rotating as it was cooled to $T = 0$, and only then was the torus slowed down.

7.12 QUANTIZED VORTICES

There is an important flaw in the theoretical analysis given here that we have to discuss now. The experiments that we have described all involved tubes filled with ground glass. This was not intended only to make the phenomenon seem still more spectacular. If the same experiments are done using a hollow tube, filled only with liquid helium, they will not work as described. In general, when liquid helium near zero temperature flows through a channel, it will behave as a superfluid as long as the flow velocity is less than some critical velocity V_c . But the critical velocity will not be equal to the slope of the line drawn in Fig. 7.9. Instead it will depend on the size of the channel, and for macroscopic channels it will be so small that the superfluid phenomena will be very difficult to observe. The source of the difficulty is not that the basic logic of the theoretical analysis is wrong, but rather that we have not taken into account all possible excited states of the system. The value of the critical velocity is determined by the ratio of the energy of an excitation to its momentum. There exist other excitations, whose nature we will describe shortly, that have much higher energies than the phonon or roton modes shown in Fig. 7.9 but that nonetheless have much lower energy-to-momentum ratios. The creation of those excitations allows energy and momentum to be transferred to the fluid at a much lower critical velocity than that determined from the phonon–roton spectrum.

To describe the nature of the excited states that we have missed, it is best to consider the case of helium within a small rotating bucket rather than the case of helium flowing through a tube (Fig. 7.12). If a bucket containing liquid helium at $T = 0$ is slowly brought into rotation, the liquid will behave in the following way. (We are now describing real experiments, not theoretical predictions, although the two things agree.) If the angular velocity of the bucket is maintained at some small value, the liquid will remain stationary as the bucket rotates around it. If the angular velocity of the bucket is increased beyond some critical angular velocity, then the stationary fluid will make an abrupt transition to a state in which there is a *vortex line* near the axis of rotation. Actually, there is a certain energy barrier (intermediate states of higher energy) between the stationary state and the state with the vortex line, so that the experimenter may be required to tap the experimental apparatus gently in order to help along the transition. But once the line has been created, further taps will not create new lines nor get rid of the one that is there. If the angular velocity

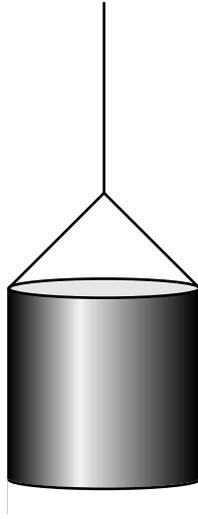


Fig. 7.12 A cylindrical bucket of liquid helium can be rotated about its symmetry axis. Actually, the bucket must be closed on top; otherwise it will empty by the liquid creeping up and down over the surface of the bucket—a characteristic of liquid helium that has not been discussed in the text.

of the bucket is below the critical angular velocity no amount of tapping will create a stable vortex line. The vortex line, running from top to bottom, is a very miniaturized version of the whirlpool created in an emptying sink or bathtub. The center of it, which is almost entirely empty, has a diameter of only a few Ångströms. The fluid flows around the line with a velocity that decreases with distance from the line. The *vorticity*, which is defined as the line integral of the local fluid velocity along any path encircling the line, is exactly equal to h/m , where h is Planck's constant and m is the mass of a helium atom.

$$\oint \mathbf{v} \cdot d\mathbf{l} = \frac{h}{m} \quad (7.102)$$

The existence of this quantum of vorticity is well understood. In fact, it was predicted theoretically long before it was experimentally observed. It can be derived by assuming that the superfluid velocity is related to the condensate wave function by the equation $m\mathbf{v}(\mathbf{r}) = \hbar\nabla\phi$, where the macroscopically occupied state is of the form $\psi = Re^{i\phi}$ (see Problem 7.32).

Returning to the experiment, if the angular velocity is increased further, at a second critical value a second vortex line appears. The two lines do not coalesce, but remain separated. Vortex lines of vorticity $2h/m$ are not fundamentally forbidden, but they are energetically unfavorable in comparison with two single lines. As the angular velocity is increased, more and more quantized vortex lines are created. Of course, the flow around each vortex line is in the direction of the bucket rotation. Once there are many lines, they will distribute themselves so that the average fluid velocity (averaged over a volume containing many vortex lines) will be the same as would exist in rigid body motion. Since an ordinary fluid would rotate (in a rotating bucket) with rigid body motion, the liquid helium, if not observed very carefully, would seem to be rotating like an ordinary fluid. Actually, once the first vortex line is created, the macroscopically occupied single-particle state is no longer a zero-momentum eigenstate. Rather, it is a quantum state with a macroscopic flow pattern that includes the vortex line. That is, the excited states that we have neglected in our analysis are not states in which a small vibration has been set up in an otherwise uniform stationary fluid, but ones in which all the fluid participates in a quantized flow with a velocity that is everywhere proportional to Planck's constant. For liquid helium flowing through a pipe, the excited states that are important in determining the critical flow velocity are states containing quantized *vortex rings*, as illustrated in Fig. 7.13. The critical velocity associated with the creation of quantized rings goes to zero as the channel size increases. However, for very narrow channels, V_c increases to about 50 m/s, a value comparable to the slope of the line in Fig. 7.9.

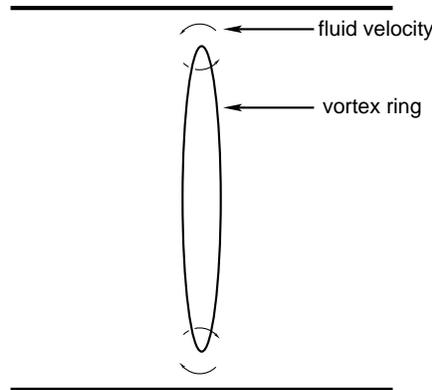


Fig. 7.13 If liquid helium is flowing through a pipe at a velocity larger than its critical velocity, it will transfer energy and momentum to the pipe by creating vortex rings, which are quantized flow patterns in which the singular vortex line is in the form of a closed ring, similar to a smoke ring (which the reader has probably never seen, since nobody smokes these days).

7.13 THE TWO-FLUID MODEL

Liquid ${}^4\text{He}$, below the λ transition, behaves as if it were composed of two interpenetrating fluids that can pass through one another without friction. The first, a normal fluid, has properties similar to helium above the λ transition. That is, it has a small but finite viscosity and interacts normally with the surface of the container. The second, a superfluid, flows without friction in a flow pattern determined by the phase of the condensate wave function. The mass density of the helium, which depends only slightly on temperature, is the sum of the mass densities of the normal and the superfluid components.

$$\rho = \rho_n(T) + \rho_s(T) \quad (7.103)$$

The superfluid and normal fractions are shown in Fig. 7.14 as functions of T at saturated vapor pressure. Notice that, below 1 K, liquid helium is almost a pure superfluid.

Now we need to clarify a subtle and easily confused point. We called the collection of particles in the macroscopically occupied single-particle state the condensate. (For liquid helium at rest the condensate state is simply the zero-momentum state, but in the presence of superfluid flow it is more complicated.) No one has yet succeeded in measuring the fraction of particles in the condensate, but it is possible to make fairly reliable theoretical estimates of the condensate fraction. At zero temperature it is estimated that about 10% of the particles are in the zero-momentum state. But, at the same temperature, all of the particles are in the superfluid. Clearly, the superfluid is not to be identified with the condensate. At zero temperature the whole system of N particles becomes locked into a complicated N -particle ground-state wave function that extends over the full macroscopic volume. If that wave function is expanded in terms of single-particle plane waves, then the zero-momentum plane wave has an average occupation of about $0.1 N$. But it is the complete system of particles in the N -particle ground state that moves coherently and constitutes the superfluid, not only those particles in the heavily occupied single-particle state.

For liquid helium, at close to zero temperature, it is not hard to answer the question: “What is the normal fluid?” The superfluid is then, by definition, everything else. We consider a system composed of liquid helium, in a very narrow stationary pipe, at equilibrium at some small but nonzero temperature. At time zero the pipe is instantaneously given some small velocity v that is less than the critical velocity. If the temperature were zero, then, according to our previous analysis, no change could take place in the fluid. However, at a finite temperature, thermal excitations already exist within the fluid.

If an excitation of momentum \mathbf{p} is scattered, at the wall, into a state of momentum \mathbf{p}' , then the change in energy of the liquid will be $\Delta E = \varepsilon_{\mathbf{p}'} - \varepsilon_{\mathbf{p}}$ and the ratio of energy change to momentum change will be $(\varepsilon_{\mathbf{p}'} - \varepsilon_{\mathbf{p}})/|\mathbf{p}' - \mathbf{p}|$. This quantity is not necessarily larger than V_c . In fact, it can have any value at all. For example, if $\mathbf{p}' \approx -\mathbf{p}$, then the ratio of ΔE to $|\Delta \mathbf{p}|$ will be very small. Therefore the energy and momentum conservation laws do not prevent the scattering of existing thermal excitations, although they do still prevent the transfer of momentum from the pipe to the fluid by the creation of new excitations. The

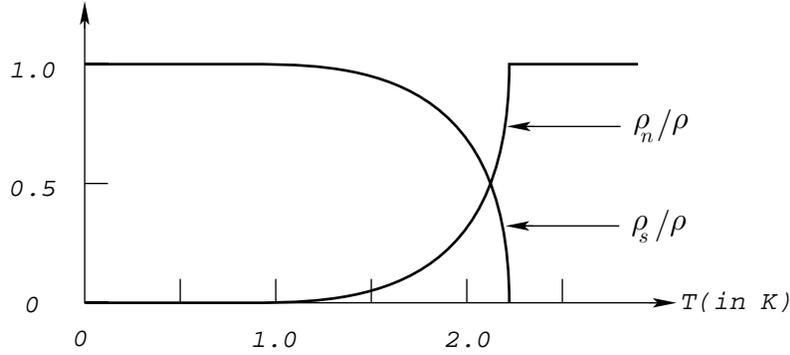


Fig. 7.14 The superfluid and normal fluid fractions, $\rho_s(T)/\rho$ and $\rho_n(T)/\rho$, between $T = 0$ and T_λ .

“quasiparticle gas” will absorb energy and momentum from the pipe, and its momentum distribution will shift until it comes into equilibrium with the pipe. Equilibrium will be established when the average group velocity of the quasiparticles is equal to the velocity of the pipe. But if the temperature is very low then the density of thermal excitations will also be very low, and equilibrium can be established with a very small transfer of energy and momentum from the pipe. Thus the system behaves as if the pipe were filled with a very low-density normal fluid. That is, the gas of thermal excitations *is* the normal fluid. The normal fluid mass density can be defined in terms of the density of momentum carried by the quasiparticle gas $\vec{\pi}$ and the velocity of the pipe \mathbf{v} , which is the same as the average group velocity of the quasiparticles.

$$\vec{\pi} = \rho_n \mathbf{v} \tag{7.104}$$

A detailed calculation of ρ_n at low temperature is left to the exercises in the supplement to this chapter.

7.14 THERMODYNAMICS OF HELIUM NEAR $T = 0$

At low temperatures, the thermodynamic properties of liquid helium, and in particular its specific heat, can be calculated by treating the system as an ideal gas of Bose–Einstein quasiparticles with the energy–momentum relation shown in Fig. 7.9. The energies of quantized vortex states are so high that those states can be completely neglected at low temperatures. Assuming that the system is contained in a cubic box of side L , the density of allowed quasiparticle momentum values is $(L/h)^3 = V/h^3$. The grand potential of the system of quasiparticles is given by Eq. (7.40), with $\zeta = -1$ and the sum converted to an integral by using the momentum state density.

$$\psi = -\frac{V}{h^3} \int \log(1 - e^{-\alpha - \beta \varepsilon_p}) d^3 \mathbf{p} \tag{7.105}$$

7.15 THE AFFINITY OF THE QUASIPARTICLE GAS

The greatest difference between the quasiparticle gas and an ordinary ideal Bose–Einstein gas is not the altered relationship between energy and momentum, but the fact that the number of quasiparticles is not a conserved quantity. The creation of a quantized sound wave does not change the number of helium atoms in the system. Thus these quantized vibrations can be freely created and absorbed at the boundary of the container. If a macroscopic variable is not constrained by a conservation law, then its value at equilibrium is determined by the maximum entropy principle of thermodynamics. That principle states that, at equilibrium,

$$\frac{\partial S}{\partial N} = 0 \tag{7.106}$$

But, by definition, $\partial S/\partial N = \alpha$, and thus, for a gas of nonconserved particles, such as the quasiparticles of liquid helium, the affinity is zero at equilibrium. (The same condition pertains to the set of quantized vibrations in a solid.) With $\alpha = 0$, the grand potential for the system is

$$\psi = -\frac{4\pi V}{h^3} \int \log(1 - e^{-\beta \varepsilon_p}) p^2 dp \tag{7.107}$$

The assumption that the quasiparticles do not interact is only valid when their density is small. As the temperature approaches T_λ , the density of quasiparticles increases to the point where their interactions strongly affect the excitation spectrum of the system. Near T_λ the system can no longer be treated as an ideal quasiparticle gas. Therefore, our present analysis is restricted to a range of temperature of about $0 < T < 2$ K. The energy at the roton minimum is ε_o , where $\varepsilon_o = 8.6$ K. Thus, below 2 K, only the states on the linear portion of the phonon curve and the roton states close to the minimum are significant. We can therefore make the approximation of replacing the single set of quasiparticles, which has a somewhat complicated spectrum, by two independent sets of quasiparticles. One set, which we will call phonons, has a purely linear energy–momentum curve with a slope given by the zero-temperature sound velocity. That is,

$$\varepsilon_p = cp \quad (7.108)$$

with $c = 244$ m/s. The other set, the rotons, have a parabolic relationship between energy and momentum, with the parameters chosen to match the experimental dispersion curve at the roton minimum. This requires that, for the rotons,

$$\varepsilon_p = \varepsilon_o + \frac{(p - p_o)^2}{2\mu} \quad (7.109)$$

where

$$\varepsilon_o/k = 8.6 \text{ K}, \quad p_o = 2.0 \times 10^{-24} \text{ kg m/s}, \quad \text{and} \quad \mu = 1.0 \times 10^{-27} \text{ kg}$$

The grand potential is the sum of the grand potentials due to the phonons and the rotons.

$$\psi = \psi_{\text{phon}} + \psi_{\text{rot}} \quad (7.110)$$

The integral for ψ_{phon} is easily calculated

$$\begin{aligned} \psi_{\text{phon}} &= -\frac{4\pi V}{h^3} \int_0^\infty \log(1 - e^{-\beta cp}) p^2 dp \\ &= -\frac{4\pi V}{(h\beta c)^3} \int_0^\infty \log(1 - e^{-x}) x^2 dx \quad (\text{with } x = \beta cp) \\ &= \frac{4\pi V}{3(h\beta c)^3} \int_0^\infty \frac{x^3 dx}{e^x - 1} \quad (\text{by partial integration}) \\ &= \frac{4\pi V}{3(h\beta c)^3} \Gamma(4)\zeta(4) \quad [\text{by Eq. (7.68)}] \\ &= \frac{4\pi^5}{45} \frac{V\tau^3}{(hc)^3} \quad (\zeta(4) = \frac{\pi^4}{90} \text{ and } \tau = \beta^{-1}) \end{aligned} \quad (7.111)$$

The roton grand potential is

$$\psi_{\text{rot}} = -\frac{4\pi V}{h^3} \int_0^\infty \log\left(1 - e^{-\beta\varepsilon_o} e^{-\beta(p-p_o)^2/2\mu}\right) p^2 dp \quad (7.112)$$

For $0 < T < 2$ K, we have $e^{-\beta\varepsilon_o} < e^{-4} = 0.018$, and therefore one can use the approximation $\log(1-x) \approx -x$, which is equivalent to using a Maxwell–Boltzmann distribution for the rotons, rather than a Bose–Einstein distribution.

$$\psi_{\text{rot}} = \frac{4\pi V}{h^3} e^{-\beta\varepsilon_o} \int_0^\infty e^{-\beta(p-p_o)^2/2\mu} p^2 dp \quad (7.113)$$

The maximum of the exponential factor in the integral, which occurs at $p = p_o$, is unity. If $p < 0$ and $T < 2$ K, then $\beta(p - p_o)^2/2\mu > 144$, which means that $\exp[-\beta(p - p_o)^2/2\mu] < e^{-144}$. Thus we can extend the integration to $-\infty$.

$$\begin{aligned} \psi_{\text{rot}} &= \frac{4\pi V}{h^3} e^{-\varepsilon_o/\tau} \int_{-\infty}^\infty e^{-(p-p_o)^2/2\mu\tau} p^2 dp \quad (\tau = kT = 1/\beta) \\ &= \frac{4\pi V}{h^3} e^{-\varepsilon_o/\tau} \int_{-\infty}^\infty e^{-q^2/2\mu\tau} (q^2 + 2p_o q + p_o^2) dq \quad (q = p - p_o) \\ &= \frac{4\pi V}{h^3} \sqrt{2\pi\mu\tau} (p_o^2 + \mu\tau) e^{-\varepsilon_o/\tau} \end{aligned} \quad (7.114)$$

These formulas for ψ_{phon} and ψ_{rot} will be used in Problem 7.31 to calculate the specific heat of liquid helium at low temperatures.

7.16 BLACKBODY RADIATION

If a cavity, whose walls are kept at a finite temperature, is completely evacuated of ordinary matter, its energy density does not become zero, because it is impossible to eliminate from the cavity the electromagnetic radiation that is constantly being emitted and absorbed by the walls. This section is devoted to a study of the physical properties of such cavity radiation. A perfectly black body (one that absorbed all radiation that was incident upon it) would, at equilibrium within the cavity, have to emit radiation with the same intensity and frequency distribution as the cavity radiation. Therefore, the type of electromagnetic radiation found within a cavity at equilibrium is also referred to as *blackbody radiation*. The electromagnetic energy within the cavity may be treated as an ideal gas of massless Bose–Einstein particles, called *photons*. Since the relation between the momentum and the wave vector, $\mathbf{p} = \hbar\mathbf{k}$, which is valid for nonrelativistic particles, is also true for zero mass photons, the allowed momentum states for photons in a periodic box of volume $V = L^3$ are the same as those for nonrelativistic particles. However, for each allowed momentum state, there are two possible values of the photon spin, corresponding to the two possible transverse polarization states of an electromagnetic wave. The energy of a photon of momentum \mathbf{p} is

$$\varepsilon_p = cp \quad (7.115)$$

Since photons are not a conserved particle species, as are electrons or neutrinos, the argument given in Section 7.15 applies, and one may conclude that the affinity α is exactly zero. Using the facts that the density of single-particle quantum states in momentum space is $2(L/h)^3$ and that $\alpha = 0$ for the photon gas, Eq. (7.40) for the grand potential can be written as

$$\psi(\beta, V) = -\frac{2V}{h^3} \int \log[1 - e^{-\beta cp}] d^3\mathbf{p} \quad (7.116)$$

Except for the factor of 2, this is the integral that is worked out in Eq. (7.111).

$$\psi(\beta, V) = \frac{8\pi^5}{45} \frac{V\tau^3}{(hc)^3} \quad (7.117)$$

The pressure and energy density of the radiation gas can now be obtained from the grand potential by the thermodynamic identities

$$p = \tau \frac{\partial \psi}{\partial V} = \frac{8\pi^5}{45} \frac{\tau^4}{(hc)^3} \quad (7.118)$$

and

$$\frac{E}{V} = -\frac{1}{V} \frac{\partial \psi}{\partial \beta} = \frac{8\pi^5}{15} \frac{\tau^4}{(hc)^3} \quad (7.119)$$

Notice that, because of the modified relationship between the energy and the momentum of the particles, the photon gas obeys a relation $p = \frac{1}{3}E/V$, rather than $p = \frac{2}{3}E/V$.

Equation (7.119) shows that the electromagnetic energy density in a cavity is proportional to the fourth power of the temperature. This relationship is called *Stefan's law*.

7.17 THE FREQUENCY DISTRIBUTION

In order to determine the frequency distribution function of the radiation, we write $E/V = -(\partial\psi/\partial\beta)/V$ as an integral, using Eq. (7.116).

$$\begin{aligned} \frac{E}{V} &= \frac{2}{h^3} \int \frac{cpe^{-\beta cp}}{1 - e^{-\beta cp}} d^3\mathbf{p} \\ &= \frac{2}{h^3} \int \frac{cp}{e^{cp/\tau} - 1} d^3\mathbf{p} \end{aligned} \quad (7.120)$$

Changing to an angular frequency variable, $\hbar\omega = cp$, and using the fact that $d^3\mathbf{p} \rightarrow 4\pi p^2 dp = 4\pi(\hbar/c)^3 \omega^2 d\omega$, gives

$$\frac{E}{V} = \frac{\hbar}{\pi^2 c^3} \int_0^\infty \frac{\omega^3}{e^{\hbar\omega/\tau} - 1} d\omega \quad (7.121)$$

The frequency distribution function, $D(\omega, T)$ is defined by saying that the energy density of radiation with angular frequency within the interval $d\omega$ at temperature T is $D(\omega, T) d\omega$. It is clear from Eq. (7.121) that

$$D(\omega, T) = \frac{\hbar}{\pi^2 c^3} \frac{\omega^3}{e^{\hbar\omega/kT} - 1} \quad (7.122)$$

At any given temperature, the dominant frequency is determined by finding the value of ω that maximizes $D(\omega, T)$. The equation $\partial D/\partial\omega = 0$ gives

$$\frac{e\omega^2}{e^{\hbar\omega/kT} - 1} - \frac{(\hbar/kT)\omega^3}{(e^{\hbar\omega/kT} - 1)^2} = 0 \quad (7.123)$$

which can be written in the form

$$\frac{\hbar\omega}{kT} = 3(1 - e^{-\hbar\omega/kT}) \quad (7.124)$$

The solution of the equation $x = 3(1 - e^{-x})$ is $x = 2.82144$, and therefore at temperature T the maximum in the frequency distribution function occurs at

$$\omega_{\max} = 2.82144 \frac{kT}{\hbar} \quad (7.125)$$

That ω_{\max} is directly proportional to T is *Wien's displacement law*. These predictions are all in excellent agreement with experimental results.

PROBLEMS

7.1 Do the ‘equivalent calculation’ mentioned just prior to Eq. (7.8).

7.2 For a system of noninteracting one-dimensional classical particles in a harmonic oscillator potential: (a) Calculate the grand potential, $\psi(\alpha, \beta)$. Note that there is no fixed “volume” for this system. (b) Obtain N and E as functions of α and β and show that they satisfy the equipartition theorem.

7.3 (a) Using the grand canonical ensemble, verify the fluctuation formulas used in Chapter 5, namely $(\Delta N)^2 = \partial^2 \psi / \partial \alpha^2$ and $(\Delta E)^2 = \partial^2 \psi / \partial \beta^2$. (b) Show that, for a macroscopic system, $\Delta N/N$ and $\Delta E/E$ are both of order $1/\sqrt{N}$ and are therefore completely negligible.

7.4 If the adsorbed particles on a surface are free to move across the surface, then they may sometimes be approximated as a two-dimensional ideal gas in which the energy of a particle of momentum (p_x, p_y) is $\varepsilon(\mathbf{p}) = (p_x^2 + p_y^2)/2m - \varepsilon_o$, where ε_o is the binding energy of the particle to the surface. Using this approximation, calculate the surface density of adsorbed particles if the pressure in the three-dimensional gas, in equilibrium with the adsorbed particles on its surface, is p .

7.5 Diatomic molecules are sometimes decomposed, upon adsorption, into their constituent atoms, attached to the surface. Consider a gas of diatomic nitrogen (N_2), and assume that the vibrational excitations can be ignored, so that Eq. (4.65) is applicable. Assuming that the gas is in equilibrium with K atomic adsorption sites, derive the equivalent of Eq. (7.24) for the fraction of occupied sites.

7.6 For a surface with K adsorption sites and a single bound state at each site, show that the entropy (in rational units) of the adsorbed particles can be written in the form

$$S^o = -K[f \log f + (1 - f) \log(1 - f)]$$

where $f = N/K$ is the fraction of sites that are filled.

7.7 It is clear from Eq. (7.7) that the grand partition function is given by $\Lambda(\alpha, \beta, V) = \sum e^{-\alpha N} Z_N(\beta, V)$, where Z_N is the canonical partition function for a system of N particles. Using the fact that $Z_N(\beta, V) = \exp \phi(N, \beta, V)$, where ϕ is the canonical potential, approximate the sum by an integral and use the method described in Section A.9 to show that

$$\psi \equiv \log \Lambda = \phi - \alpha N = S^o - \alpha N - \beta E$$

where $N(\alpha, \beta, V)$ is the solution of $\alpha = \partial \phi(N, \beta, V) / \partial N$.

7.8 (a) Equation (7.47) gives the grand potential $\psi = \beta pV$ for a gas of spin- $\frac{1}{2}$ fermions. By a partial integration, show that $pV = \frac{2}{3}E$ for the Fermi–Dirac ideal gas. (b) Do the same for a gas of spinless bosons.

7.9 If a hydrogen atom is placed in a magnetic field, its nucleus (a proton) can have its spin, and therefore its magnetic moment, oriented either parallel or antiparallel to the field. The energy levels of the two orientations are $\pm \mu B$, where $\mu = 2.79255 \mu_N$. ($\mu_N = e\hbar/2M_p = 5.05 \times 10^{-27}$ J/T is the *Bohr nuclear magneton*.) (a) In a field of 2 Tesla, at a temperature of 300 K, what is the ratio $R(T) = (N_- - N_+) / (N_- + N_+)$. (N_- and N_+ are the numbers of parallel and antiparallel spins, respectively.) (b) If a substance containing hydrogen is placed in a magnetic field and subjected to electromagnetic radiation at a frequency $\nu = 2\mu B/h$, energy will be absorbed from the radiation field, causing transitions between the two nuclear magnetic energy states. The absorption rate is proportional to $R(T)$. This is the phenomenon of *nuclear magnetic resonance*. (c) For a field of 2 T, in what range is the nuclear magnetic resonance frequency (infrared, microwave, etc.)?

7.10 Shown in Fig. 7.15 is an impurity atom in a cubic crystal of lattice constant a . The atom has become ionized by transferring an electron to one of its six nearest neighbors. Assuming that, in the absence of an electric field, the six positions are equivalent, determine the average polarization of the ion-electron system when an electric field \mathbf{E} is imposed in the z direction.

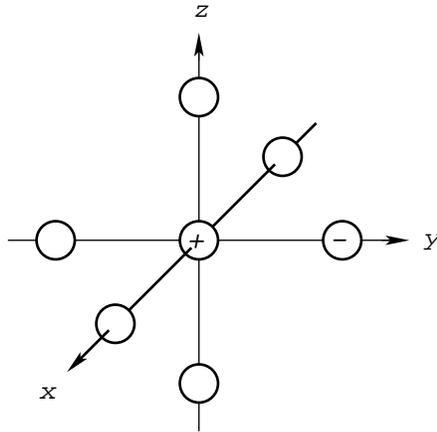


Fig. 7.15

7.11 In the grand canonical ensemble, the probability of finding the system with exactly N particles in some particular state is given by Eq. (7.6). Assume that the system is an ideal monatomic gas in a volume V , at temperature T . (a) Calculate \bar{N} , the average number of particles in the system, as a function of the affinity α . (b) Show that ΔN , the uncertainty in N , satisfies Eq. (5.73). That is, that $(\Delta N)^2 = -\partial\bar{N}/\partial\alpha$. (c) For one mole of gas at STP, calculate $\Delta N/\bar{N}$.

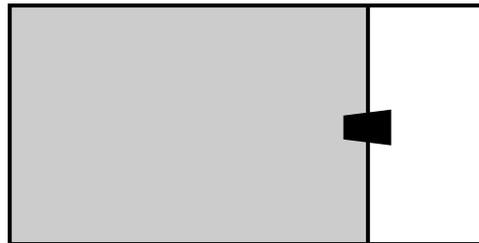


Fig. 7.16

7.12 Consider the system shown in Fig. 7.16. The volume on the left is $\frac{3}{4}$ of the total volume. In the left-hand side is a Fermi–Dirac gas at zero temperature. In the initial state $\varepsilon_F = 1$ eV. The right-hand side is completely empty, and the system is totally isolated. At $t = 0$ the plug is pulled. What is the temperature when the system comes to equilibrium?

7.13 If the Fermi energy is much larger than the rest energy of an electron ($\varepsilon_F \gg m_e c^2$), then the relationship between energy and momentum can be approximated by that for zero-mass particles; that is, $E = cp$. For such an ultrarelativistic electron gas, obtain an expansion for the energy and pressure up to order τ^2 .

7.14 Massless particles have the energy–momentum relationship $\varepsilon = cp$. (a) For a system of spinless one-dimensional Fermi–Dirac massless particles, determine the exact relationship involving N , μ , and τ . (b) Show that, at $\tau = 0$, $\mu = \varepsilon_F$.

7.15 Neutrinos are zero-mass spin- $\frac{1}{2}$ Fermi–Dirac particles. Although neutrinos have spin- $\frac{1}{2}$, there is only one neutrino state for each momentum, because of the fact that the spin angular momentum of a neutrino is always antiparallel to its momentum vector. Treating the neutrino number as a strictly conserved quantity, obtain expansions for p and E/N , up to order τ^2 , for a neutrino gas.

7.16 The antiparticle to the neutrino is the antineutrino, a particle with the same properties as the neutrino, but with its spin angular momentum always parallel to its linear momentum. In fact, the neutrino number N_ν and the antineutrino number $N_{\bar{\nu}}$ are not separately conserved, but only the *lepton number*, $L = N_\nu - N_{\bar{\nu}}$,

is conserved. Due to creation of neutrino–antineutrino pairs, the total number of particles, $N = N_\nu + N_{\bar{\nu}}$, can change spontaneously. A neutrino–antineutrino gas may be treated as two interpenetrating Fermi–Dirac ideal gases with a chemical reaction, $\nu + \bar{\nu} \leftrightarrow 0$. Using the chemical equilibrium equation, calculate the pressure of such a system as an expansion in τ , separately, for the two cases $L = 0$ and $L > 0$. (Note: This problem requires the solution of Problem 7.15.)

7.17 Calculate the specific heat at low temperature of a two-dimensional Fermi–Dirac ideal gas of spin- $\frac{1}{2}$ particles.

7.18 The baloneyon is an imaginary Fermi–Dirac particle with spin- $\frac{1}{2}$ and the following relationship between energy and momentum.

$$E = B|\mathbf{p}|^4$$

where B is the baloney constant. What is the Fermi energy of a system of baloneyons as a function of the particle density?

7.19 Consider a mixture of N α particles and $2N$ electrons within a volume V . When the average kinetic energy of the electrons, due to the Pauli Exclusion Principle, is much larger than the binding energy of an electron bound to an α particle, then the electrons will be stripped off the α particles and the system can be approximated as an interpenetrating Fermi–Dirac electron gas and a classical gas of α particles, rather than as a gas of helium atoms, which it would become at lower densities. This situation exists in high-density stars. (a) Determine the mass density of the system when the average kinetic energy of the electrons (at 0 K) is ten times the binding energy of a single electron to an α particle in free space. (b) How does it compare with the estimated mass densities at the center of the sun (10^5 kg/m^3) and in a white dwarf ($2 \times 10^9 \text{ kg/m}^3$)? (c) The internal temperature of white dwarf stars is about 10^7 K . What is the ratio of τ to ε_F in a white dwarf? (This ratio determines whether the zero-temperature approximation is accurate.)

7.20 Copper has a density of about 8.9 g/cm^3 . Copper has one conduction electron per atom. (a) Calculate the pressure of the conduction electron gas at 0 K. (b) Calculate the increase in pressure when the temperature is raised to 300 K. (c) What is holding copper together against the pressures obtained in (a) and (b)?

7.21 The pressure in a finite-density Fermi–Dirac ideal gas does not go to zero as the temperature approaches zero. Show that the entropy satisfies the limit equations mentioned in Section 5.18; namely

$$\lim_{E \rightarrow E_0} \left(\frac{\partial S}{\partial V} \right) = \infty \quad \text{and} \quad \frac{\partial}{\partial V} \left(\lim_{E \rightarrow E_0} S \right) = 0$$

7.22 In this problem we want to show that, below the Bose–Einstein condensation temperature, it is not necessary to treat any state except the zero momentum state individually. Consider the thermodynamic limit, $N = nL^3 \rightarrow \infty$, with fixed n and β . Show that the number of particles in any fixed finite number of momentum states that does not include the zero-momentum state, divided by N , approaches zero, even for $\alpha = 0$. (Hint: The most heavily occupied nonzero momentum states are the ones next to the zero momentum state.)

7.23 Show that, in an ideal Bose gas, the Bose–Einstein transition occurs when the number of particles in a cubic thermal de Broglie wavelength is equal to 2.612. That is, when $n\lambda^3 = \zeta\left(\frac{3}{2}\right)$.

7.24 Using Eqs. (7.68) and (7.71), derive the function $\alpha(n, \tau)$ in phase II of an ideal Bose–Einstein gas.

7.25 For an ideal Bose–Einstein gas, calculate the ratio of the condensate density to the total density as a function of τ/τ_c . [τ_c is defined in Eq. (7.78).]

7.26 (a) For a two-dimensional gas of spin-zero particles in a periodic box of area L^2 , calculate the number of momentum eigenstates with energies within the interval ε to $\varepsilon + d\varepsilon$. (b) Use the result of (a) to obtain an integral formula for N/A as a function of α and τ for a 2D Bose–Einstein gas. (c) Show that the

result obtained in (b) implies that no Bose–Einstein condensation occurs for the two-dimensional ideal Bose–Einstein gas.

7.27 (a) Consider a system of conserved bosons for which the relationship between energy and momentum is not $\varepsilon = p^2/2m$, but $\varepsilon = cp$, where $p = |\mathbf{p}|$. For this system, calculate the Bose–Einstein condensation temperature τ_c as a function of the particle density. (b) For a system of particles in which $\varepsilon = cp^3$, show that there is no Bose–Einstein condensation.

7.28 For a particle in a gravitational potential $U = mgz$, the Schrödinger equation for the ground state is

$$-\frac{\hbar^2}{2m} \frac{d^2\psi(z)}{dz^2} + U\psi(z) = E_0\psi(z)$$

Assume that a “hard floor” exists at $z = 0$, so that ψ has the boundary condition $\psi(0) = 0$. (a) Show that the ground-state wave function has the form $\psi(z) = u(z/s)$, where $s = (\hbar^2/m^2g)^{1/3}$ and $u(x)$ satisfies an eigenvalue equation that does not contain the parameters \hbar , m , or g . Thus the parameter s gives the scale height for a quantum particle in a gravitational potential. For an ideal Bose–Einstein gas at zero temperature, all the particles will go into this single-particle ground state. (b) Evaluate s for the earth’s gravitational field and m equal to the mass of a ${}^4\text{He}$ atom.

7.29 (a) Write the ground-state wave function for a single particle of mass m in a hard-walled box of volume L^3 . (b) For an N -particle Bose–Einstein ideal gas in such a hard-walled box, determine the particle density as a function of position at temperature zero.

7.30* (a) It is a mathematical theorem that a function $f(x, y)$ is strictly convex if and only if $\partial^2 f/\partial x^2 < 0$, $\partial^2 f/\partial y^2 < 0$, and $(\partial^2 f/\partial x^2)(\partial^2 f/\partial y^2) > (\partial^2 f/\partial x \partial y)^2$. Prove that $s^o(n, \varepsilon)$, given in Eq. (7.87), is a strictly convex function. (b) Show that the peculiar characteristic of the ideal Bose gas illustrated in Fig. 7.7 disappears for the Bose gas with mean-field interactions.

7.31 Using Eq.s 7.111 and 7.114, separately calculate and plot the contributions to the specific heat, $C = \partial E/\partial \tau$, of liquid helium due to phonons and rotons.

7.32 Assume that the condensate wave function has the form $\psi(\mathbf{r}) = R \exp[i\phi(\mathbf{r})]$ and that the superfluid velocity at point \mathbf{r} is related to ψ by $m\mathbf{v} = \hbar \nabla\phi(\mathbf{r})$. From the single valuedness of ψ , derive the quantization of vorticity [Eq. (7.102)].

7.33 Calculate the number of photons in a 1 cm cube at 300 K.

7.34 Consider a small area dA on the inside surface of a cavity at temperature T . Show that the electromagnetic energy that falls upon that area, per second, can be written as $I(\omega, T) dA$, where the *spectral intensity function* $I(\omega, T) = (c/4)D(\omega, T)$. Thus, the frequency distribution function $D(\omega, T)$ also gives the frequency distribution of the radiation that would pour out of a hole in a cavity at temperature T . This is not true for the speed distribution for nonrelativistic particles. The speed distribution for particles within a box (see Problem 2.8) is not the same as the speed distribution of particles exiting from a small hole in the box. Explain what is the essential characteristic of photons that makes I proportional to D .