

18

QUANTUM FLUIDS

18-1 QUANTUM PARTICLES: A “FERMION PRE-GAS MODEL”

At this point we might be tempted to test the grand canonical formalism on the ideal gas, not to obtain new results of course, but to compare the analytic convenience and power of the various formalisms. Remarkably, the grand canonical formalism proves to be extremely *uncongenial* to the classical ideal gas model! The catastrophe of nonextensivity that plagued the calculation in the canonical formalism becomes even more awkward in the grand canonical formalism¹.

As so often happens in physics, the formalism points the way to reality. The awkwardness of the formalism is a signal that the *model* is unphysical—that there are no classical particles in nature! There are only fermions and bosons, two types of quantum mechanical particles. For these the grand canonical formalism becomes extremely simple!

Fermions are the quantum analogues of the material particles of classical physics. Electrons, protons, neutrons, and a panoply of more esoteric particles are fermions. The nineteenth century “law of impenetrability of matter” is replaced by an antisymmetry condition on the quantum mechanical wave function². This condition implies (as the only consequence of which we shall have need) that *only a single fermion can occupy a given orbital state*.

Bosons are the quantum analogues of the “waves” of classical physics. Photons, the quanta of light, are typical bosons. Just as waves can be freely superposed classically, *so an arbitrary number of bosons can occupy a single orbital state*. Furthermore, there exist bosons with zero rest mass—such bosons, like classical waves, can be freely created or annihili-

¹The root of the difficulty lies in the fact that the grand canonical formalism focusses not on the particles, but on the *orbital states*. There is then no natural way to count the states “as if the particles had labels” (later to be corrected by division by $N!$).

²The wave function must be antisymmetric under interchange of two fermions, thereby interposing a node between the fermions and preventing two fermions (of the same spin state) from occupying the same spatial position.

lated. The radiation of electromagnetic waves by a hot body is described in quantum terminology as the creation and emission of photons.

The fundamental particles in nature possess intrinsic angular momentum, or "spin." The (immutable) magnitude of this intrinsic angular momentum is necessarily a multiple of $\hbar/2$; those particles with odd multiples of $\hbar/2$ are fermions, and those with even multiples of $\hbar/2$ are bosons.

The orientation of the intrinsic angular momentum is also quantized. For fermions of "spin $\frac{1}{2}$ " (angular momentum = $\hbar/2$) the angular momentum can have either of two orientations (along any arbitrarily designated axis). These two orientations are designated by *up* and *down*, or by the two values $m_s = \frac{1}{2}$ and $m_s = -\frac{1}{2}$ of the "magnetic quantum number" m_s .

Finally, an orbital state of a quantum particle is labeled by the quantum numbers of its spatial wave function *and* by the magnetic quantum number m_s of its spin orientation. For a particle in a cubic container the three spatial quantum numbers are the three components of the wave vector \mathbf{k} (recall equation 16.37), so that an orbital state is completely labeled by \mathbf{k} and m_s .

Preparatory to the application of the grand canonical formalism to Fermi and Bose ideal gases, it is instructive to consider a simpler model that exhibits the physics in greater clarity. This model has only three energy levels, so that all summations over states can be exhibited explicitly. Except for this simplification, the analysis stands in strict step by step correspondence with the analysis of quantum gases to be developed in the following sections; hence the name *pre-gas model*.

We consider first the spin- $\frac{1}{2}$ fermion pre-gas model. The model system is such that only three spatial orbits are permitted; particles in these spatial orbits have energies ϵ_1 , ϵ_2 , and ϵ_3 . The model system is in contact with a thermal reservoir and with a reservoir of spin- $\frac{1}{2}$ Fermi particles; the reservoirs impose fixed values of the temperature T and of the molar Gibbs potential μ (which, for fermion systems, is also known as the *Fermi level*).

Each spatial orbit corresponds to two orbital states, one of spin up and one of spin down. There are therefore six orbital states, which can be numbered (n, m_s) with $n = 1, 2, 3$ and $m_s = -\frac{1}{2}, +\frac{1}{2}$.

The grand canonical partition sum factors with respect to the six orbital states

$$\mathcal{Z} = z_{1,-1/2} z_{1,1/2} z_{2,-1/2} z_{2,1/2} z_{3,-1/2} z_{3,1/2} \quad (18.1)$$

and each orbital state partition sum has two terms, corresponding to the state being either empty or occupied. In the absence of a magnetic field,

$$z_{n,m_s} = 1 + e^{-\beta(\epsilon_n - \mu)} \quad (18.2)$$

Alternatively we can pair the two orbital states with the same n but with $m_s = \pm \frac{1}{2}$

$$z_{n,1/2}z_{n,-1/2} = [1 + e^{-\beta(\epsilon_n - \mu)}]^2 = 1 + 2e^{-\beta(\epsilon_n - \mu)} + e^{-2\beta(\epsilon_n - \mu)} \quad (18.3)$$

This product can be interpreted in terms of the *four* states of given n : the empty state, two singly occupied states, and one doubly occupied state.

The probability that the orbital state (n, m_s) is empty is $1/z_{n,m}$, and the probability that it is occupied is

$$f_{n,m} = \frac{e^{-\beta(\epsilon_n - \mu)}}{z_{n,m}} = \frac{1}{e^{\beta(\epsilon_n - \mu)} + 1} \quad (18.4)$$

The fundamental equation follows directly from equations 18.1 to 18.3

$$e^{-\beta\Psi} = \mathcal{Z} = [1 + e^{-\beta(\epsilon_1 - \mu)}]^2 [1 + e^{-\beta(\epsilon_2 - \mu)}]^2 [1 + e^{-\beta(\epsilon_3 - \mu)}]^2 \quad (18.5)$$

We can find the mean number of particles in the system by differentiation ($\tilde{N} = -\partial\Psi/\partial\mu$). Alternatively we can sum the probability of occupation $f_{n,m}$ over all six orbital states

$$\tilde{N} = \sum_{n,m} f_{n,m} = \frac{2}{e^{\beta(\epsilon_1 - \mu)} + 1} + \frac{2}{e^{\beta(\epsilon_2 - \mu)} + 1} + \frac{2}{e^{\beta(\epsilon_3 - \mu)} + 1} \quad (18.6)$$

The entropy of the system can be obtained by differentiation of the fundamental equation ($S = -\partial\Psi/\partial T$). Alternatively it can be calculated from the occupation probabilities (Problem 18.1-1).

The energy is found thermodynamically by differentiation: $U = (\partial\beta\Psi/\partial\beta)_{\beta\mu}$ (equation 17.27). Alternatively, from the probability interpretation of $f_{n,m}$

$$U = \sum_{n,m} \epsilon_{n,m} f_{n,m} = \frac{2\epsilon_1}{e^{\beta(\epsilon_1 - \mu)} + 1} + \frac{2\epsilon_2}{e^{\beta(\epsilon_2 - \mu)} + 1} + \frac{2\epsilon_3}{e^{\beta(\epsilon_3 - \mu)} + 1} \quad (18.7)$$

If the system of interest is actually in contact with T and μ reservoirs, these results are in convenient form. But it may happen that the physical system that we wish to describe is enclosed in nonpermeable walls that impose constancy of the particle number \tilde{N} rather than of μ . Nevertheless *the fundamental equation is an attribute of the thermodynamic system, independent of boundary conditions*, so that the preceding formalism re-

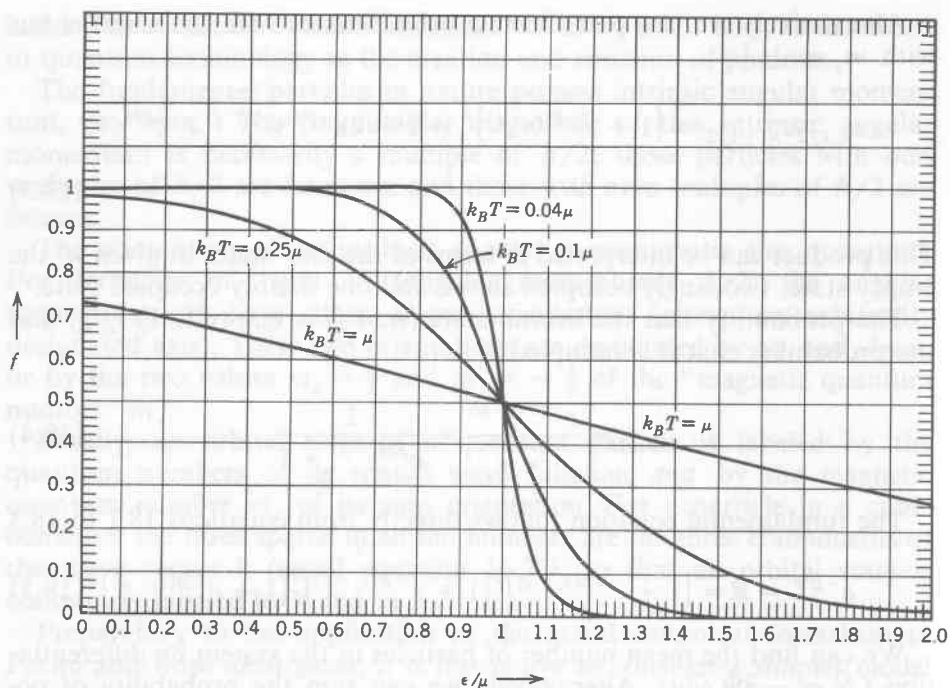


FIGURE 18.1

The probability of occupation, by a fermion, of an orbital state of energy ϵ at temperature T .

mains valid. However, the Fermi level μ is not a known quantity. Instead the value of μ adjusts to a change in temperature in such a way as to maintain \tilde{N} constant—a response governed by equation 18.6.

Unfortunately equation 18.6 does not lend itself easily to explicit solution for μ as a function of T and \tilde{N} . However the solution can be obtained numerically or by series expansions in certain temperature regions, as we shall soon see. It is instructive first to reconsider the preceding analysis in more pictorial terms.

The occupation probability f of an orbital state of energy ϵ (as given by equation 18.4) is shown in Fig. 18.1. This occupation probability is more general than the present model, of course. It applies to any orbital state of a fermion. In the limit of zero temperature, any state of energy $\epsilon < \mu$ is occupied and any state of energy $\epsilon > \mu$ is empty. As the temperature is raised the states with energies slightly less than μ become partially depopulated, and the states with energies slightly greater than μ become populated. The range of energies within which this population transfer occurs is of the order of $4k_B T$ (see Problems 18.1-4, 18.1-5, 18.1-6).

The probability of occupation of a state with energy equal to μ is always one half, and a plot of $f(\epsilon, T)$ as a function of ϵ (such as in Fig. 18.1) is symmetric under inversion through the point $\epsilon = \mu$, $f = \frac{1}{2}$ (see Problem 18.1-5).

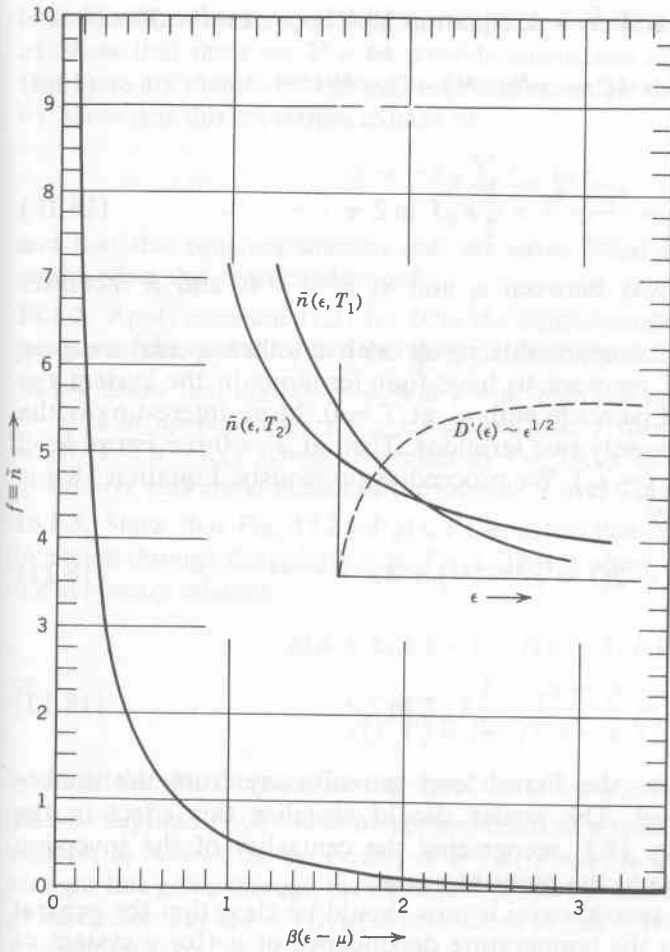


FIGURE 18.2
 The Bose mean occupation number \bar{n} of an orbital state of energy ϵ , at given T and μ .
 The insert is schematic, for $T_2 < T_1$ and $\mu_2 < \mu_1$.

With these pictorial insights we can explore the dependence of μ on T for the fermion pre-gas model. For definiteness suppose the system to contain four fermions. Furthermore, suppose that two of the energy levels coincide, with $\epsilon_1 = \epsilon_2$, and with $\epsilon_3 > \epsilon_2$. At $T = 0$ the four fermions fill the four orbital states of energy $\epsilon_1 (= \epsilon_2)$, and the two states of energy ϵ_3 are empty. The Fermi level must lie somewhere between ϵ_2 and ϵ_3 , but the precise value of μ must be found by considering the limiting value as $T \rightarrow 0$. For very low T

$$f \equiv \frac{1}{e^{\beta(\epsilon - \mu)} + 1} \approx \begin{cases} e^{-\beta(\epsilon - \mu)} & \text{for } \epsilon > \mu \text{ and } T \approx 0 \\ 1 - e^{\beta(\epsilon - \mu)} & \text{for } \epsilon < \mu \text{ and } T \approx 0 \end{cases} \quad (18.8)$$

Thus, if $\varepsilon_1 = \varepsilon_2 < \varepsilon_3$, and $\tilde{N} = 4$, equation 18.6 becomes, for $T \approx 0$

$$4 = 4(1 - e^{\beta(\varepsilon_1 - \mu)}) + 2e^{-\beta(\varepsilon_3 - \mu)} \quad (18.9)$$

or

$$\mu = \frac{\varepsilon_1 + \varepsilon_3}{2} + \frac{1}{2}k_B T \ln 2 + \dots \quad (18.10)$$

In this case μ is midway between ε_1 and ε_3 at $T = 0$, and μ increases linearly as T increases.

It is instructive to compare this result with another special case, in which $\varepsilon_1 < \varepsilon_2 = \varepsilon_3$. If we were to have four fermions in the system the Fermi level (μ) would coincide with ε_2 at $T = 0$. More interesting is the case in which there are only two fermions. Then at $T = 0$ the Fermi level lies between ε_1 and $\varepsilon_2 (= \varepsilon_3)$. We proceed as previously. Equation 18.9 is replaced, for $T \approx 0$, by

$$2 = 2(1 - e^{\beta(\varepsilon_1 - \mu)}) + 4e^{-\beta(\varepsilon_3 - \mu)} \quad (18.11)$$

and

$$\mu = \frac{\varepsilon_1 + \varepsilon_3}{2} - \frac{1}{2}k_B T \ln 2 + \dots \quad (18.12)$$

In each of the cases the Fermi level moves away from the doubly degenerate energy level. The reader should visualize this effect in the pictorial terms of Fig. 18.1, recognizing the centrality of the inversion symmetry of f relative to the point at $\varepsilon = \mu$.

From these several special cases it now should be clear that the general principles that govern the temperature dependence of μ (for a system of constant \tilde{N}) are:

- (a) The occupation probability departs from zero or unity over a region of $\Delta\varepsilon \approx \pm 2k_B T$ around μ .
- (b) As T increases, the Fermi level μ is "repelled" by high densities of states within this region.

PROBLEMS

18.1-1. Obtain the mean number of particles in the fermion pre-gas model by differentiating Ψ , as given in equation 18.5. Show that the result agrees with \tilde{N} as given in equation 18.6.

18.1-2. The entropy of a system is given by $S = -k_B \sum_j f_j \ln f_j$, where f_j is the probability of a microstate of the system. Each microstate of the fermion pre-gas

model is described by specifying the occupation of *all six* orbital states.

a) Show that there are $2^6 = 64$ possible microstates of the model system, and that there are therefore 64 terms in the expression for the entropy.

b) Show that this expression reduces to

$$S = -k_B \sum_{n,m} f_{nm} \ln f_{nm}$$

and that this equation contains only six terms. What special properties of the model effect this drastic reduction?

18.1-3. Apply equation 17.27 for U to the fundamental equation of the fermion pre-gas model, and show that this gives the same result for U as in equation 18.7.

18.1-4. Show that $df/d\varepsilon = -\beta/4$ at $\varepsilon = \mu$. With this result show that f falls to $f = 0.25$ at approximately $\varepsilon \approx \mu + k_B T$ and that f rises to $f = 0.75$ at approximately $\varepsilon \approx \mu - k_B T$ (check this result by Fig. 18.1). This rule of thumb gives a qualitative and useful picture of the range of ε over which f changes rapidly.

18.1-5. Show that Fig. 17.2 [of $f(\varepsilon, T)$ as a function of ε] is symmetric under inversion through the point $\varepsilon = \mu$, $f = \frac{1}{2}$. That is, show that $f(\varepsilon, T)$ is subject to the symmetry relation

$$f(\mu + \Delta, T) = 1 - f(\mu - \Delta, T)$$

or

$$f(\varepsilon, T) = 1 - f(2\mu - \varepsilon, T)$$

and explain why this equation expresses the symmetry alluded to.

18.1-6. Suppose $f(\varepsilon, T)$ is to be approximated as a function of ε by three linear regions, as follows. In the vicinity of $\varepsilon \approx \mu$, $f(\varepsilon, \mu)$ is to be approximated by a straight line going through the point ($\varepsilon = \mu$, $f = \frac{1}{2}$) and having the correct slope at that point. For low ε , $f(\varepsilon, \mu)$ is to be taken as unity. And at high ε , $f(\varepsilon, \mu)$ is to be taken as zero.

What is the slope of the central straight line section? What is the “width,” in energy units, of the central straight line section? Compare this result with the “rule of thumb” given in Problem 18.1-4.

18-2 THE IDEAL FERMI FLUID

We turn our attention to the “ideal Fermi fluid,” a model system of wide applicability and deep significance. The ideal Fermi fluid is a quantum analogue of the classical ideal gas; it is a system of fermion particles between which there are no (or negligibly small) interaction forces.

Conceptually, the simplest ideal Fermi fluid is a collection of neutrons, and such a fluid is realized in neutron stars and in the nucleus of heavy atoms (as one component of the neutron-proton “two-component fluid”).

Composite "particles," such as atoms, behave as fermion particles if they contain an odd number of fermion constituents. Thus helium-three (^3He) atoms (containing two protons, one neutron, and two electrons) behave as fermions. Accordingly, a gas of ^3He atoms can be treated as an "ideal Fermi fluid." In contrast, ^4He atoms, containing an additional neutron, behave as bosons. The spectacular difference between the properties of ^3He and ^4He fluids at low temperatures, despite the fact that the two types of atoms are chemically indistinguishable, is a striking confirmation of the statistical mechanics of these quantum fluids.

Electrons in a metal are another Fermi fluid of great interest, to which we shall address our attention in Section 18.4.

We first consider the statistical mechanics of a general ideal, Fermi fluid. The analysis will follow the pattern of the fermion pre-gas model of the preceding section. Since the number of orbital states of the fluid is very large, rather than being the mere six orbital states of the pre-gas model, summations will be replaced by integrals. But otherwise the analyses stand in strict step by step correspondence.

To calculate the fundamental relation of an ideal fermion fluid we choose to consider it as being in interaction with a thermal and a particle reservoir, of temperature T and electrochemical potential μ . We stress again that the particular system being studied in the laboratory may have different boundary conditions—it may be closed, or it may be in diathermal contact only with a thermal reservoir, and so forth. But thermodynamic fundamental relations do not refer to any particular boundary condition, and we are free to choose any convenient boundary condition that facilitates the calculation. We choose the boundary conditions appropriate to the grand canonical formalism.

The orbital states available to the fermions are specified by the wave vector \mathbf{k} of the wave function (recall equation 16.43) and by the orientation of the spin ("up" or "down" for a spin- $\frac{1}{2}$ fermion). The partition sum factors over the possible orbital states

$$\mathcal{Z} = \prod_{\mathbf{k}, m_s} z_{\mathbf{k}, m_s} \quad (18.13)$$

where m_s can take two values, $m_s = \frac{1}{2}$ implying spin up and $m_s = -\frac{1}{2}$ implying spin down. Each orbital state can be either empty or singly occupied. The energy of an empty orbital state is zero, and the energy of an occupied orbital state \mathbf{k}, m_s is

$$\epsilon_{\mathbf{k}, m_s} = \frac{p^2}{2m} = \frac{\hbar^2 k^2}{2m} \quad (\text{independent of } m_s) \quad (18.14)$$

so that the partition sum of the orbital state \mathbf{k}, m_s is

$$z_{\mathbf{k}, m_s} = 1 + e^{-\beta((\hbar^2 k^2 / 2m) - \mu)} \quad (18.15)$$

It is conventional to refer to the product $z_{\mathbf{k}, 1/2} \cdot z_{\mathbf{k}, -1/2}$ as $z_{\mathbf{k}}$, the

“partition sum of the mode k ”

$$\begin{aligned} \mathcal{Z} &= \prod_{\mathbf{k}, m_s} z_{\mathbf{k}, m_s} = \prod_{\mathbf{k}} z_{\mathbf{k}, 1/2} z_{\mathbf{k}, -1/2} \\ &= \prod_{\mathbf{k}} \left[1 + 2e^{-\beta((\hbar^2 k^2 / 2m) - \mu)} + e^{-\beta((2\hbar^2 k^2 / 2m) - 2\mu)} \right] \end{aligned} \quad (18.16)$$

The three terms refer then to the totally empty mode, to the singly occupied mode (with two possible spin orientations), and to the doubly occupied mode (with one spin up and one down).

Each orbital state (\mathbf{k}, m_s) is independent, and the probability of occupation is

$$f_{\mathbf{k}, m_s} = \frac{e^{-\beta((\hbar^2 k^2 / 2m) - \mu)}}{z_{\mathbf{k}, m_s}} = \frac{1}{e^{\beta((\hbar^2 k^2 / 2m) - \mu)} + 1} \quad (18.17)$$

This function is shown in Fig. 18.1.

At this point we can proceed by either of two routes. The fundamental algorithm instructs us to calculate the grand canonical potential Ψ ($= -k_B T \ln \mathcal{Z}$), thereby obtaining a fundamental relation. Alternatively, we can calculate all physical quantities of interest directly from equation 18.17. We shall first calculate the fundamental relation and then return to explore the (parallel) information available from knowledge of the “orbital-state distribution function” $f_{\mathbf{k}, m_s}$.

The grand canonical potential is

$$\Psi = -k_B T \sum_{\mathbf{k}} \ln z_{\mathbf{k}} = -k_B T \sum_{\mathbf{k}} \ln \left[1 + e^{-\beta((\hbar^2 k^2 / 2m) - \mu)} \right]^2 \quad (18.18)$$

The density of orbital states (of a *single* spin orientation) is $D(\epsilon) d\epsilon$, which has been calculated in Equation 16.47.

$$D(\epsilon) d\epsilon = \frac{V}{2\pi^2} k^2 \frac{dk}{d\epsilon} d\epsilon = \frac{V}{4\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} \epsilon^{1/2} d\epsilon \quad (18.19)$$

Inserting a factor of 2 to account for the two possible spin orientations, Ψ can then be written as

$$\begin{aligned} \Psi &= -2k_B T \int_0^\infty \ln(1 + e^{-\beta(\epsilon - \mu)}) D(\epsilon) d\epsilon \\ &= -k_B T \frac{V}{2\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} \int_0^\infty \epsilon^{1/2} \ln(1 + e^{-\beta(\epsilon - \mu)}) d\epsilon \end{aligned} \quad (18.20)$$

Unfortunately the integral cannot be evaluated in closed form. Quantities of direct physical interest, obtained by differentiation of Ψ , must also be

expressed in terms of integrals. Such quantities can be calculated to any desired accuracy by numerical quadrature or by various approximation schemes. In principle the statistical mechanical phase of the problem is completed with equation 18.20.

It is of interest to calculate the number of particles \tilde{N} in the gas. By differentiation of Ψ

$$\begin{aligned}\tilde{N} &= -\frac{\partial \Psi}{\partial \mu} = 2 \int_0^\infty \frac{1}{e^{\beta(\epsilon-\mu)} + 1} D(\epsilon) d\epsilon \\ &= \frac{V}{2\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} \int_0^\infty \frac{\epsilon^{1/2}}{e^{\beta(\epsilon-\mu)} + 1} d\epsilon\end{aligned}\quad (18.21)$$

The first form of this equation reveals most clearly that it is identical to a summation of occupation probabilities over all states. Similarly the energy obtained by differentiation is identical to a summation of ϵf over all states

$$\begin{aligned}U &= \left(\frac{\partial \beta \Psi}{\partial \beta} \right)_{\beta\mu} = 2 \int_0^\infty \frac{\epsilon}{e^{\beta(\epsilon-\mu)} + 1} D(\epsilon) d\epsilon \\ &= \frac{V}{2\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} \int_0^\infty \frac{\epsilon^{3/2}}{e^{\beta(\epsilon-\mu)} + 1} d\epsilon\end{aligned}\quad (18.22)$$

A flow-chart for the statistical mechanics of quantum fluids is shown in Table 18.1. Bose fluids are included, although we shall consider them explicitly only in later sections. The analysis differs only in several changes in sign, as will emerge in Section 18.5.

Before exploring these general results in specific detail it is wise to corroborate that for high temperature they do reduce to the classical ideal gas, and to explore the criterion that separates the classical from the quantum mechanical regime.

PROBLEMS

18.2-1. Prove equations c, g, h, i, and j of Table 18.1 (for fermions only).

18-3 THE CLASSICAL LIMIT AND THE QUANTUM CRITERION

The hallmark of the quantum regime is that a fermion particle is not free to occupy any arbitrarily chosen orbital state, for some states may already be filled. However at low density or high temperature the probability of occupation of each orbital state is small, thereby minimizing the

TABLE 18.1

Statistical Mechanics of Quantum Fluids. The upper sign refers to fermions and the lower to bosons.

(a) The partition sum factors. The number of spin orientations is $g_0 = 2S + 1$ ($g_0 = 1$ for bosons of spin zero; $g_0 = 2$ for fermions of spin $\frac{1}{2}$, etc.)

(b) $z_{\mathbf{k}}$ is the partition sum of a single orbital state (of definite \mathbf{k} and m_s).

(c) $f_{\mathbf{k}, m_s}$ is the mean occupation number (or "occupation probability") of the orbital state \mathbf{k}, m_s .

(d, e, and f) $D(\epsilon)$ is the density of orbital states of a single spin orientation.

(g) $\Psi(T, \mu)$ is a fundamental relation.

(h, i, and j) $P = P(U, V)$ is an equation of state, common to both fermion and bosons.

$$\mathcal{Z} = \prod_{\mathbf{k}, m_s} z_{\mathbf{k}, m_s} = \prod_{\mathbf{k}} z_{\mathbf{k}}^{g_0} \tag{a}$$

$$z_{\mathbf{k}} = [1 \pm e^{-\beta(\epsilon_{\mathbf{k}} - \mu)}]^{\pm 1} \tag{b}$$

$$f_{\mathbf{k}, m_s} = \frac{1}{e^{\beta(\epsilon_{\mathbf{k}} - \mu)} \pm 1} \tag{c}$$

$$-\beta\Psi = \ln \mathcal{Z} = g_0 \sum_{\mathbf{k}} \ln z_{\mathbf{k}} = \pm g_0 \sum_{\mathbf{k}} \ln [1 \pm e^{-\beta(\epsilon_{\mathbf{k}} - \mu)}] \tag{d}$$

$$= \pm g_0 \int_0^\infty \ln [1 \pm e^{-\beta(\epsilon - \mu)}] D(\epsilon) d\epsilon \tag{e}$$

$$D(\epsilon) = \frac{V}{(2\pi)^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} \epsilon^{1/2} \tag{f}$$

Integrating by parts

$$\Psi = -\frac{2}{3} \frac{g_0 V}{(2\pi)^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} \int_0^\infty \frac{\epsilon^{3/2}}{e^{\beta(\epsilon - \mu)} \pm 1} d\epsilon \quad (\text{Fundamental Equation}) \tag{g}$$

Note $\Psi = -\frac{2}{3} \int_0^\infty \epsilon f(\epsilon) g_0 D(\epsilon) d\epsilon = -\frac{2}{3} U \tag{h}$

Also $\Psi = -PV \quad (\text{for simple systems}) \tag{i}$

$$\therefore P = \frac{2}{3} \frac{U}{V} \quad (\text{equation of state}) \tag{j}$$

effect of the fermion prohibition against multiple occupancy. All gases become classical at low density or high temperature, in which conditions relatively few particles are distributed over many states.

The probability of occupancy of a state of energy ϵ is $[e^{\beta(\epsilon - \mu)} + 1]^{-1}$, and this is small (for all ϵ) if $e^{-\beta\mu}$ is large, or if the fugacity $e^{\beta\mu}$ is small:

$$e^{\beta\mu} \ll 1 \quad (\text{classical regime}) \tag{18.23}$$

In this classical regime the occupation probability reduces to

$$f_{\mathbf{k}, m_s} \simeq e^{\beta\mu} e^{-\beta\epsilon} \quad (18.24)$$

In terms of Fig. 18.1, the classical region corresponds to the recession of the Fermi level μ to such large negative values that all physical orbitals lie on the "tail" of the $f(\epsilon, T)$ curve.

We first corroborate that the occupation probability of equation 18.24 does reproduce classical results, and we then explore the physical condition that leads to a small fugacity.

The number of particles \tilde{N} is expressed by equation 18.21 which, for small fugacity, becomes

$$\tilde{N} \simeq \frac{g_0 V}{(2\pi)^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} e^{\beta\mu} \int_0^\infty e^{-\beta\epsilon} \epsilon^{1/2} d\epsilon = \frac{g_0 V}{\lambda_T^3} e^{\beta\mu} \quad (18.25)$$

where λ_T (a quantity to be given a physical interpretation momentarily) is defined by

$$\lambda_T = \frac{h}{\sqrt{2\pi m k_B T}} \quad (18.26)$$

and where $g_0 = 2S + 1$ is the number of permissible spin orientations (equal to two for the spin $\frac{1}{2}$ case). Similarly the energy, as expressed in equation 17.62, becomes

$$U = \frac{2V}{(2\pi)^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} e^{\beta\mu} \int_0^\infty e^{-\beta\epsilon} \epsilon^{3/2} d\epsilon = \frac{3}{2} k_B T \frac{g_0 V}{\lambda_T^3} e^{\beta\mu} \quad (18.27)$$

Dividing

$$U = \frac{3}{2} \tilde{N} k_B T \quad (18.28)$$

This is the well-known equation of state of the classical ideal gas. In addition the individual equations 18.25 and 18.27 can be corroborated as valid for the classical ideal gas.

With the reassurance that the Fermi gas does behave appropriately in the classical limit, we may inquire as to the criterion that divides the quantum and classical regimes. It follows from our discussion that this division occurs when the fugacity is of the order of unity

$$e^{\beta\mu} \simeq 1 \quad (\text{classical-quantum boundary}) \quad (18.29)$$

or, from equation 18.25

$$\lambda_T^3 / \left(\frac{g_0 V}{\tilde{N}} \right) \approx 1 \quad (\text{classical-quantum boundary}) \quad (18.30)$$

This “quantum criterion” acquires a revealing pictorial interpretation when we explore the significance of λ_T . In fact λ_T is the quantum mechanical wave length of a particle with kinetic energy $k_B T$ (see Problem 18.3-2), whence λ_T is known as the “thermal wave length.” From equation 18.25 we see that *in the classical limit the fugacity is the ratio of the “thermal volume” λ_T^3 to the volume per particle (of a single spin orientation) $V/(\tilde{N}/g_0)$. The system is in the quantum regime if the thermal volume is larger than the actual volume per particle (of a single spin orientation) either by virtue of large \tilde{N} or by virtue of low T (and consequently of large λ_T).*

PROBLEMS

18.3-1. Calculate the definite integrals appearing in equations 18.25 and 18.26 by letting $\epsilon = x^2$ and noting that each of the resulting integrals is the derivative (with respect to β) of a simpler integral.

18.3-2. Validate the interpretation of λ_T as the “thermal wavelength” by identifying the wavelength with the momentum p by the quantum mechanical definition $p = h/\lambda$, and by comparing the energy $p^2/2m$ to $k_B T$.

18-4 THE STRONG QUANTUM REGIME: ELECTRONS IN A METAL

The electrons in a metal would appear, at first thought, to be a very poor example of an ideal Fermi fluid, for the charges on the electrons ostensibly imply strong interparticle forces. However the background positive charges of the fixed ions tend to neutralize the negative charges of the electrons, at least on the average. And the very long range of the Coulomb force ensures that the average effect is the dominant effect, for the potential at any point is the resultant of contributions from enormously many electrons and positive ions—some nearby and many further removed in space. All of this can be made quantitative, and the accuracy of the approximation can be estimated and controlled by the methodology of solid state physics. We proceed by simply accepting the model of electrons in a metal as an ideal fermion gas, on the basis of the slender plausibility of these remarks.

An estimate of the Fermi level (to be made shortly) will reveal that for all reasonable temperatures $\mu \gg k_B T$. Thus electrons in a metal are an example of an ideal Fermi gas in the strong quantum regime. The analysis of this section is simply an examination of the Fermi gas in this strong quantum regime, with the allusion to electrons in a metal only to provide a physical context for the more general discussion.

Consider first the state of the electrons at zero temperature, and denote the value of the Fermi level at $T = 0$ as μ_0 (the “Fermi energy”). The occupation probability f is unity for $\epsilon < \mu_0$ and is zero for $\epsilon > \mu_0$, so that (from equation 18.21)

$$\tilde{N} = \frac{\sqrt{2} m^{3/2} V}{\pi^2 \hbar^3} \int_0^{\mu_0} \epsilon^{1/2} d\epsilon = \frac{(2m)^{3/2} V}{3\pi^2 \hbar^3} \mu_0^{3/2} \quad (18.31)$$

or

$$\mu_0 = \frac{\hbar^2}{2m} \left(3\pi^2 \frac{\tilde{N}}{V} \right)^{2/3} \quad (18.32)$$

The number of conduction electrons per unit volume in metals is of the order of 10^{22} to 10^{23} electrons/cm³ (corresponding to one or two electrons per ion and an interionic distance of ≈ 5 Å). Consequently for electrons in metals the Fermi energy μ_0 (or the “Fermi temperature” μ_0/k_B) is of the magnitude

$$\frac{\mu_0}{k_B} \approx 10^4 \text{ K to } 10^5 \text{ K} \quad (18.33)$$

For other previously cited Fermi fluids the Fermi temperature may be even higher—of the order of 10^9 K for the electrons in white dwarf stars or 10^{12} K for the nucleons in heavy atomic nuclei and in neutron stars.

The enormously high Fermi temperature implies that the energy of the electron gas is correspondingly high. The energy at zero temperature is

$$U(T = 0) = 2 \int_0^{\mu_0} \epsilon D(\epsilon) d\epsilon = \frac{3}{5} \tilde{N} \mu_0 \quad (18.34)$$

Thus the energy per particle is $\frac{3}{5} \mu_0$, or approximately 10^4 K in equivalent temperature units.

As the temperature rises, the Fermi level decreases (being “repelled” by the higher density of states at high energy, as we observed in the “fermion pre-gas model” of Section 18.1). Furthermore some electrons are “promoted” from orbitals below μ to orbitals above μ , increasing the energy of the system. To explore these effects quantitatively it is convenient to

invoke a general result for integrals of the form $\int \phi(\epsilon)f(\epsilon, T) d\epsilon$, where $\phi(\epsilon)$ is an arbitrary function and $f(\epsilon, T)$ is the Fermi occupation probability. This integral can be expanded in a power series in the temperature by invoking the step-function shape of $f(\epsilon, T)$ at low temperatures (Problem 18.4-2), giving

$$\int_0^\infty \phi(\epsilon)f(\epsilon, T) d\epsilon = \int_0^\mu \phi(\epsilon) d\epsilon + \frac{\pi^2}{6}(k_B T)^2 \phi'(\mu) + \frac{7\pi^4}{360}(k_B T)^4 \phi'''(\mu) + \dots \quad (18.35)$$

where ϕ' and ϕ''' are the first and third derivatives of ϕ with respect to ϵ , evaluated at $\epsilon = \mu$. It should be noted that μ is the temperature dependent Fermi level (not the zero-temperature Fermi energy μ_0).

We first find the dependence of the Fermi energy on the temperature. The Fermi energy is determined by equation 18.21

$$\tilde{N} = 2 \int_0^\infty f(\epsilon, T) D(\epsilon) d\epsilon = \frac{V}{2\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} \int_0^\infty \epsilon^{1/2} f(\epsilon, T) d\epsilon \quad (18.36)$$

Then taking $\phi(\epsilon) = \epsilon^{1/2}$ in equation 18.35

$$\tilde{N} = \frac{V}{3\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} \mu^{3/2} \left[1 + \frac{\pi^2}{8} \left(\frac{k_B T}{\mu} \right)^2 + \dots \right] \quad (18.37)$$

At zero temperature we recover equation (18.32) for μ_0 . To carry the solution to second order in T it is sufficient to replace μ by μ_0 in the second-order term, whence

$$\mu(T) = \mu_0 \left[1 - \frac{\pi^2}{12} \left(\frac{k_B T}{\mu_0} \right)^2 + \dots \right] \quad (18.38)$$

This result corroborates our expectation that the Fermi level decreases with increasing temperature. But for a typical value of μ_0/k_B (on the order of 10^4 K) the Fermi level at room temperature is decreased by only around 0.1% from its zero-temperature value!

The energy is given in an identical fashion, merely replacing $\epsilon^{1/2}$ by $\epsilon^{3/2}$, giving

$$U = \frac{V}{5\pi^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} \mu^{5/2} \left[1 + \frac{5}{8} \pi^2 \left(\frac{k_B T}{\mu} \right)^2 + \dots \right] \quad (18.39)$$

Comparison with equation 18.32 corroborates that at $T = 0$ we recover the relationship $U = \frac{3}{5}\tilde{N}\mu_0$ (equation 18.34). This suggests dividing equation 18.39 by equation 18.37, giving

$$U = \frac{3}{5}\tilde{N}\mu \left[1 + \frac{1}{2}\pi^2 \left(\frac{k_B T}{\mu} \right)^2 + \dots \right] \quad (18.40)$$

Replacing $\mu(T)$ by equation 18.38 we finally find

$$U = \frac{3}{5}\tilde{N}\mu_0 \left[1 + \frac{5}{12}\pi^2 \left(\frac{k_B T}{\mu_0} \right)^2 + \dots \right] \quad (18.41)$$

and the heat capacity is

$$C = \frac{3}{2}\tilde{N}k_B \left(\frac{\pi^2}{3} \frac{k_B T}{\mu_0} \right) + O(T^3) \quad (18.42)$$

The prefactor $\frac{3}{2}\tilde{N}k_B$ is the classical result, and the factor in parentheses is the “quantum correction factor” due to the quantum properties of the fermions. The quantum correction factor is of the order of $\frac{1}{10}$ at room temperature (for $\mu_0/k_B \approx 10^4$ K). This drastic reduction of the heat capacity from its classically expected value is in excellent agreement with experiment for essentially all metals.

In order to compare the observed heat capacity of metals with theory it must be recalled (Section 16.6) that the lattice vibrations also contribute a term proportional to T^3 , in addition to the linear and cubic terms contributed by the electrons

$$C = AT + BT^3 + \dots \quad (18.43)$$

The coefficient A is equal to the coefficient in equation 18.42 whereas B arises both from the cubic terms in equation 18.42 and (predominately) from the coefficient in the Debye theory. It is conventional to plot experimental data in the form C/T versus T^2 , so that the coefficient A is obtained as the $T = 0$ intercept and the coefficient B is the slope of the straight line. In fact such plots of experimental data do give excellent straight lines, with values of A and B in excellent agreement with equation 18.42 and the Debye theory (16.51).

The heat capacity (18.42) can be understood semiquantitatively and intuitively. As the temperature rises from $T = 0$, electrons are “promoted” from energies just below μ_0 to energies just above μ_0 . This population

transfer occurs primarily within a range of energies of the order of $2k_B T$ (recall Fig. 18.1 and Problem 18.1-7). The number of electrons so promoted is then of the order of $D(\mu_0)2k_B T$, and each increases its energy by roughly $k_B T$. Thus the increase in energy is of the order of

$$U - U_0 \approx 2D(\mu_0)(k_B T)^2 \quad (18.44)$$

But $D(\mu_0) = 3\tilde{N}/2\mu_0$, so that

$$U - U_0 \approx \frac{3\tilde{N}(k_B T)^2}{\mu_0} \quad (18.45)$$

and

$$C \approx \frac{3}{2}\tilde{N}k_B \left(2\frac{k_B T}{\mu_0}\right) \quad (18.46)$$

This rough estimate is quite close to the quantitative result calculated in equation 18.42, which merely substitutes $\pi^2/3$ for the factor 2 in the parentheses of equation 18.46.

PROBLEMS

18.4-1. Show that equation 18.32 can be interpreted as $\mu_0 = \hbar^2 k_F^2 / 2m$ where k_F is the radius of the sphere in k -space such that one octant contains $2\tilde{N}$ particles (recall Section 16.6). Why $2\tilde{N}$ rather than \tilde{N} particles?

18.4-2. Derive equation 18.35 by the following sequence of operations:

a) Denoting the integral in equation 18.35 by I , first integrate by parts and let $\Phi \equiv \int_0^\epsilon \phi(\epsilon') d\epsilon'$. Then expanding $\Phi(\epsilon)$ in a power series in $(\epsilon - \mu)$ to third order, show that

$$I = - \sum_{m=0}^{\infty} \frac{1}{m!} \frac{d^m \Phi(\mu)}{d\mu^m} I_m$$

with

$$I_m = \int_0^\infty (\epsilon - \mu)^m \frac{df}{d\epsilon} d\epsilon = -\beta^{-m} \int_{-\beta\mu}^\infty \frac{e^x}{(e^x + 1)^2} x^m dx$$

b) Show that only an exponentially small error is made by taking the lower limit of integration as $-\infty$, and that then all terms with m odd vanish.

c) Evaluate the first two nonvanishing terms and show that these agree with equation 18.35.

18-5 THE IDEAL BOSE FLUID

The formalism for the ideal Bose fluid bears a strikingly close similarity to that for the ideal Fermi fluid. As was anticipated in Table 18.1, and as we shall validate here, the formalisms differ only in several changes in sign. But the consequences are dramatically different. Whereas fermions at low temperatures tend to “saturate” orbital states up to some specific Fermi energy, bosons all tend to “condense” into the single lowest orbital state. This condensation happens precipitously, at (and below) a sharply defined “condensation temperature.” The resultant phase transition leads to superfluidity in ^4He (a phenomenon *not* seen in ^3He , which is a fermion fluid) and it leads to superconductivity in lead and in various other metals.

We consider an ideal Bose fluid, composed of particles of integral spin. The number of spin orientations is then $g_0 = 2S + 1$, where S is the magnitude of the spin.

The possible orbital states of the bosons in the fluid are labeled by \mathbf{k} and m_s , precisely as in the fermion case, and again the grand canonical partition sum factors with respect to the orbital states (as in line *a* of Table 18.1).

The partition sum of a single orbital state is independent of m_s , and is, for *each* value of m_s

$$\begin{aligned} z_{\mathbf{k}} = z_{\mathbf{k}, m_s} &= 1 + e^{-\beta(\epsilon_{\mathbf{k}} - \mu)} + e^{-\beta(2\epsilon_{\mathbf{k}} - 2\mu)} + e^{-\beta(3\epsilon_{\mathbf{k}} - 3\mu)} + \dots \\ &= \frac{1}{1 - e^{-\beta(\epsilon_{\mathbf{k}} - \mu)}} \end{aligned} \quad (18.47)$$

This validates line (b) of Table 18.1.

The average number of bosons in the orbital state \mathbf{k}, m_s is

$$\begin{aligned} \bar{n}_{\mathbf{k}, m_s} &= [e^{-\beta(\epsilon_{\mathbf{k}} - \mu)} + 2e^{-\beta(2\epsilon_{\mathbf{k}} - 2\mu)} + 3e^{-\beta(3\epsilon_{\mathbf{k}} - 3\mu)} + \dots] / z_{\mathbf{k}, m_s} \\ &= k_B T \frac{\partial}{\partial \mu} \ln z_{\mathbf{k}, m_s} \end{aligned} \quad (18.48)$$

which is just the analogue of the relation $\beta N = \partial / \partial \mu \ln \mathcal{Z}$, but is now applied to a single orbital state. Carrying out the differentiation we find

$$\bar{n}_{\mathbf{k}, m_s} \equiv f_{\mathbf{k}, m_s} = \frac{1}{e^{\beta(\epsilon_{\mathbf{k}} - \mu)} - 1} \quad (18.49)$$

and this is the result listed in line *c* of Table 18.1. It is important to note that, in contrast to the fermion case, $f_{\mathbf{k}, m_s}$ is not necessarily less than (or

equal to) unity. The quantity f_{k, m_i} is frequently referred to as an “occupation probability,” but it is more properly identified as a “mean occupation number” \bar{n}_{k, m_i} .

A moment’s reflection on the form of \bar{n}_{k, m_i} reveals that for a gas of material Bose particles the molar Gibbs function must be negative. For if μ were positive the orbital state with ϵ_k equal to μ would have an infinite occupation number! We thus conclude that for a gas with a bounded number of particles (and with a choice of energy scale in which the lowest energy orbital has zero energy) *the molar Gibbs potential μ is always negative.*

The form of \bar{n} as a function of $\beta(\epsilon - \mu)$ is shown in Fig. 18.2. The occupation number falls from an infinite value at $\epsilon = \mu$ to unity at $\epsilon = \mu + 0.693k_B T$. In the insert of Fig. 18.2, the orbital occupation number is shown schematically as a function of ϵ for two different temperatures ($T_2 > T_1$) and for two choices of μ .

If the system of interest is in contact with a particle reservoir, so that μ is constant, then the curve of $\bar{n}(\epsilon, T_2)$ in the insert should be shifted to the right. The number of particles in such a system increases with temperature. If the system of interest is maintained at constant particle number, the integral of $\bar{n}(\epsilon, T)D(\epsilon)$ is conserved. As is evident from the figure, the molar Gibbs potential μ then must decrease with increasing temperature (just as it does in the Fermi gas).

The grand canonical potential Ψ is the logarithm of \mathcal{Z} which, in turn, is the product of the z_{k, m_i} given in equation 18.47. Thus, as in Table 18.1 (lines d to g),

$$\beta\Psi = g_0 \int_0^\infty \ln [1 - e^{-\beta(\epsilon - \mu)}] D(\epsilon) d\epsilon \tag{18.50}$$

or, integrating by parts

$$\Psi = -\frac{2}{3} \frac{g_0 V}{(2\pi)^2} \left(\frac{2m}{\hbar^2}\right)^{3/2} \int_0^\infty \frac{\epsilon^{3/2}}{e^{\beta(\epsilon - \mu)} - 1} d\epsilon \tag{18.51}$$

and again the mechanical equation of state is $P = 2U/3V$ (lines i and j of Table 18.1).

For a system of particles maintained at constant μ by a particle reservoir the thermodynamics follows in a straightforward fashion. But for a system at constant \bar{N} the apparently innocuous formalism conceals some startling and dramatic consequences, with no analogues in either fermion or classical systems. As a preliminary to such considerations it is useful to turn our attention to systems in which the particle number is physically nonconserved.

18-6 NONCONSERVED IDEAL BOSON FLUIDS: ELECTROMAGNETIC RADIATION REVISITED

As we observed in Section 18.1, bosons are the quantum analogues of the “waves” of classical physics. A residue of this classical significance is that, unlike fermions, bosons need not be conserved. In some cases, as in a fluid of ^4He atoms, the boson particles are conserved; in other cases, as in a “photon gas” (recall Section 3.6), the bosons are not conserved. There exist processes, for instance, in which two photons interact through a nonlinear coupling to produce three photons. How then are we to adapt the formalism of the ideal Bose fluid to this possibility of nonconservation?

We recall the reasoning in Sections 17.2 and 17.3, leading to the grand canonical formalism. We there maximized the disorder subject to auxiliary constraints on the energy (equation 17.30) and on the number of particles (equation 17.31). These constraints introduced Lagrange parameters λ_2 and λ_3 (equation 17.33), which were then physically identified as $\lambda_2 = \beta$ and as $\lambda_3 = \beta\mu$. *Treatment of nonconserved particles simply requires that we omit the constraint equation on particle number.* Omission of the parameter λ_3 is equivalent to taking $\lambda_3 = 0$, or to taking $\mu = 0$. We thus arrive at the conclusion that *the molar Gibbs potential of a nonconserved Bose gas is zero.*

For $\mu = 0$ the grand canonical formalism becomes identical to the canonical formalism. Hence the grand canonical analysis of the photon gas simply reiterates the canonical treatment of electromagnetic radiation as developed in Section 16.7. The reader should trace this parallelism through in step by step detail, referring to Table 18.1 and Section 16.7 (see also Problem 18.6-2).

It is instructive to reflect on the different viewpoints taken in Section 16.7 and in this section. In the previous analysis our focus was on the *normal modes of the electromagnetic field*, and this led us to the canonical formalism. In this section our focus shifted to the *quanta of the field*, or the *photons*, for which the grand canonical formalism is the more natural. But the nonconservation of the particles requires μ to vanish and thereby achieves exact equivalence between the two formalisms. Only the language changes!

The number of photons of energy ε is $(e^{\beta\varepsilon} - 1)^{-1}$, where the permitted energies are given by

$$\varepsilon = \hbar\omega = \hbar c \frac{2\pi}{\lambda} = \frac{hc}{\lambda} \quad (18.52)$$

Here c is the velocity of light and λ is the quantum mechanical wavelength of the photon (or the wavelength of the normal mode, in the mode language of Section 16.7). The population of bosons of infinitely long

wavelength is unbounded³. The energy of these long wavelength photons vanishes, so that no divergence of the energy is associated with the formal divergence of the boson number.

To recapitulate, electromagnetic radiation can be conceptualized either in terms of the normal modes or in terms of the quanta of excitation of these modes. The former view leads to a canonical formalism. The latter leads to the concept of a nonconserved Bose gas, to the conclusion that the molar Gibbs potential of the gas is zero, and to an unbounded population of (unobservable) zero energy bosons in the lowest orbital state.

All of this might appear to be highly contrived and formally baroque were it not to have a direct analogy in *conserved* boson systems, giving rise to such startling physical effects as superfluidity in ⁴He and superconductivity in metals, to which we now turn.

PROBLEMS

18.6-1. Calculate the number of photons in the lowest orbital state in a cubic vessel of volume 1 m³ at a temperature of 300 K. What is the total energy of these photons? What is the number of photons in a single orbital state with a wavelength of 5000 Å, and what is the total energy of these photons?

18.6-2.

(a) In applying the grand canonical formalism to the photon gas can we use the density of orbital states function $D(\epsilon)$ as in equation (f) of Table 18.1? Explain.

(b) Denoting the velocity of light by c , show that writing $c = (\text{wavelength}/\text{period})$ implies $\omega = ck$. From this relation and from Section 16.5 find the density of orbital states $D(\epsilon)$.

(c) Show that the grand canonical analysis of the photon gas corresponds precisely with the theory given in Section 16.8.

18-7 BOSE CONDENSATION

Having the interlude of Section 18.6 to provide perspective, we focus on a system of conserved particles enclosed in impermeable walls. Then, as we saw in Fig. 18.2 and the related discussion, the molar Gibbs potential μ must increase as the temperature decreases (just as in the fermion case).

Assuming the bosons to be material particles of which the kinetic energy is $\epsilon = p^2/2m$, the density of orbital states is proportional to $\epsilon^{1/2}$

³Of course such infinite-wavelength photons can be accommodated only in a infinitely large container, but the number of photons can be increased beyond any preassigned bound in a finite container of sufficiently large size.

(equation f of Table 18.1) and the number of particles is

$$\tilde{N}_e = \frac{g_0 V}{(2\pi)^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} \int_0^\infty \frac{\epsilon^{1/2}}{\xi^{-1} e^{\beta\epsilon} - 1} d\epsilon \quad (18.53)$$

where ξ is the fugacity

$$\xi \equiv e^{\beta\mu} \quad (18.54)$$

and where the subscript e is affixed to \tilde{N}_e for reasons that will become understandable only later; for the moment \tilde{N}_e is simply another notation for \tilde{N} . The molar Gibbs potential is always negative (for conserved particles) so that the fugacity lies between zero and unity.

$$0 < \xi < 1 \quad (18.55)$$

This observation encourages us to expand the integral in equation 18.53 in powers of the fugacity, giving

$$\tilde{N}_e = \left[\frac{g_0 V}{(2\pi)^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} \right] \frac{\sqrt{\pi}}{2} (k_B T)^{3/2} F_{3/2}(\xi) = \frac{g_0 V}{\lambda_T^3} F_{3/2}(\xi) \quad (18.56)$$

where λ_T is the “thermal wavelength” (equation 18.26) and

$$F_{3/2}(\xi) = \sum_{r=1}^{\infty} \frac{\xi^r}{r^{3/2}} = \xi + \frac{\xi^2}{2\sqrt{2}} + \frac{\xi^3}{3\sqrt{3}} + \dots \quad (18.57)$$

At high temperature the fugacity is small and $F_{3/2}(\xi)$ can be replaced by ξ (its leading term), in which case equation 18.56 reduces to its classical form 18.25.

Similarly

$$U = \left[\frac{g_0 V}{(2\pi)^2} \left(\frac{2m}{\hbar^2} \right)^{3/2} \right] \frac{3\sqrt{\pi}}{4} (k_B T)^{5/2} F_{5/2}(\xi) = \frac{3}{2} k_B T \frac{g_0 V}{\lambda_T^3} F_{5/2}(\xi) \quad (18.58)$$

where

$$F_{5/2}(\xi) \equiv \sum_{r=1}^{\infty} \frac{\xi^r}{r^{5/2}} = \xi + \frac{\xi^2}{4\sqrt{2}} + \frac{\xi^3}{9\sqrt{3}} + \dots \quad (18.59)$$

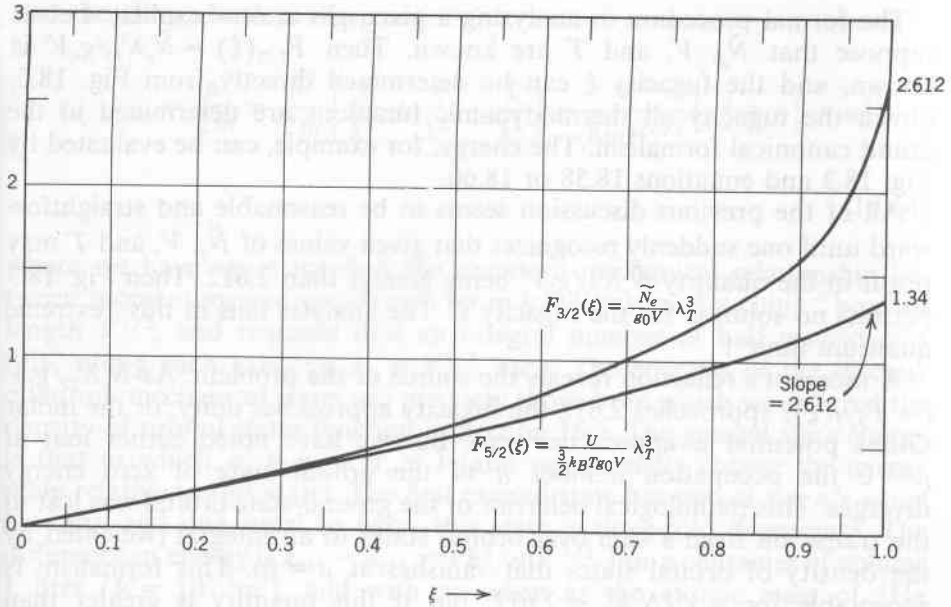


FIGURE 18.3

The functions $F_{3/2}(\xi)$ and $F_{5/2}(\xi)$ that characterize the particle number and the energy (equations 18.57–18.60) of a gas of conserved bosons.

Again the equation for U reduces to its classical form 18.27 if $F_{5/2}(\xi)$ is replaced by ξ , the leading term in the series.

Dividing 18.58 by 18.56

$$U = \frac{3}{2} \tilde{N}_e k_B T \frac{F_{5/2}(\xi)}{F_{3/2}(\xi)} \quad (18.60)$$

so that the ratio $F_{5/2}(\xi)/F_{3/2}(\xi)$ measures the deviation from the classical equation of state.

For both $F_{3/2}(\xi)$ and $F_{5/2}(\xi)$ all the coefficients in their defining series are positive, so that both functions are monotonically increasing functions of ξ , as shown in Fig. 18.3. Each function has a slope of unity at $\xi = 0$. At $\xi = 1$ the functions $F_{3/2}$ and $F_{5/2}$ have the value 2.612 and 1.34, respectively.

The two functions satisfy the relation

$$\frac{d}{d\xi} F_{5/2}(\xi) = \frac{1}{\xi} F_{3/2}(\xi) \quad (18.61)$$

from which it follows that the slope of $F_{5/2}(\xi)$ at $\xi = 1$ is equal to $F_{3/2}(1)$, or 2.612. The slope of $F_{3/2}(\xi)$ at $\xi = 1$ is infinite (Problem 18.7-2).

The formal procedure in analyzing a given gas is now explicit. Let us suppose that \tilde{N}_e , V , and T are known. Then $F_{3/2}(\xi) = \tilde{N}_e \lambda_T^3 / g_0 V$ is known, and the fugacity ξ can be determined directly from Fig. 18.3. Given the fugacity all thermodynamic functions are determined in the grand canonical formalism. The energy, for example, can be evaluated by Fig. 18.3 and equations 18.58 or 18.60.

All of the previous discussion seems to be reasonable and straightforward until one suddenly recognizes that given values of \tilde{N}_e , V , and T may result in the quantity $\tilde{N}_e \lambda_T^3 / g_0 V$ being greater than 2.612. Then Fig. 18.3 permits no solution for the fugacity ξ ! The analysis fails in this "extreme quantum limit"!

A moment's reflection reveals the source of the problem. As $\tilde{N}_e \lambda_T^3 / g_0 V (= F_{3/2}(\xi))$ approaches 2.612 the fugacity approaches unity, or the molar Gibbs potential μ approaches zero. But we have noted earlier that at $\mu = 0$ the occupation number \bar{n} of the orbital state of zero energy diverges. This pathological behavior of the ground-state orbital was lost in the transition from a sum over orbital states to an integral (weighted by the density of orbital states that vanishes at $\mu = 0$). This formalism is acceptable for $g_0 V / \tilde{N}_e \lambda_T^3 < 2.612$, but if this quantity is greater than 2.612 we must treat the replacement of a sum over states by an integral with greater care and delicacy.

We postpone briefly the corrections to the analysis that are required if $g_0 V / \tilde{N}_e \lambda_T^3 \geq 2.612$, to first evaluate the temperature at which the failure of the "integral analysis" (as opposed to the "summation analysis") occurs. Setting $g_0 V / \tilde{N}_e \lambda_T^3 = 2.612$ we find

$$k_B T_c = \frac{2\pi\hbar^2}{m} \left(\frac{1}{2.612} \frac{\tilde{N}}{g_0 V} \right)^{2/3} \quad (18.62)$$

where T_c is called the Bose condensation temperature. *For temperature greater than T_c the "integral analysis" is valid. At and below T_c a "Bose condensation" occurs, associated with an anomalous population of the orbital ground state.*

If the atomic mass m and the observed number density $\tilde{N}_e / g_0 V$ of liquified ${}^4\text{He}$ are inserted in equation 18.62 one finds a condensation temperature reasonably close (≈ 3 K) to the temperature (2.17 K) at which superfluidity and other nonclassical effects occur. This agreement is reasonable in light of the gross approximation involved in treating ${}^4\text{He}$ liquid as an ideal noninteracting gas.

To explore the population of the orbital ground state, and of other low-lying excited orbital states, we recall that the total number of particles is

$$\tilde{N}_e = \sum_{\mathbf{k}, m_s} \bar{n}(\varepsilon_{\mathbf{k}}) = g_0 \sum_{\mathbf{k}} [e^{\beta(\varepsilon_{\mathbf{k}} - \mu)} - 1]^{-1} \quad (18.63)$$

and the allowed values of $\epsilon_{\mathbf{k}}$ are

$$\epsilon_{n_x, n_y, n_z} = \frac{p^2}{2m} = \frac{h^2}{2m} \left(\frac{1}{\lambda_x^2} + \frac{1}{\lambda_y^2} + \frac{1}{\lambda_z^2} \right) = \frac{h^2}{8mV^{2/3}} (n_x^2 + n_y^2 + n_z^2) \quad (18.64)$$

where we have again invoked the quantum mechanical relationship between momentum and wavelength ($p = h/\lambda$), assumed a cubic "box" of length $V^{1/3}$, and required that an integral number of half wavelengths "fit" along each axis ($\frac{1}{2}n_x\lambda_x = V^{1/3}$, etc.). The energies of the discrete quantum mechanical states are precisely those from which we inferred the density of orbital states function in Section 16.5. The ground state energy is that in which $n_x = n_y = n_z = 1$ (and we normally choose the energy scale relative to this state). The first excited state has two of the n 's equal to unity and one equal to two—this state is three-fold degenerate. The difference in energy is $\epsilon_{211} - \epsilon_{111} = 6h^2/mV^{2/3}$. For a container of volume 1 liter ($V = 10^{-3} \text{ m}^3$), and with m taken as the atomic mass of ${}^4\text{He}$ ($\approx 6.6 \times 10^{-27} \text{ Kg}$), the energy of the first excited state (relative to the ground state energy is)

$$\epsilon_{211} - \epsilon_{111} = 6h^2/mV^{2/3} \approx 2.5 \times 10^{-37} \text{ J}$$

or

$$(\epsilon_{211} - \epsilon_{111})/k_B \approx 2 \times 10^{-14} \text{ K} \quad (18.65)$$

Thus the discrete states are indeed *very* closely spaced in energy—far closer than $k_B T$ at any reasonable temperature. We might well have felt confident in replacing the sum by an integral!

But let us examine more closely the population of each state as the chemical potential approaches ϵ_{111} from below. In particular we inquire as to the value of μ for which the population of the orbital ground state alone is comparable to the entire number of particles in the gas. Let n_0 be the number of particles in the ground state orbital, so that $[\exp \beta(\epsilon_{111} - \mu) - 1]^{-1} = n_0$. Then if $n_0 \gg 1$ it follows that $\beta(\epsilon_{111} - \mu) \ll 1$ and we can expand the exponential to first order, so that $n_0 \sim k_B T / (\epsilon_{111} - \mu)$. Thus the population of the orbital ground state becomes comparable to the entire number of particles in the system (say $n_0 \approx 10^{22}$) if $\beta(\epsilon_{111} - \mu) \sim 10^{-22}$.

What, then, is the population of the first excited orbital state? The energy difference $(\epsilon_{111} - \mu)/k_B$ is $\approx 10^{-21} \text{ K}$ (for $T \approx 10 \text{ K}$) whereas $(\epsilon_{211} - \epsilon_{111})/k_B \approx 10^{-14} \text{ K}$ (equation 18.65). It follows that $n_{211}/n_0 \approx 10^{-7}$. The population of higher states continues to fall extremely rapidly.

As the temperature decreases in a Bose gas the molar Gibbs potential increases and approaches the energy of the ground state orbital. The population of the ground state orbital increases, becoming a nonnegligible fraction of the total number of bosons in the gas at the critical temperature T_c . The occupation number of any individual other state is relatively negligible.

As the temperature decreases further μ cannot approach closer to the ground state energy than $\beta(\mu - \varepsilon_{111}) = 1/\tilde{N} \approx 10^{-23}$ (at which value the ground state alone would host all N particles in the gas!). Hence the ground state shields all other states from too close an approach of μ , and each other state individually can host only a relatively small number of particles. Together, of course, the remaining states host all the particles not in the ground state.

With this understanding of the mechanism of the Bose condensation it is a simple matter to correct the analysis. All orbital states other than the ground state are adequately represented by the integral over the density of orbital states function. The ground state energy must be separately and explicitly listed in the sum over states.

The number of particles is, then

$$\tilde{N} = n_0 + \tilde{N}_e \quad (18.66)$$

where n_0 is the number of particles in the ground state orbital

$$n_0 = (e^{-\beta\mu} + 1)^{-1} = \frac{\xi}{1 - \xi} \quad (18.67)$$

and where \tilde{N}_e is the number of particles in "excited states" (i.e., in all orbital states other than the ground orbital state). The number of "excited particles" \tilde{N}_e is as given in equation 18.54.

The expression 18.59 for the energy remains correct, since the population of the zero energy orbitals makes no contribution to the energy. Thus *the entire correction to the theory consists of the reinterpretation of \tilde{N}_e as the number of excited particles, and the adjuncture of the two additional equations 18.67 and 18.68.*

Equivalently, we can simply add the ground state term to our previous expression for the grand canonical potential (equation 18.51), giving the fundamental relation

$$\Psi = g_0 k_B T \ln(1 - \xi) - g_0 k_B T \frac{V}{\lambda_T^3} F_{5/2}(\xi) \quad (18.68)$$

where, of course, ξ is the fugacity $e^{\beta\mu}$.

With equations 18.56 to 18.60 and 18.66 to 18.67, we can explore a variety of observable properties of Bose fluids. These properties are summarized in Table 18.2 and illustrated schematically in Fig. 18.4.

TABLE 18.2
Properties of the Ideal Bose Fluid

Fundamental equation

$$\Psi = k_B T \ln(1 - \xi) - k_B T (V/\lambda_T^3) F_{5/2}(\xi)$$

Condensation temperature

$$k_B T_c = \frac{2\pi\hbar^2}{m} \left(\frac{1}{2.612} \frac{\tilde{N}}{g_0 V} \right)^{3/2}$$

Condensed and excited bosons

$$\tilde{N} = n_0 + \tilde{N}_e, \quad n_0 = \frac{\xi}{1 - \xi}, \quad \tilde{N}_e = \frac{V}{\lambda^3} F_{3/2}(\xi)$$

$$T > T_c: \quad n_0 \ll \tilde{N}, \quad \tilde{N}_e \approx \tilde{N} = \frac{V}{\lambda^3} F_{3/2}(\xi)$$

$$T < T_c: \quad n_0/\tilde{N} = 1 - \tilde{N}_e/\tilde{N} = 1 - \left(\frac{T}{T_c} \right)^{3/2}$$

Energy

$$T > T_c: \quad U = \frac{3}{2} \tilde{N} k_B T \frac{F_{5/2}(\xi)}{F_{3/2}(\xi)}$$

$$T < T_c: \quad U = \frac{3}{2} \tilde{N} k_B T \frac{F_{5/2}(1)}{F_{3/2}(1)} \left(\frac{T}{T_c} \right)^{3/2} = 0.76 \tilde{N} k_B T_c \left(\frac{T}{T_c} \right)^{5/2}$$

Heat capacity c_v (per particle)

$$T > T_c: \quad c_v = \frac{3}{2} k_B \left[\frac{5}{2} \frac{F_{5/2}(\xi)}{F_{3/2}(\xi)} - \frac{3}{2} \frac{F'_{5/2}(\xi)}{F'_{3/2}(\xi)} \right]$$

$$T < T_c: \quad c_v = 1.9 k_B \left(\frac{T}{T_c} \right)^{3/2}$$

Entropy

$$T > T_c: \quad S = \frac{5}{2} k_B \frac{V}{\lambda_T^3} F_{5/2}(\xi) - \tilde{N} k_B \ln \xi$$

$$T < T_c: \quad S = \frac{5}{2} k_B \frac{V}{\lambda_T^3} F_{5/2}(1) = 3.35 k_B \frac{V}{\lambda_T^3}$$

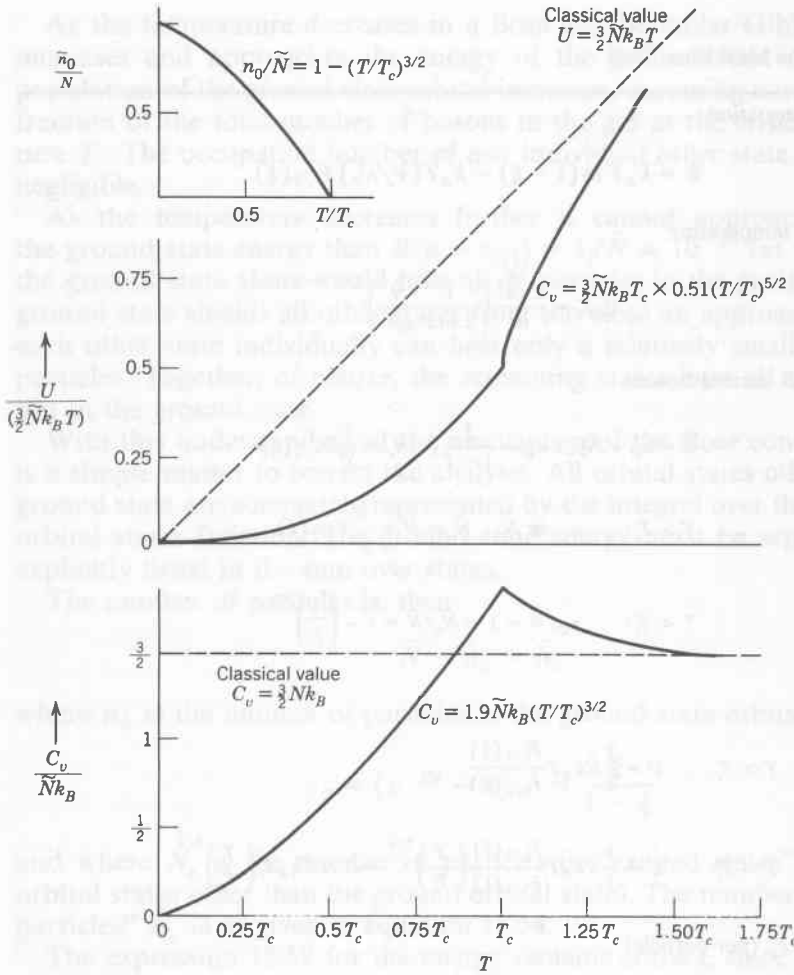


FIGURE 18.4 Properties of an ideal Bose fluid. The energy and heat capacity for $T > T_c$ are schematic.

First, consider the temperature dependence of the number of bosons in the orbital ground state. For $T < T_c$ the maximum number of bosons that can be accommodated in excited states is

$$\tilde{N}_e = \frac{g_0 V}{\lambda_T^3} F_{3/2}(1), \quad T < T_c \tag{18.69}$$

and in particular, as $T \rightarrow T_c$, $\tilde{N}_e \rightarrow \tilde{N}$, so that

$$\tilde{N} = \frac{g_0 V}{\lambda_c^3} F_{3/2}(1) \tag{18.70}$$

where λ_c is the value of λ_T at $T = T_c$. Dividing

$$\frac{\tilde{N}_e}{\tilde{N}} = \left(\frac{\lambda_c}{\lambda_T} \right)^3 = \left(\frac{T}{T_c} \right)^{3/2} \quad (18.71)$$

The number of particles in the ground state is then

$$\frac{n_0}{\tilde{N}} = 1 - \frac{\tilde{N}_e}{\tilde{N}} = 1 - \left(\frac{T}{T_c} \right)^{3/2} \quad (18.72)$$

This dependence is sketched in Fig. 18.4.

The energy of the system is also of great interest as its derivative is the heat capacity, an easily observable quantity. For $T > T_c$ the energy is given by equation 18.60. For $T < T_c$ equation 18.58 can be written in the form

$$\begin{aligned} U &= \frac{3}{2} k_B T \frac{g_0 V}{\lambda_T^3} F_{5/2}(1) = \frac{3}{2} k_B T \frac{\tilde{N}_e}{F_{3/2}(1)} F_{5/2}(1) \\ &= \frac{3}{2} \tilde{N} k_B T \frac{F_{5/2}(1)}{F_{3/2}(1)} \frac{\tilde{N}_e}{\tilde{N}} = \frac{3}{2} \tilde{N} k_B T (0.51) \left(\frac{T}{T_c} \right)^{3/2} \\ &= 0.76 \tilde{N} k_B T_c \left(\frac{T}{T_c} \right)^{5/2}, \quad T < T_c \end{aligned} \quad (18.73)$$

For $T > T_c$ the energy is given by equation 18.60, or $U = \frac{3}{2} \tilde{N} k_B T [F_{5/2}(\xi)/F^{3/2}(\xi)]$, so that the energy is always less than its classical value. The fugacity is determined as a function of T by Fig. 18.2.

Calculation of the molar heat capacity for $T < T_c$ follows directly by differentiation of equation 18.73

$$c_v = 1.9 \tilde{N} k_B \left(\frac{T}{T_c} \right)^{3/2}, \quad T < T_c \quad (18.74)$$

It is of particular interest that $c_v = 1.9 N k_B$ at $T = T_c$, a value well above the classical value $1.5 N k_B$ which is approached in the classical regime at high temperature.

Calculation of the heat capacity at $T > T_c$ requires differentiation of equation 18.60 at constant \tilde{N} , and elimination of $(d\xi/dT)_{\tilde{N}}$ by equation 18.56. The results are indicated schematically in Fig. 18.4 and given in Table 18.2.

The unique cusp in the heat capacity at $T = T_c$ is a signature of the Bose condensation. A strikingly similar discontinuity is observed in ^4He

fluids; its detailed shape appears to be in agreement with the renormalization group predictions for the universality class of a two-dimensional order parameter (recall the penultimate paragraph of Chapter 12).

Finally we note that the Bose condensation in ^4He is accompanied by striking physical properties of the fluid. Below T_c the fluid flows freely through the finest capillary tubes. It runs up and over the side of breakers. It is, as its name denotes, "superfluid." The explanation of these properties lies outside the scope of statistical mechanics. It is sufficient to say that it is the "condensed phase," or the *ground state component*, that alone flows so freely through narrow tubes. This component cannot easily dissipate energy through friction, as it is already in the ground state. More significantly, the condensed phase has a *quantum coherence* with no classical analogue; the bosons that share a single state are correlated in a fashion totally different from the excited particles (which are randomly distributed over enormously many states).

A similar Bose condensation occurs in the electron fluid in certain metals. By an interaction involving phonons, pairs of electrons bind together in correlated motion. These electron pairs then act as bosons. The Bose condensation of the pairs leads to superconductivity, the analogue of the superfluidity of ^4He .

PROBLEMS

18.7-1. Show that equations 18.56 and 18.58, for \tilde{N}_e and U , respectively, approach their proper classical limits in the classical regime.

18.7-2. Show that $F_{3/2}(1)$, $F_{5/2}(1)$, and $F_{5/2}'(1)$ are all finite, whereas $F_{3/2}'(1)$ is infinite. Here $F_{3/2}'(1)$ denotes the derivative of $F_{3/2}(x)$, evaluated at $x = 1$.

Hint: Use the integral test of convergence of infinite series, whereby $\sum_{n=1}^{\infty} f(n)$ converges or diverges with $\int_1^{\infty} f(x) dx$ (if $0 < f_{n+1} < f_n$ for all n).

18.7-3. Show that the explicit inclusion of the orbital ground state contributes $g_0 k_B T \ln(1 - \xi)$ to the grand canonical partition sum, thereby validating equation 18.68.