

Chapter 5 Quantum Statistical Mechanics

5.1 Review of the Ideal Classical Gas

In the previous chapter, we dealt with the ideal classical gas. Recall that this is a system of **independent, indistinguishable** particles in a box. The assumption of **independence** means that the energy eigenstates of the N particle system may be found in terms of the single particle energy eigenstates. For monatomic particles, these are simply the familiar stationary states of a single particle in a three-dimensional box. We saw that the assumption of **indistinguishability** means that it is not possible to say that a particular particle is in a particular single-particle state. Instead, all we can do to label the N -particle states is to specify the numbers of particles in each of the single-particle states. We called these the **occupation numbers** of the single-particle states. A state r of the N particle system is thus a list of occupation numbers $r = (n_1, n_2, \dots, n_s, \dots)$.

If we deal with a gas containing of only **one** particle in a box, the Boltzmann distribution gives the probability of that particle being in each of the energy eigenstates, i.e.,

$$p_s = \exp(-\beta\varepsilon_s) / Z_1(\beta) \quad (5.1)$$

where s labels the single-particle eigenstate of energy ε_s . When we considered N particles, the average occupation number \bar{n}_s of the s th single-particle energy eigenstate was found to be

$$\bar{n}_s = N p_s = \frac{N \exp(-\beta\varepsilon_s)}{Z_1(\beta)}, \quad (5.2)$$

where for the classical approximation to apply, it was assumed that for every s ,

$$\bar{n}_s \ll 1. \quad (5.3)$$

Although equation (5.2) seems obvious, it is in fact **not** true in general. The condition (5.3) is necessary (together with indistinguishability) to make the approximation

$$Z_N \approx \frac{Z_1^N}{N!} \quad (5.4)$$

and it is this result which leads to (5.2). Equation (5.2) defines what is meant by **Maxwell-Boltzmann statistics**, and we shall see in this chapter how it is an approximation to the actual distribution functions which arise from quantum statistical mechanics.

We close this review with figures illustrating the approximations involved in calculating a density of states and a summary of how the average occupation numbers are used to find the number density of various particle energies when the discrete energy levels are so close together that they may be replaced by a continuum. We shall be considering this process several times in this chapter and so it is useful to consider it first in a familiar setting.

For a particle of mass m in a cube of side L , the energy eigenvalues are

$$\varepsilon_s = \frac{(n_x^2 + n_y^2 + n_z^2) \pi^2 \hbar^2}{2mL^2} \quad (5.5)$$

where n_x , n_y and n_z are positive integers. Given a particular energy ε , we can define $F(\varepsilon)$ to be the number of single-particle states with energy $\leq \varepsilon$. A simple program that counts these states produces the graph shown in Figure 5.1. By using the volume of the positive octant of a sphere as in the last chapter, we can calculate an approximation to the number of states. In the inset, the actual number of states is shown as the shaded grey region while the approximation is shown by the line. For low values of the energy, the discreteness is important, and the approximation using the volume is an over-estimate of the true number of states. In the main graph, these relationships are plotted using a log-log scale over a much larger range of

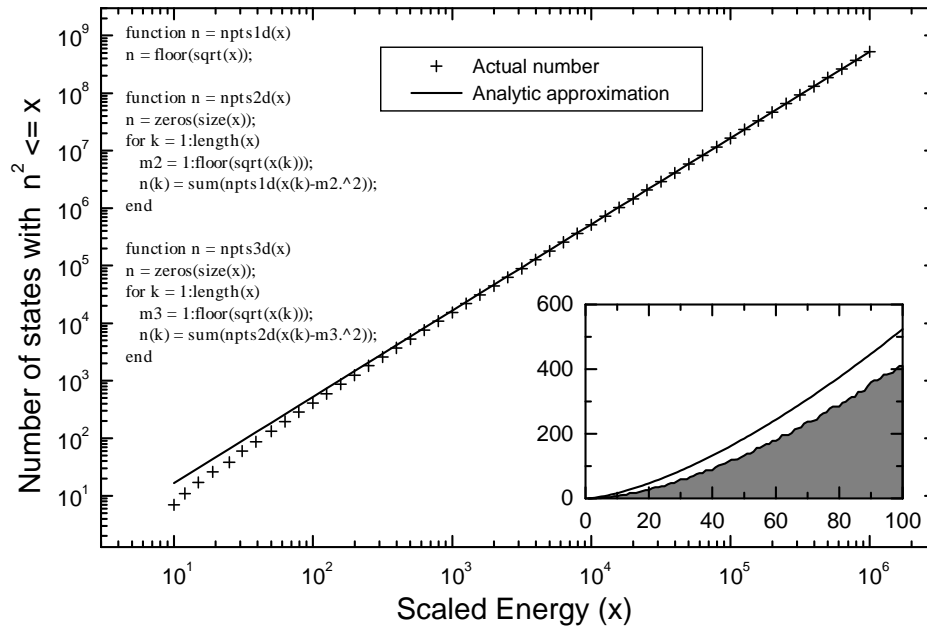


Figure 5.1 Actual and analytic approximation to the number of states with $n_x^2 + n_y^2 + n_z^2 \leq x$, where n_x , n_y and n_z are positive integers. Main graph is on log-log axes, inset is on linear axes for small values of x .

energies. It is clear that for larger energies, the power-law $F(\varepsilon) \propto \varepsilon^{3/2}$ calculated using the volume argument is quite accurate. The density of states $f(\varepsilon)$ is defined so that

$$F(\varepsilon) = \int_0^\varepsilon f(\varepsilon') d\varepsilon' \quad (5.6)$$

from which it is apparent that $f(\varepsilon) = F'(\varepsilon) \propto \varepsilon^{1/2}$.

What we would like is to find $dN(\varepsilon)$ which gives the number of particles in the gas with energies lying in the range ε to $\varepsilon + d\varepsilon$. This is the product of two factors. The first is mean occupation number of the single particle states which we called \bar{n}_s . When we are dealing with a continuum, this is replaced by $\bar{n}(\varepsilon)$. The second is the number of single-particle states lying in the energy range ε to $\varepsilon + d\varepsilon$. In the previous chapter, we called the density of single-particle states $f(\varepsilon)$ and so this second factor is $f(\varepsilon) d\varepsilon$. Thus in summary, we have

$$dN(\varepsilon) = \bar{n}(\varepsilon) f(\varepsilon) d\varepsilon \quad (5.7)$$

or

$$\frac{dN}{d\varepsilon} = \bar{n}(\varepsilon) f(\varepsilon) \quad (5.8)$$

This calculation is shown graphically in Figure 5.2. As we shall see in this chapter, interesting effects arise from choosing systems with different $f(\varepsilon)$ and with different $\bar{n}(\varepsilon)$.

From dN we can find quantities such as the total number of particles and the total energy of the gas using

$$N = \int_0^\infty dN(\varepsilon) \quad (5.9)$$

$$E = \int_0^\infty \varepsilon dN(\varepsilon) \quad (5.10)$$

and related formulas.

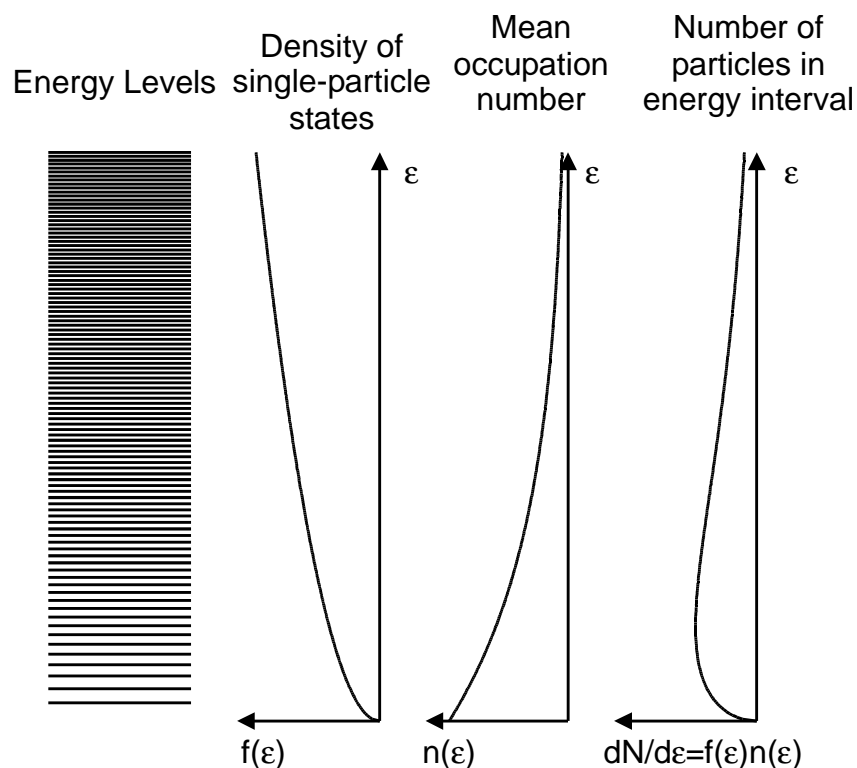


Figure 5.2 Calculation of number of particles dN with energies in an interval $d\varepsilon$ about ε . This figure shows $f(\varepsilon)$ and $\bar{n}(\varepsilon)$ appropriate for particles of matter obeying Maxwell-Boltzmann statistics.

5.2 The Quantum Gas of Identical Particles

Let us consider more carefully the transition between the quantum mechanics of single particle and that of a gas of N independent, **indistinguishable** particles. Let us suppose that the single-particle energy eigenvalues are

$$\varepsilon_1 \leq \varepsilon_2 \leq \varepsilon_3 \leq \dots \leq \varepsilon_s \leq \dots \quad (5.11)$$

For an energy eigenstate of N indistinguishable particles, we cannot say which single-particle energy eigenstate each particle is found in. Instead, we have to deal with **occupation numbers** (n_1, n_2, \dots) which tell us how many particles are in each single-particle eigenstate. If there are a total N particles,

$$n_1 + n_2 + \dots + n_s + \dots = N \quad (5.12)$$

and for non-interacting particles the total energy of the eigenstate is

$$n_1\varepsilon_1 + n_2\varepsilon_2 + \dots + n_s\varepsilon_s + \dots = E \quad (5.13)$$

We have so far implicitly assumed that the values of n_s can take on any value from zero to the total number of particles. This is in fact not always the case. Rather unexpectedly, it turns out that all particles fall into one of two categories. Particles of the first category are called **bosons**, and for such particles, the occupation numbers can indeed take on any value. However, for particles of the second category, which are called **fermions**, it turns out that the only possible occupation numbers allowed are zero and one. The fact that for fermions, it is not possible to place more than one particle in a single-particle eigenstate is called the **Pauli exclusion principle**. It turns out that particles with half-integer spin such as protons, neutrons and electrons are fermions, whereas particles with integer spin such as photons and mesons are bosons. For composite particles such as atoms, the **total** spin determines whether the particle is a boson or a fermion. For example, a sodium 23 atom with 11 protons, 12 neutrons and 11 electrons has a total of 34 particles with half-integer spin and so is a boson overall. On the other hand, an atom of the helium 3 isotope has two

protons, one neutron and two electrons. This is an odd number of particles with half-integer spin and so the resulting atom is a fermion.

When evaluating the partition function for a quantum gas, we must be sure to do the sum only over the allowed occupation numbers for the type of particles being considered. As always,

$$Z = \sum_r \exp(-\beta E_r) \quad (5.14)$$

where r labels the energy eigenstates. Here we have

$$Z = \sum_{n_1} \sum_{n_2} \cdots \sum \exp[-\beta(n_1 \varepsilon_1 + n_2 \varepsilon_2 + \dots)] \quad (5.15)$$

where the sum is over all n_1, n_2, \dots . If the particles are fermions, each n_s can either be zero or one, whereas if the particles are bosons, each n_s can take on any value. For material particles which can neither be created nor destroyed, we have the additional constraint that

$$n_1 + n_2 + \dots + n_s + \dots = N. \quad (5.16)$$

5.3 Blackbody Radiation

We consider the radiation present within a cavity whose walls are in thermal equilibrium with the radiation at temperature T . This thought of either as a problem involving electromagnetic waves (analogous to the vibrational modes in a solid) or as a noninteracting “gas” of photons. We shall adopt the model of a photon gas.

Since photons have spin one, they are bosons and so their occupation numbers can take on any value. Unlike material particles, however, the number of photons within a cavity at constant temperature is **not** fixed, but can fluctuate as photons are continually absorbed and re-emitted by the atoms in the walls. It is thus **not** appropriate to use the total number constraint (5.16) for photons. Instead, the partition function is found by carrying out an unrestricted sum over all values of n_1, n_2 , etc. Thus, for photons, we see that

$$Z = \sum_{n_1=0}^{\infty} \sum_{n_2=0}^{\infty} \cdots \sum \exp[-\beta(n_1 \varepsilon_1 + n_2 \varepsilon_2 + \dots)] \quad (5.17)$$

$$= \left(\sum_{n_1=0}^{\infty} \exp[-\beta n_1 \varepsilon_1] \right) \left(\sum_{n_2=0}^{\infty} \exp[-\beta n_2 \varepsilon_2] \right) \dots \quad (5.18)$$

$$= \prod_s \left(\sum_{n_s=0}^{\infty} \exp[-\beta n_s \varepsilon_s] \right) \quad (5.19)$$

Each infinite sum is a simple geometric series which may be summed explicitly, giving the result

$$Z = \prod_s \frac{1}{1 - \exp(-\beta \varepsilon_s)} = \prod_s Z_s. \quad (5.20)$$

where $Z_s = [1 - \exp(-\beta \varepsilon_s)]^{-1}$. From the expression for Z we shall proceed to find the mean energy etc., in the usual way.

5.3.1 Occupation Numbers of Single-Particle Energy Eigenstates

Before calculating an explicit form for Z , let us look more closely at the **occupation number** n_s of the **single-particle energy eigenstate** s when the system is in thermal equilibrium. Although n_s can take on

any (non-negative integer) value for bosons, the above suggests that probability that n_s takes on different values is given by the Boltzmann distribution, with

$$p(n_s) = \frac{\exp(-\beta n_s \varepsilon_s)}{Z_s} \quad (5.21)$$

The **mean occupation number** of single-particle energy eigenstate s is thus

$$\bar{n}_s = \bar{n}(\varepsilon_s) = \sum_{n_s=0}^{\infty} n_s p(n_s) = -\frac{1}{\beta} \frac{\partial}{\partial \varepsilon_s} (\log Z_s) = \frac{1}{\exp(\beta \varepsilon_s) - 1} \quad (5.22)$$

5.3.2 The Density of States

Let us now proceed to calculate the **single-particle energy eigenstates** labelled by s . For the classical gas, these are simply the familiar eigenstates of a particle in a box, obtained by solving the Schrödinger equation. What can be the corresponding single-particle eigenstates for a photon? It should be clear that we cannot just take over the results for the particle in the box, because in Schrödinger's equation we assumed that the kinetic energy is $p^2/(2m)$ which is correct for a (non-relativistic) particle but certainly not right for a photon. Instead, we have to consider what energy eigenvalues a photon can have when it is bouncing around inside a box. For a photon, the energy depends on the frequency via Planck's relationship $E = \hbar\omega$. In order to determine the available frequencies, it is only necessary to ask what **standing waves** can propagate within the box subject to the **boundary conditions**.

Using a cube with a side of length L , we see that there must be an integer number of half wavelengths in L for each of the three directions. Hence if the propagation vector is \mathbf{k} , with Cartesian components (k_x, k_y, k_z) , we must have that

$$k_x = \frac{n_x \pi}{L}, \quad k_y = \frac{n_y \pi}{L} \quad \text{and} \quad k_z = \frac{n_z \pi}{L} \quad (5.23)$$

where n_x, n_y and n_z are from the set $\{1, 2, 3, \dots\}$. Associated with each \mathbf{k} , the energy of the photon is $\hbar\omega = \hbar|\mathbf{k}|c$ where c is the speed of light. The relationship between the single-particle energy and the lattice point (n_x, n_y, n_z) is thus

$$\varepsilon_s = \hbar c \sqrt{k_x^2 + k_y^2 + k_z^2} = \frac{\hbar c \pi}{L} \sqrt{n_x^2 + n_y^2 + n_z^2} \quad (5.24)$$

Since there are two independent transverse polarizations of light, the single particle state label s may be thought of as (n_x, n_y, n_z, σ) where σ is 0 or 1, indicating the polarization. If we compare (5.5) and (5.24) we see that the differences between material particles and photons has led to a different expression for the single-particle energy eigenvalues.

In order to calculate the partition function, we need to carry out a product over all the single particle energy eigenstates in (5.20). As usual, we do this by taking the logarithm to turn the product into a sum and use the density of states to replace the sum by an integral. The number of states with energy less than ε is twice (remember two polarizations!) the number of positive integer triples (n_x, n_y, n_z) with the property that

$$\frac{\hbar c \pi}{L} \sqrt{n_x^2 + n_y^2 + n_z^2} \leq \varepsilon \quad (5.25)$$

Using the now-familiar argument of taking the volume of the octant of a sphere of radius $\varepsilon L/(\hbar c \pi)$, we see that

$$\begin{aligned} F(\varepsilon) &= 2 \times \frac{1}{8} \times \frac{4}{3} \pi \left(\frac{\varepsilon L}{\hbar c \pi} \right)^3 \\ &= \frac{\varepsilon^3 V}{3\pi^2 \hbar^3 c^3} \end{aligned} \quad (5.26)$$

where $V = L^3$ is the volume of the box. The density of states is the derivative of this cumulative distribution function, i.e.,

$$f(\varepsilon) = \frac{\varepsilon^2 V}{\pi^2 \hbar^3 c^3}. \quad (5.27)$$

Taking the logarithm of (5.20), we see that

$$\log Z = \sum_s \log \left[\frac{1}{1 - \exp(-\beta \varepsilon_s)} \right] \quad (5.28)$$

Replacing the sum by an integral, recalling that $f(\varepsilon) d\varepsilon$ is the number of single-particle states with energies between ε and $\varepsilon + d\varepsilon$,

$$\log Z = \int_0^\infty f(\varepsilon) \log \left[\frac{1}{1 - \exp(-\beta \varepsilon)} \right] d\varepsilon \quad (5.29)$$

5.3.3 The Distribution of Photon Energies (Blackbody Spectrum)

The mean energy is

$$\bar{E} = -\frac{\partial}{\partial \beta} \log Z = \int_0^\infty \frac{\varepsilon f(\varepsilon)}{\exp(\beta \varepsilon) - 1} d\varepsilon \quad (5.30)$$

Comparing this with (5.22), we see that this may be written as

$$\bar{E} = \int_0^\infty \varepsilon \bar{n}(\varepsilon) f(\varepsilon) d\varepsilon \quad (5.31)$$

which is identical to (5.10), and which confirms that

$$dN(\varepsilon) \equiv \bar{n}(\varepsilon) f(\varepsilon) d\varepsilon \quad (5.32)$$

may be interpreted as the number of photons with energy between ε and $\varepsilon + d\varepsilon$ as in (5.7). Substituting the expressions for $\bar{n}(\varepsilon)$ and $f(\varepsilon)$ we see that

$$dN(\varepsilon) \equiv \frac{V}{\pi^2 \hbar^3 c^3} \frac{\varepsilon^2}{\exp(\beta \varepsilon) - 1} d\varepsilon \quad (5.33)$$

Since $\varepsilon = \hbar \omega$, we can find the number of photons within the angular frequency range ω to $\omega + d\omega$. This is

$$dN(\omega) = \frac{V}{\pi^2 c^3} \frac{\omega^2}{\exp(\beta \hbar \omega) - 1} d\omega \quad (5.34)$$

The energy carried by the photons in this angular frequency range is $\hbar \omega dN(\omega)$, or

$$dE(\omega) = \frac{V}{\pi^2 c^3} \frac{\hbar \omega^3}{\exp(\beta \hbar \omega) - 1} d\omega \quad (5.35)$$

The **energy density** within the cavity corresponding to this angular frequency range is $u(\omega, T)$, where

$$u(\omega, T) d\omega = \frac{\hbar \omega^3}{\pi^2 c^3 [\exp(\beta \hbar \omega) - 1]} d\omega \quad (5.36)$$

This is the celebrated **Planck blackbody radiation law** which gives the distribution of energy density as a function of frequency for radiation at thermal equilibrium. It depends only on the temperature T and is in excellent agreement with observations.

From equation (5.36) for the blackbody spectrum, we may find the frequency at which u is a maximum. This occurs for

$$0 = \frac{d}{d\omega} \left\{ \frac{\hbar \omega^3}{\pi^2 c^3 [\exp(\beta \hbar \omega) - 1]} \right\} \quad (5.37)$$

Carrying out the differentiation, we find that we need to solve the transcendental equation

$$3 + (x - 3) e^x = 0, \quad (5.38)$$

where $x = \beta \hbar \omega_{\max}$. This can be done numerically, giving

$$\omega_{\max} = \frac{2.822 kT}{\hbar}. \quad (5.39)$$

This proportionality of ω_{\max} on temperature is called **Wien's displacement law**, which is in excellent agreement with experiment.

At low frequencies, $\exp(\beta\hbar\omega) - 1 \approx \beta\hbar\omega$ and so

$$u(\omega, T) d\omega \approx \frac{kT}{\pi^2 c^3} \omega^2 d\omega \quad (5.40)$$

This is called the **Rayleigh-Jeans law**, which is also the prediction of classical (non-quantum) mechanics. The fact that it diverges at large ω was called the “ultraviolet catastrophe” and historically was the motivation for Planck's development of quantum mechanics.

At high frequencies, $\exp(\beta\hbar\omega) \gg 1$ and

$$u(\omega, T) d\omega \approx \frac{\hbar\omega^3}{\pi^2 c^3} \exp(-\beta\hbar\omega) d\omega \quad (5.41)$$

This is called **Wien's law** which was first proposed as an empirical fit to the experimental spectrum.

5.3.4 The Mean Energy and the Free Energy

Carrying out the integral in (5.31), we obtain

$$\bar{E} = \frac{V}{\pi^2 \hbar^3 c^3} \int_0^\infty \frac{\varepsilon^3}{\exp(\beta\varepsilon) - 1} d\varepsilon \quad (5.42)$$

$$= \frac{Vk^4 T^4}{\pi^2 \hbar^3 c^3} \int_0^\infty \frac{x^3}{e^x - 1} dx \quad (5.43)$$

where we have set $x = \beta\varepsilon$. The value of the integral is $\pi^4/15$ so that

$$\bar{E} = aVT^4 \quad (5.44)$$

where

$$a = \frac{\pi^2 k^4}{15 \hbar^3 c^3} \quad (5.45)$$

The dependence of \bar{E} on the fourth power of T is called the **Stefan-Boltzmann law**. The constant a is related to the Stefan-Boltzmann constant σ by $a = 4\sigma/c$.

The above method of calculating \bar{E} was somewhat indirect as we first wanted an expression for the spectrum of radiation (which involves finding the variation of energy with frequency). The more usual route is to calculate the partition function from (5.29) which after substituting for $f(\varepsilon)$ is

$$\log Z = - \int_0^\infty \frac{\varepsilon^2 V}{\pi^2 \hbar^3 c^3} \log(1 - \exp(-\beta\varepsilon)) d\varepsilon \quad (5.46)$$

Substituting $x = \beta\varepsilon$ we obtain

$$\log Z = - \frac{V}{\pi^2 \hbar^3 c^3 \beta^3} \int_0^\infty x^2 \log(1 - e^{-x}) dx \quad (5.47)$$

The last integral may be evaluated by parts

$$- \int_0^\infty x^2 \log(1 - e^{-x}) dx = \frac{1}{3} \int_0^\infty \frac{x^3}{e^x - 1} dx = \frac{\pi^4}{45} \quad (5.48)$$

Thus the free energy is

$$F = -kT \log Z = -kT \left(\frac{V}{\pi^2 \hbar^3 c^3 \beta^3} \right) \left(\frac{\pi^4}{45} \right) = -\frac{1}{45} \frac{\pi^2 k^4 T^4 V}{\hbar^3 c^3} \quad (5.49)$$

$$= -\frac{1}{3} aVT^4 \quad (5.50)$$

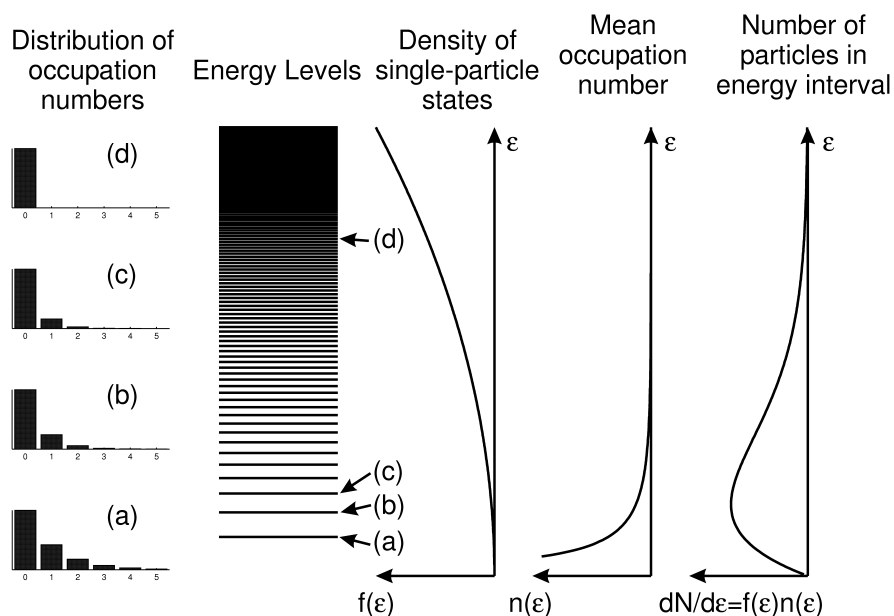


Figure 5.3 Summary diagram showing distribution of photon energies in the blackbody spectrum. The distributions of occupation numbers on the left are for the four single-particle energy eigenstates indicated.

where we have used definition (5.45) for a . Since $dF = -SdT - PdV$, we see that

$$S = - \left(\frac{\partial F}{\partial T} \right)_V = \frac{4}{3} aVT^3 \quad (5.51)$$

and so

$$E = F + TS = \left(-\frac{1}{3} aVT^4 \right) + T \left(\frac{4}{3} aVT^3 \right) \quad (5.52)$$

$$= aVT^4 \quad (5.53)$$

which agrees with the previous result (5.31) obtained by integrating the spectrum. We also see that

$$P = - \left(\frac{\partial F}{\partial V} \right)_T = \frac{1}{3} aT^4 = \frac{1}{3} \frac{E}{V} \quad (5.54)$$

which is the usual equation of state for radiation.

5.3.5 Summary

In Figure 5.3, the calculation outlined above is depicted graphically. The quadratic dependence on energy of the density of single-particle states is shown as $f(\epsilon)$. For each of the single particle states, the occupation number is given by the Boltzmann distribution. In the first column, these distributions are shown for the four energy levels indicated. Notice that for low-energy photons, the Boltzmann distribution is relatively flat, so there is a greater probability of larger occupation numbers. For high-energy photons on the other hand, the most probable occupation number is zero. Since photons are bosons, all occupation numbers are possible in principle. The mean of the occupation numbers computed over the Boltzmann distributions is shown as $\bar{n}(\epsilon)$. We note that even though each n_s is distributed exponentially, the mean is not an exponential function of the energy, unlike the case for the Maxwell-Boltzmann statistics discussed previously in Figure 5.2. The product of $f(\epsilon)$ and $\bar{n}(\epsilon)$ yields $dN/d\epsilon$, from which the Planck blackbody spectrum may be calculated as outlined in (5.33) through (5.36).

5.4 The Gibbs' Distribution

We now return to the problem of considering material particles which are neither created nor destroyed (under normal non-relativistic circumstances). Calculation of the partition function is complicated because we need to restrict the summation to those occupation numbers which satisfy the total number constraint $n_1 + n_2 + \dots = N$. Although this can be done, W. Gibbs devised an alternative formalism which avoids many of the difficulties. Just as we found that a macroscopic system at equilibrium in contact with a heat reservoir has an energy (at a given temperature) which has only very small fluctuations even though there is no explicit constraint upon the energy, Gibbs came up with the idea of a **particle reservoir** which determines the number of particles in the system at equilibrium.

We consider a system of fixed volume in contact with an environment such that both heat and particles may flow through the boundary. As usual, we regard the system and reservoir together as an isolated composite system and regard the total energy, particle number and volume as constants.

$$E_{\text{tot}} = E + E_{\text{res}} \quad (5.55)$$

$$N_{\text{tot}} = N + N_{\text{res}} \quad (5.56)$$

$$V_{\text{tot}} = V + V_{\text{res}}, \text{ where } V \text{ and } V_{\text{res}} \text{ are kept fixed.} \quad (5.57)$$

In these equations, the quantities without subscripts refer to the system. We wish to calculate the probability that at equilibrium, the system is in microstate (N, r) where N denotes the number of particles in the system and r denotes the particular N -particle energy eigenstate. If we denote the system energy in this microstate by ε_{Nr} , the reservoir energy is $E_{\text{tot}} - \varepsilon_{Nr}$ and the number of particles in the reservoir is $N_{\text{tot}} - N$. Denoting the statistical weight of the reservoir by Ω_{res} , we see that

$$p_{Nr} = \frac{\Omega_{\text{res}}(E_{\text{tot}} - \varepsilon_{Nr}, V_{\text{res}}, N_{\text{tot}} - N)}{\sum_{N'} \sum_{r'} \Omega_{\text{res}}(E_{\text{tot}} - \varepsilon_{N'r'}, V_{\text{res}}, N_{\text{tot}} - N')} \quad (5.58)$$

Since $\Omega = \exp(S/k)$,

$$p_{Nr} \propto \exp \left[\frac{1}{k} S_{\text{res}}(E_{\text{tot}} - \varepsilon_{Nr}, V_{\text{res}}, N_{\text{tot}} - N) \right] \quad (5.59)$$

$$\approx \exp \left[\frac{1}{k} \left\{ S_{\text{res}}(E_{\text{tot}}, V_{\text{res}}, N_{\text{tot}}) - \varepsilon_{Nr} \frac{\partial S_{\text{res}}}{\partial E} - N \frac{\partial S_{\text{res}}}{\partial N} \right\} \right] \quad (5.60)$$

As before, $\partial S_{\text{res}}/\partial E$ is simply T^{-1} where T is the temperature of the environment. We introduce the quantity μ defined such that

$$\frac{\mu}{T} = - \left(\frac{\partial S_{\text{res}}}{\partial N} \right) \quad (5.61)$$

μ is called the **chemical potential** of the environment. A difference of chemical potential between the environment and the system causes particles to flow through the boundary in order to equalize the chemical potentials. With these definitions,

$$p_{Nr} \propto \exp[\beta(\mu N - \varepsilon_{Nr})] \quad (5.62)$$

where $\beta = 1/(kT)$. The normalization factor involves

$$\mathcal{Z}(\beta, V, \mu) = \sum_N \sum_r \exp[\beta(\mu N - \varepsilon_{Nr})] \quad (5.63)$$

which is called the **grand partition function**. This is a function of β (or temperature T), V and μ unlike the partition function Z which is a function of β (or temperature T), V and N . Putting these together, we obtain

$$p_{Nr} = \frac{\exp[\beta(\mu N - \varepsilon_{Nr})]}{\mathcal{Z}(\beta, V, \mu)} \quad (5.64)$$

which is called the **Gibbs' distribution** for the probability that the system is in microstate Nr when it is in equilibrium with the environment. It is analogous to the Boltzmann distribution for a system of fixed volume in thermal contact with its environment.

Recall that the usual **partition function** $Z(\beta, V, N)$ is given by

$$Z(\beta, V, N) = \sum_r \exp(-\beta \varepsilon_{Nr}) \quad (5.65)$$

and so we see that the grand partition function is related to the usual partition functions by

$$\mathcal{Z}(\beta, V, \mu) = \sum_N Z(\beta, V, N) \exp(\beta \mu N). \quad (5.66)$$

If we can write the grand partition function as a power series in $\lambda = \exp(\beta \mu)$, the coefficients of the power series are the partition functions.

5.4.1 Gibbs' distribution for systems of non-interacting particles

We shall specialize from this point onwards to the situation of non-interacting particles for which we can infer the energy eigenstates of a system of N particles from the energy eigenstates of a system consisting of a single particle. For such a system, we can speak of occupation numbers n_s associated with the single-particle eigenstates s with energy ε_s . We have that

$$N = \sum_s n_s \text{ and } \varepsilon_{Nr} = \sum_s n_s \varepsilon_s \quad (5.67)$$

The Gibbs' distribution for such systems is

$$p_{Nr} = \frac{\exp[\beta(\mu \sum_s n_s - \sum_s n_s \varepsilon_s)]}{\mathcal{Z}} = \frac{\exp[\sum_s n_s \beta(\mu - \varepsilon_s)]}{\mathcal{Z}} \quad (5.68)$$

This factorizes into

$$p_{Nr} = \left(\frac{\exp[n_1 \beta(\mu - \varepsilon_1)]}{\mathcal{Z}_1} \right) \left(\frac{\exp[n_2 \beta(\mu - \varepsilon_2)]}{\mathcal{Z}_2} \right) \cdots \left(\frac{\exp[n_s \beta(\mu - \varepsilon_s)]}{\mathcal{Z}_s} \right) \cdots \quad (5.69)$$

$$= \prod_s p_s(n_s) \quad (5.70)$$

where

$$p_s(n_s) = \frac{\exp[n_s \beta(\mu - \varepsilon_s)]}{\mathcal{Z}_s} \text{ and } \mathcal{Z}_s = \sum_{n_s} \exp[n_s \beta(\mu - \varepsilon_s)] \quad (5.71)$$

We may regard $p_s(n_s)$ as the probability that the single-particle energy eigenstate s has n_s particles in it. In Figure 5.3, this was called the distribution of occupation numbers. We see that the probability distribution of occupation numbers is always **exponential** in n_s (see Figure 5.4).

The range of values that each n_s can take depends on the type of particles under consideration. For **fermions** which obey Fermi-Dirac (FD) statistics, n_s can only take the values 0 or 1 due to the Pauli exclusion principle. On the other hand, for **bosons** which obey Bose-Einstein (BE) statistics, n_s can range from zero to infinity. We can readily work out \mathcal{Z}_s in each case. For FD statistics

$$\mathcal{Z}_s = 1 + \exp[\beta(\mu - \varepsilon_s)] \quad (5.72)$$

whereas for BE statistics,

$$\mathcal{Z}_s = \frac{1}{1 - \exp[\beta(\mu - \varepsilon_s)]} \quad (5.73)$$

where we have summed the geometric series. We may combine these two expressions as

$$\mathcal{Z}_s = \{1 \pm \exp[\beta(\mu - \varepsilon_s)]\}^{\pm 1} \quad (5.74)$$

where the upper sign denotes Fermi-Dirac statistics and the lower sign denotes Bose-Einstein statistics.

From these distributions of occupation numbers, we can find the mean occupation number of single-particle state s

$$\bar{n}_s = \sum_{n_s} n_s p_s(n_s) = \frac{1}{\beta} \frac{\partial (\log \mathcal{Z}_s)}{\partial \mu} = -\frac{1}{\beta} \frac{\partial (\log \mathcal{Z}_s)}{\partial \varepsilon_s} \quad (5.75)$$

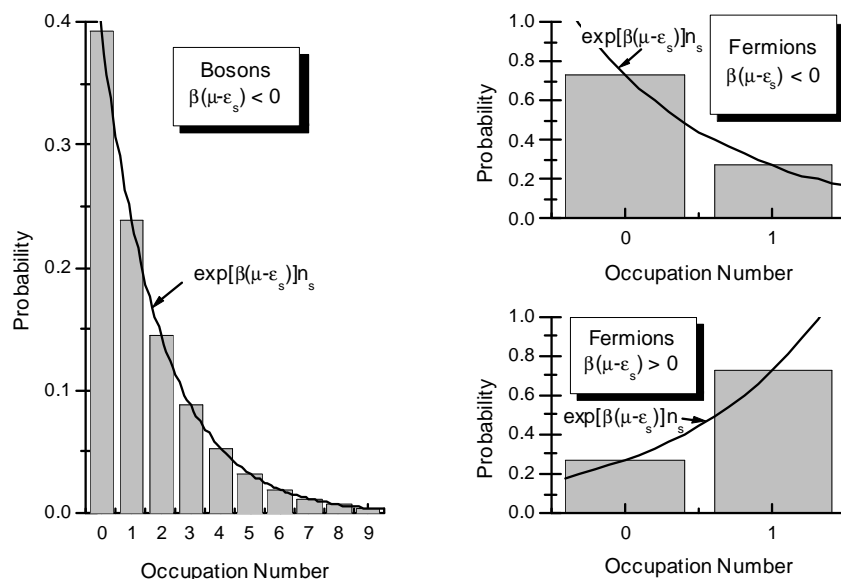


Figure 5.4 Distributions of occupation numbers for bosons and fermions, showing exponential dependence on n_s . For bosons, all values of n_s are possible and so $\beta(\mu - \varepsilon_s)$ must be negative. For fermions, n_s is restricted to be zero or one and $\beta(\mu - \varepsilon_s)$ may be of either sign.

For FD statistics

$$\bar{n}_s = \frac{1}{\exp[\beta(\varepsilon_s - \mu)] + 1}, \quad (5.76)$$

whereas for BE statistics

$$\bar{n}_s = \frac{1}{\exp[\beta(\varepsilon_s - \mu)] - 1}. \quad (5.77)$$

This is the same as the result (5.22) for photons, except that for light, $\mu = 0$. Again, the two expressions may conveniently be combined into

$$\bar{n}_s = \frac{1}{\exp[\beta(\varepsilon_s - \mu)] \pm 1} \quad (5.78)$$

where the upper sign is for FD statistics and the lower sign is for BE statistics.

5.4.2 Using the Gibbs' Distribution

Although the Gibbs' distribution is formulated for a system in thermal and diffusive contact with a bath, the more usual situation is to consider a system with a **fixed** number of particles N maintained at some temperature T . We model this situation by regarding μ as a parameter that has to be adjusted so that the mean number of particles \bar{N} is equal to the given number of particles N . For independent indistinguishable particles with single-particle energy eigenstates ε_s , the mean occupation number of the s 'th eigenstate is $\bar{n}_s(\beta, V, \mu)$ as calculated above. We must choose μ so that

$$\sum_s \bar{n}_s(\beta, V, \mu) = N \quad (5.79)$$

Having found $\mu(\beta, V, N)$, we can determine quantities such as the mean energy

$$\bar{E}(\beta, V, N) = \sum_s \varepsilon_s \bar{n}_s(\beta, V, \mu(\beta, V, N)) \quad (5.80)$$

and from this find the heat capacity etc.

Instead of considering the energy eigenstates individually, it is usual to approximate the sum by an **integral** over a density of single-particle states $f(\varepsilon)$. The equation to determine μ then becomes

$$\int_0^{\infty} f(\varepsilon) \bar{n}(\varepsilon) d\varepsilon = N \quad (5.81)$$

and the mean energy is

$$\bar{E} = \int_0^{\infty} \varepsilon f(\varepsilon) \bar{n}(\varepsilon) d\varepsilon \quad (5.82)$$

where f depends implicitly on V and \bar{n} depends implicitly on β , V and N . We may always solve the problem of finding μ numerically and I have written a Matlab program (which should be on the lab computers) which does this for a variety of choices for f and for \bar{n} . In the following, however, we seek approximate **analytic** solutions for a few specific cases.

Note that for Fermi-Dirac statistics at absolute zero, \bar{n}_s is one for $\varepsilon_s < \mu$ and \bar{n}_s is zero for $\varepsilon_s > \mu$. If there are a total of N fermions at absolute zero, they simply fill up the N available single-particle states of lowest energy. Since the Pauli exclusion principle prohibits more than one fermion in each single-particle state, successive fermions occupy states of higher and higher energy until as many states are filled as there are fermions. The value of μ has to be adjusted in order to make this happen. On the other hand, for Bose-Einstein statistics at absolute zero, all the bosons are able to occupy the ground state, since no exclusion principle applies.

5.5 The Free Electron Model of Metals

In conductors, the valence electrons are only loosely bound to the lattice of positive ions and are essentially free to move throughout the material. They are responsible for electrical conduction and are thus called conduction electrons. In the free electron model, these conduction electrons may be treated as a perfect gas obeying Fermi-Dirac statistics. Their interactions with the positive ions and with each other are ignored.

The density of single particle states is the same as for a point particle in a box, with one modification. Since an electron has spin half, there are two energy eigenstates for an electron (spin up and spin down) corresponding to each energy eigenstate of the featureless particle. From the previous chapter, we saw that the number of states for a featureless particle with energy between ε and $\varepsilon + d\varepsilon$ in a box of volume V is given by

$$\left(\frac{2m}{\hbar^2}\right)^{3/2} \frac{V\varepsilon^{1/2}}{4\pi^2} d\varepsilon, \quad (5.83)$$

and so the density of states for an electron in a box is

$$f(\varepsilon) = \left(\frac{2m}{\hbar^2}\right)^{3/2} \frac{V\varepsilon^{1/2}}{2\pi^2} = \frac{4\pi V}{h^3} (2m)^{3/2} \varepsilon^{1/2}. \quad (5.84)$$

The mean occupation number for the single-particle state of energy ε for particles obeying Fermi-Dirac statistics is given by

$$\bar{n}(\varepsilon) = \frac{1}{\exp[\beta(\varepsilon - \mu)] + 1}, \quad (5.85)$$

and so the mean number of electrons with energies between ε and $\varepsilon + d\varepsilon$ is given by

$$d\bar{N}(\varepsilon) = f(\varepsilon) \bar{n}(\varepsilon) d\varepsilon = \frac{4\pi V}{h^3} (2m)^{3/2} \frac{\varepsilon^{1/2}}{\exp[\beta(\varepsilon - \mu)] + 1} d\varepsilon. \quad (5.86)$$

The mean number of electrons in the system (summed over all energies) is thus

$$\bar{N} = \frac{4\pi V}{h^3} (2m)^{3/2} \int_0^{\infty} \frac{\varepsilon^{1/2}}{\exp[\beta(\varepsilon - \mu)] + 1} d\varepsilon. \quad (5.87)$$

Let us recall the physical situation to which this applies. We have our system in thermal and chemical contact with an environment at temperature $T = (k\beta)^{-1}$ and with chemical potential μ . As we adjust T and μ , the energy within the system and the number of particles in the system changes. We are usually given the number of particles in the system N , rather than the value of μ . In the Gibbs' distribution, we regard μ as a parameter we adjust so that the mean number of particles \bar{N} in the system turns out equal to the actual number of particles N . For a macroscopic system, the fluctuations in the particle number are small so that we can drop the distinction between N and \bar{N} . By using this trick, we do not need to include a constraint on the total number in the initial formulation. Note that for each value of T and V the value of μ must be adjusted to give the correct value of N . We may thus regard μ as a function of T , V and N and write $\mu(T, V, N)$.

Once we have chosen μ so that the number of electrons is correct, the mean energy of the system is

$$\bar{E} = \int_0^\infty \varepsilon dN(\varepsilon) = \frac{4\pi V}{h^3} (2m)^{3/2} \int_0^\infty \frac{\varepsilon^{3/2}}{\exp[\beta(\varepsilon - \mu)] + 1} d\varepsilon \quad (5.88)$$

By calculating how \bar{E} changes as T is varied, we can find the heat capacity due to the conduction electrons.

We now turn to the problem of calculating μ . At absolute zero, $\beta \rightarrow \infty$ and so the expression for $\bar{n}(\varepsilon)$ simplifies to

$$\bar{n}(\varepsilon) = \begin{cases} 1 & \text{if } \varepsilon < \mu \\ 0 & \text{if } \varepsilon > \mu \end{cases} \quad (5.89)$$

Thus we must choose μ so that

$$N = \frac{4\pi V}{h^3} (2m)^{3/2} \int_0^\mu \varepsilon^{1/2} d\varepsilon = \left[\frac{4\pi V}{h^3} (2m)^{3/2} \right] \frac{2}{3} \mu^{3/2} \quad (5.90)$$

whence

$$\mu(0, V, N) = \frac{h^2}{2m} \left(\frac{3}{8\pi} \frac{N}{V} \right)^{2/3}. \quad (5.91)$$

The value of the chemical potential at zero temperature is called the **Fermi energy** $\varepsilon_F(V, N)$ and so

$$\varepsilon_F = \frac{h^2}{2m} \left(\frac{3}{8\pi} \frac{N}{V} \right)^{2/3}. \quad (5.92)$$

Let us now consider raising the temperature so that $\bar{n}(\varepsilon)$ changes from being the solid line in Figure 5.5(a) to the dashed line. In Figure 5.5(b) the product $dN/d\varepsilon = f(\varepsilon)\bar{n}(\varepsilon)$ is shown for these different temperatures. To the lowest order of approximation, the number of electrons (the area under the curves) does not change if μ is fixed and the temperature is varied. A more careful calculation however shows that in order to keep N fixed, it is necessary to adjust μ with temperature so that

$$\mu(T, V, N) \approx \varepsilon_F \left[1 - \frac{\pi^2}{12} \left(\frac{kT}{\varepsilon_F} \right)^2 \right] \quad (5.93)$$

provided that $kT \ll \varepsilon_F$.

In order to establish this, we need a preliminary result. If $\phi(\varepsilon)$ is any function, then for $kT \ll \mu$,

$$\int_0^\infty \frac{\phi(\varepsilon)}{e^{(\varepsilon-\mu)/(kT)} + 1} d\varepsilon = \int_0^\mu \phi(\varepsilon) d\varepsilon + \frac{\pi^2}{6} (kT)^2 \phi'(\mu). \quad (5.94)$$

Proof:

$$\int_0^\infty \frac{\phi(\varepsilon)}{e^{(\varepsilon-\mu)/(kT)} + 1} d\varepsilon - \int_0^\mu \phi(\varepsilon) d\varepsilon = \int_0^\mu \phi(\varepsilon) \left[\frac{1}{e^{(\varepsilon-\mu)/(kT)} + 1} - 1 \right] d\varepsilon \quad (5.95)$$

$$+ \int_\mu^\infty \frac{\phi(\varepsilon)}{e^{(\varepsilon-\mu)/(kT)} + 1} d\varepsilon \quad (5.96)$$

$$= - \int_0^\mu \frac{\phi(\varepsilon)}{e^{-(\varepsilon-\mu)/(kT)} + 1} d\varepsilon + \int_\mu^\infty \frac{\phi(\varepsilon)}{e^{(\varepsilon-\mu)/(kT)} + 1} d\varepsilon \quad (5.97)$$

$$= -kT \int_0^{\mu/kT} \frac{\phi(\mu - kTx)}{e^x + 1} dx + kT \int_0^\infty \frac{\phi(\mu + kTx)}{e^x + 1} dx \quad (5.98)$$

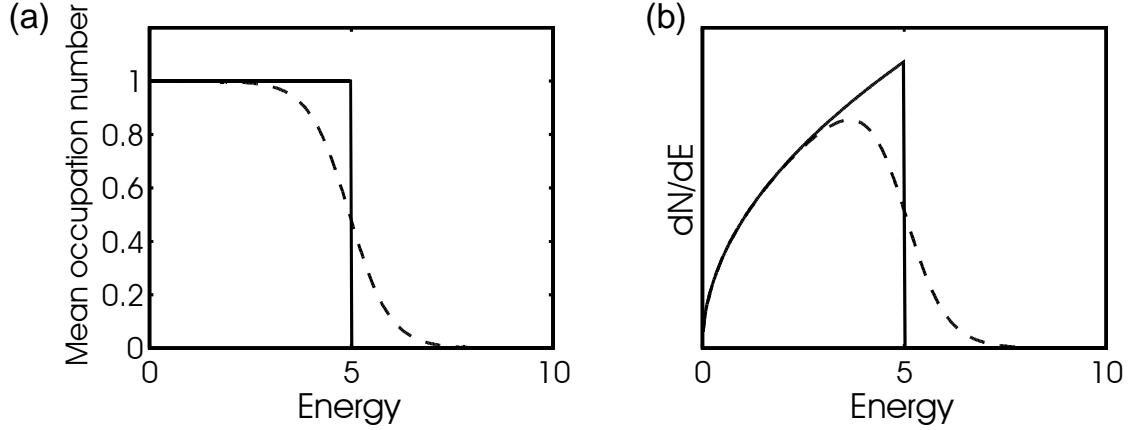


Figure 5.5 (a) Mean occupation number $\bar{n}(\varepsilon)$ and (b) number of particles with specified energies $dN/d\varepsilon = f(\varepsilon)\bar{n}(\varepsilon)$ for a fermions in a box at zero temperature (solid line) and at finite temperature (dashed line).

where we have set $x = \pm(\mu - \varepsilon)/kT$ to obtain the first and second integrals respectively. If $\mu \gg kT$, we can replace the upper limit in the first integral by infinity. Expanding the expressions for ϕ to first order about μ , we see that the right hand side of the above is

$$-kT \int_0^\infty \frac{\phi(\mu) - kTx\phi'(\mu)}{e^x + 1} dx + kT \int_0^\infty \frac{\phi(\mu) + kTx\phi'(\mu)}{e^x + 1} dx = 2(kT)^2 \phi'(\mu) \int_0^\infty \frac{x}{e^x + 1} dx \quad (5.99)$$

$$= \frac{\pi^2}{6} (kT)^2 \phi'(\mu) \quad (5.100)$$

Where we have used the fact that the last integral evaluates to $\pi^2/12$. Hence

$$\int_0^\infty \frac{\phi(\varepsilon)}{\exp[(\varepsilon - \mu)/kT] + 1} d\varepsilon - \int_0^\mu \phi(\varepsilon) d\varepsilon \approx \frac{\pi^2}{6} (kT)^2 \phi'(\mu) \quad (5.101)$$

as required.

Let us now establish the temperature dependence of μ , which is required in order to keep the number of particles equal to N . Since

$$N = \frac{4\pi V}{h^3} (2m)^{3/2} \int_0^\infty \frac{\varepsilon^{1/2}}{\exp[\beta(\varepsilon - \mu)] + 1} d\varepsilon \quad (5.102)$$

$$\approx \frac{4\pi V}{h^3} (2m)^{3/2} \left(\int_0^\mu \varepsilon^{1/2} d\varepsilon + \frac{\pi^2}{6} (kT)^2 \left(\frac{1}{2} \mu^{-1/2} \right) \right) \quad (5.103)$$

$$= \frac{4\pi V}{h^3} (2m)^{3/2} \left(\frac{2}{3} \mu^{3/2} + \frac{\pi^2 k^2 T^2}{12} \mu^{-1/2} \right) \quad (5.104)$$

and from the result (5.92) at absolute zero, we have that

$$N = \left[\frac{4\pi V}{h^3} (2m)^{3/2} \right] \frac{2}{3} \varepsilon_F^{3/2} \quad (5.105)$$

Combining these, we see that

$$\varepsilon_F^{3/2} \approx \mu^{3/2} \left(1 + \frac{\pi^2 k^2 T^2}{8\mu^2} \right) \quad (5.106)$$

For low temperatures ($kT \ll \varepsilon_F$), we expect that μ will be very close to ε_F and so the second term in the parentheses will be small compared to 1. Using the Binomial theorem, we see that

$$\varepsilon_F \approx \mu \left(1 + \frac{\pi^2 k^2 T^2}{12\mu^2} \right) \quad (5.107)$$

and so

$$\mu \approx \varepsilon_F \left(1 - \frac{\pi^2 k^2 T^2}{12\mu^2} \right) \quad (5.108)$$

Since $\mu \approx \varepsilon_F$ in this regime, we can replace μ^2 in the denominator by ε_F^2 while still being correct to this order in T . Hence

$$\mu \approx \varepsilon_F \left(1 - \frac{\pi^2 k^2 T^2}{12\varepsilon_F^2} \right) \quad (5.109)$$

establishing the relation (5.93).

In order to find the heat capacity, we require $\partial \bar{E} / \partial T$. We start from equation (5.88) and note that as the temperature changes, we have also to take into account of how μ changes with T . Using result (5.94), we see that

$$\bar{E} = \frac{4\pi V}{h^3} (2m)^{3/2} \int_0^\infty \frac{\varepsilon^{3/2}}{\exp[\beta(\varepsilon - \mu)] + 1} d\varepsilon \quad (5.110)$$

$$\approx \frac{4\pi V}{h^3} (2m)^{3/2} \left(\int_0^\mu \varepsilon^{3/2} d\varepsilon + \frac{\pi^2}{6} (kT)^2 \left(\frac{3}{2} \mu^{1/2} \right) \right) \quad (5.111)$$

$$= \frac{8\pi V}{5h^3} (2m)^{3/2} \mu^{5/2} \left(1 + \frac{5}{8} \frac{\pi^2 k^2 T^2}{\mu^2} \right) \quad (5.112)$$

We now substitute (5.93) for μ and use the binomial theorem to obtain

$$\bar{E} \approx \frac{8\pi V}{5h^3} (2m)^{3/2} \varepsilon_F^{5/2} \left(1 - \frac{5\pi^2 k^2 T^2}{24\varepsilon_F^2} \right) \left(1 + \frac{5}{8} \frac{\pi^2 k^2 T^2}{\varepsilon_F^2} \left[1 + \frac{\pi^2 k^2 T^2}{12\varepsilon_F^2} \right] \right) \quad (5.113)$$

Retaining terms up to order $k^2 T^2 / \varepsilon_F^2$ (which is assumed to be small), we see that

$$\bar{E} \approx \frac{8\pi V}{5h^3} (2m)^{3/2} \varepsilon_F^{5/2} \left(1 + \frac{5}{12} \frac{\pi^2 k^2 T^2}{\varepsilon_F^2} \right) \quad (5.114)$$

The coefficient can be simplified with the help of (5.92) which yields

$$\bar{E} = \frac{3}{5} N \varepsilon_F \left(1 + \frac{5}{12} \frac{\pi^2 k^2 T^2}{\varepsilon_F^2} \right) \quad (5.115)$$

The heat capacity (at low temperatures) is thus given by

$$C_V = \frac{\partial E}{\partial T} = \frac{\pi^2}{2} \left(\frac{kT}{\varepsilon_F} \right) Nk \quad (5.116)$$

This is a linear function of the temperature, which is responsible for the offset in the graph of C_V/T vs T^2 for conductors at low temperatures. (Recall that in chapter 3, it was stated that at low temperatures, $C_V/T = \alpha T^2 + \gamma$. Debye's theory helps explain the αT^2 term, and the above theory explains the γ term for metals.)

Figure 5.6 shows a summary of the calculation carried out above for the energy distribution of fermions in a box. Note that the occupation number for each level is zero or one. For energy levels below μ , it is more likely that the occupation number is one while for energy levels above μ , it is more likely that the occupation number is zero.

5.6 Bose-Einstein Condensation

We now consider the equilibrium state of a collection of indistinguishable bosons of mass $m > 0$ in a box maintained at temperature T . We find that at conditions of high density and low temperature, an interesting quantum mechanical phenomenon occurs.

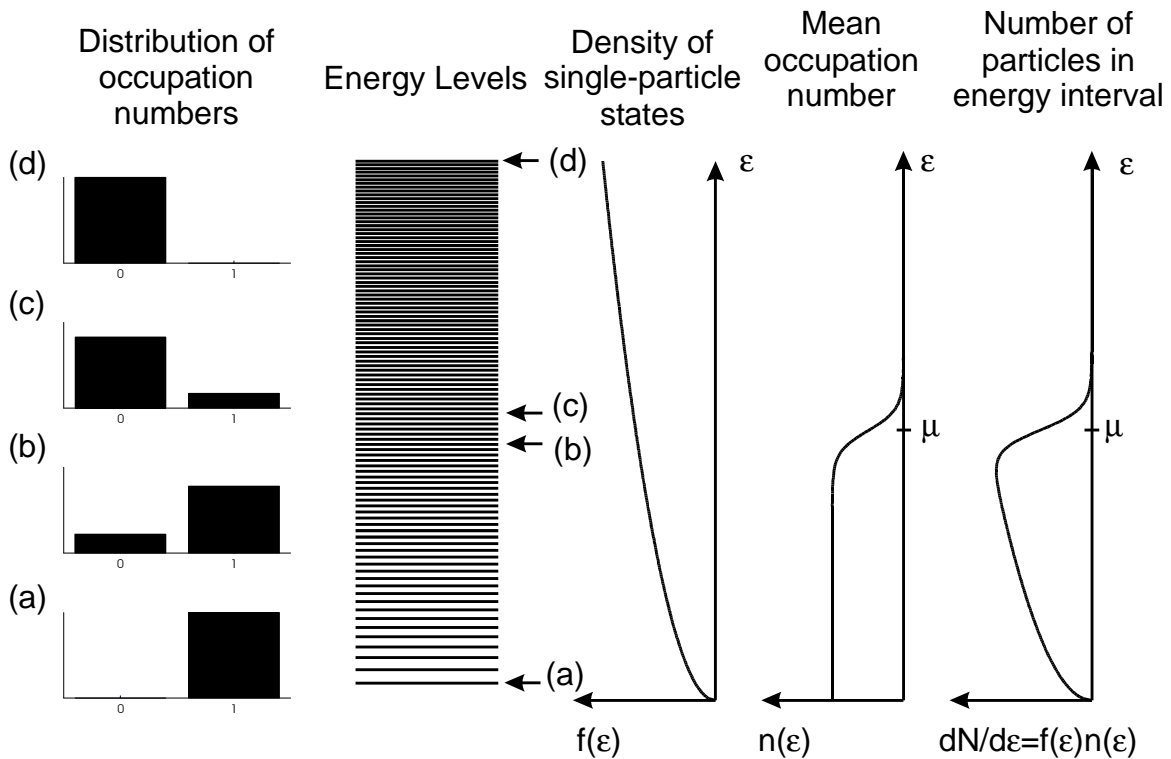


Figure 5.6 Summary diagram showing distribution of energies for fermions in a box. The distributions of occupation numbers on the left are for the four single-particle energy eigenstates indicated.

For bosons of zero spin, the density of states in a box of volume V is given by

$$f(\varepsilon) = \frac{2\pi V}{h^3} (2m)^{3/2} \varepsilon^{1/2} \quad (5.117)$$

This is half the value given above for electrons since particles of spin zero have only one state of polarization. We note that this is an **approximation** to the actual situation in which there are **discrete** energy levels. As we shall see, this approximation actually breaks down under the conditions we shall be interested in, but for the moment, let us persist with making this continuum approximation to the energy levels.

The mean occupation number for single-particle energy eigenstates for independent bosons is

$$\bar{n}_s = \frac{1}{\exp[\beta(\varepsilon_s - \mu)] - 1} \quad (5.118)$$

and so the number of particles with energy between ε and $\varepsilon + d\varepsilon$ is given by

$$dN(\varepsilon) = 2\pi V \left(\frac{2m}{h^2}\right)^{3/2} \frac{\varepsilon^{1/2}}{\exp[\beta(\varepsilon - \mu)] - 1}. \quad (5.119)$$

We choose the chemical potential μ of the environment so as to satisfy the total number constraint, namely

$$N = 2\pi V \left(\frac{2m}{h^2}\right)^{3/2} \int_0^\infty \frac{\varepsilon^{1/2}}{\exp[\beta(\varepsilon - \mu)] - 1} d\varepsilon \quad (5.120)$$

If we write $x = \beta\varepsilon$ in the integral, we find that

$$\int_0^\infty \frac{\varepsilon^{1/2}}{\exp[\beta(\varepsilon - \mu)] - 1} d\varepsilon = \beta^{-3/2} \int_0^\infty \frac{x^{1/2} e^{-(x-\beta\mu)}}{1 - e^{-(x-\beta\mu)}} dx \quad (5.121)$$

If $\mu \leq 0$, the integral converges and we can evaluate it by expanding $[1 - e^{-(x-\beta\mu)}]^{-1}$ using the binomial

theorem since the exponential is less than unity.

$$\int_0^\infty \frac{x^{1/2} e^{-x}}{1 - e^{-(x-\beta\mu)}} dx = \int_0^\infty x^{1/2} e^{-(x-\beta\mu)} \left(1 + e^{-(x-\beta\mu)} + e^{-2(x-\beta\mu)} + \dots\right) dx \quad (5.122)$$

$$= \sum_{n=1}^\infty \int_0^\infty x^{1/2} e^{-n(x-\beta\mu)} dx \quad (5.123)$$

$$= \sum_{n=1}^\infty \frac{e^{n\beta\mu}}{\bar{n}^{3/2}} \left(\int_0^\infty y^{1/2} e^{-y} dy \right) = \frac{\sqrt{\pi}}{2} \sum_{n=1}^\infty \frac{e^{n\beta\mu}}{\bar{n}^{3/2}} \quad (5.124)$$

where we have substituted $y = nx$ and recognized the last integral as $\Gamma(3/2)$. On the other hand, if $\mu > 0$, the value of \bar{n} diverges at a point within the integration interval and so the integral diverges. Thus, if we define

$$G(z) = \sum_{n=1}^\infty \frac{e^{nz}}{\bar{n}^{3/2}} \quad (5.125)$$

then the constraint equation for determining μ becomes

$$\frac{N}{V} = \left(\frac{2\pi mkT}{h^2} \right)^{3/2} G\left(\frac{\mu}{kT}\right) \quad (5.126)$$

The behaviour of G with μ is interesting. As μ is increased from $-\infty$, the value of G rises monotonically from zero. When $\mu = 0$, the value of G is $\zeta(3/2) = 2.612$ and if μ is increased above zero, G becomes infinite. This means that in this model, the density $\rho = N/V$ can only take on values from zero to a maximum value

$$\left(\frac{N}{V}\right)_{\max} = 2.612 \left(\frac{2\pi mkT}{h^2}\right)^{3/2} \quad (5.127)$$

Another way of looking at this is to say that if the density of the system is given, there is a temperature T_c above which we can find $\mu \leq 0$ and satisfy the constraint equation for the total particle number. If the temperature is reduced below T_c , the model breaks down. The value of T_c for a given (N/V) is

$$T_c = \left(\frac{h^2}{2\pi mk}\right) \left(\frac{N}{2.612V}\right)^{2/3} \quad (5.128)$$

As will be discussed later, T_c is called the **condensation temperature** or the **degeneracy temperature**.

If we look carefully at the behaviour of $dN(\varepsilon)$ as T approaches T_c , it is possible to understand what is going on. Even though the density of states $f(\varepsilon) \rightarrow 0$ as $\varepsilon \rightarrow 0$, the dependence of $\bar{n}(\varepsilon)$ is rising so rapidly as $\varepsilon \rightarrow \mu \leq 0$ that the model is trying to place a large number of particles in states of low energy. At low energies, the discrete nature of the energy levels is poorly approximated by a continuous density of states. Since $f(0) = 0$, it is not possible in this model for there to be a finite number of particles in the ground state. If we had used the true formula for N as a sum over discrete states, this problem would not have arisen.

Since it is difficult to obtain analytic results with discrete states, a trick is used in which the ground state is treated specially as a discrete state while all the higher energy states are treated as a continuum with the density of states given by $f(\varepsilon)$. In effect, we include a discrete state at $\varepsilon = 0$ in order to compensate for the fact that the continuous approximation (incorrectly) places a zero there. The mean occupation number of this ground state is given by

$$\bar{n}_0 = \frac{1}{\exp(-\beta\mu) - 1} \quad (5.129)$$

since we have set $\varepsilon = 0$ in the usual expression for the mean occupation number for bosons in an energy eigenstate. Including the particles in the ground state, equation (5.81) is replaced by

$$\bar{n}_0 + \int_0^\infty f(\varepsilon) \bar{n}(\varepsilon) d\varepsilon = N \quad (5.130)$$

Again we are supposed to adjust μ so that this is satisfied. Above T_c , \bar{n}_0 is very small and so this reduces to the previous problem. Below the critical temperature however, the value of μ is very close to zero, but

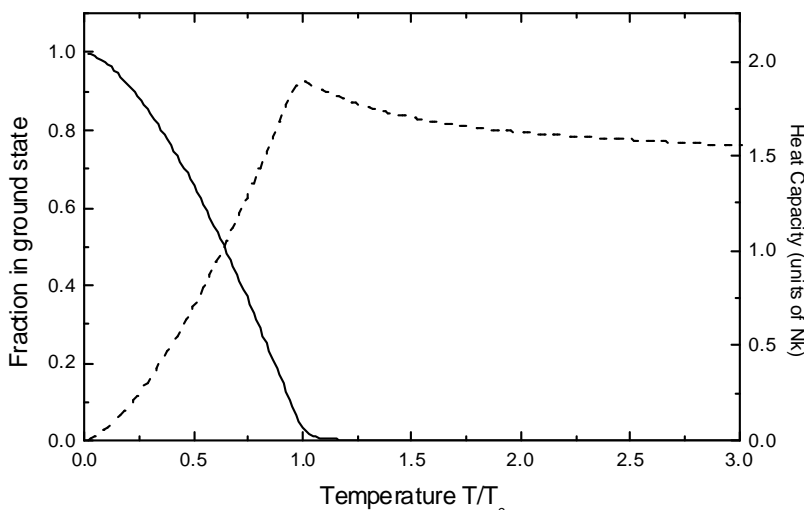


Figure 5.7 Fraction of bosons in the ground state (solid line) and heat capacity (dashed line) from a numerical simulation showing Bose-Einstein condensation at temperature T_c .

slightly negative. The exact value of μ affects \bar{n}_0 greatly, but does not significantly change the value of the integral $\int_0^\infty f(\varepsilon) \bar{n}(\varepsilon) d\varepsilon$, which is taken over all the states above the ground state. Thus, to a very good approximation, we can set $\mu = 0$ in the integral part to obtain

$$\int_0^\infty f(\varepsilon) \bar{n}(\varepsilon) d\varepsilon = \left(\frac{2\pi mkT}{h^2} \right)^{3/2} VG(0) = 2.612 \left(\frac{2\pi mkT}{h^2} \right)^{3/2} V \quad (5.131)$$

$$= N \left(\frac{T}{T_c} \right)^{3/2}, \quad (5.132)$$

where we have used (5.128) for the condensation temperature T_c associated with N particles in volume V . Substituting this back into (5.130) we find that

$$\bar{n}_0 + N \left(\frac{T}{T_c} \right)^{3/2} = N \quad (5.133)$$

or

$$\frac{\bar{n}_0}{N} = 1 - \left(\frac{T}{T_c} \right)^{3/2} \quad (5.134)$$

for $T < T_c$. For temperatures above T_c , the number of particles in the ground state is very small. The solid line in Figure 5.7 shows a graph of the fraction of particles in the ground state as a function of the temperature from a numerical simulation. Below T_c , the number of particles in the ground state rapidly grows. At zero temperature, all the particles are in the ground state. Note that T_c is usually much **higher** than the temperatures for which $kT \ll \varepsilon_2 - \varepsilon_1$, so this phenomenon of a large population in the ground state is **not** simply because the particles have insufficient thermal energy to populate the higher-lying levels. Rather, it arises from the quantum mechanical tendency of bosons to be in the same single-particle energy eigenstate which makes the mean occupation number of the lowest-lying state very much larger than all the others. The development of a macroscopic population in a single state represents a phase transition called **Bose-Einstein condensation**. Before 1995, the theory of Bose-Einstein condensation was only applicable to liquid Helium 4 below 2.17 K which exhibits a phase transition to a superfluid. Since the atoms in liquid He are actually quite strongly interacting, there is only a qualitative correspondence with the above theory. In 1995, a much more nearly ideal form of Bose-Einstein condensation in a dilute weakly-interacting gas was achieved using rubidium and more recently using sodium. Studying the quantum mechanical properties of a Bose-Einstein condensate is currently an active research field.

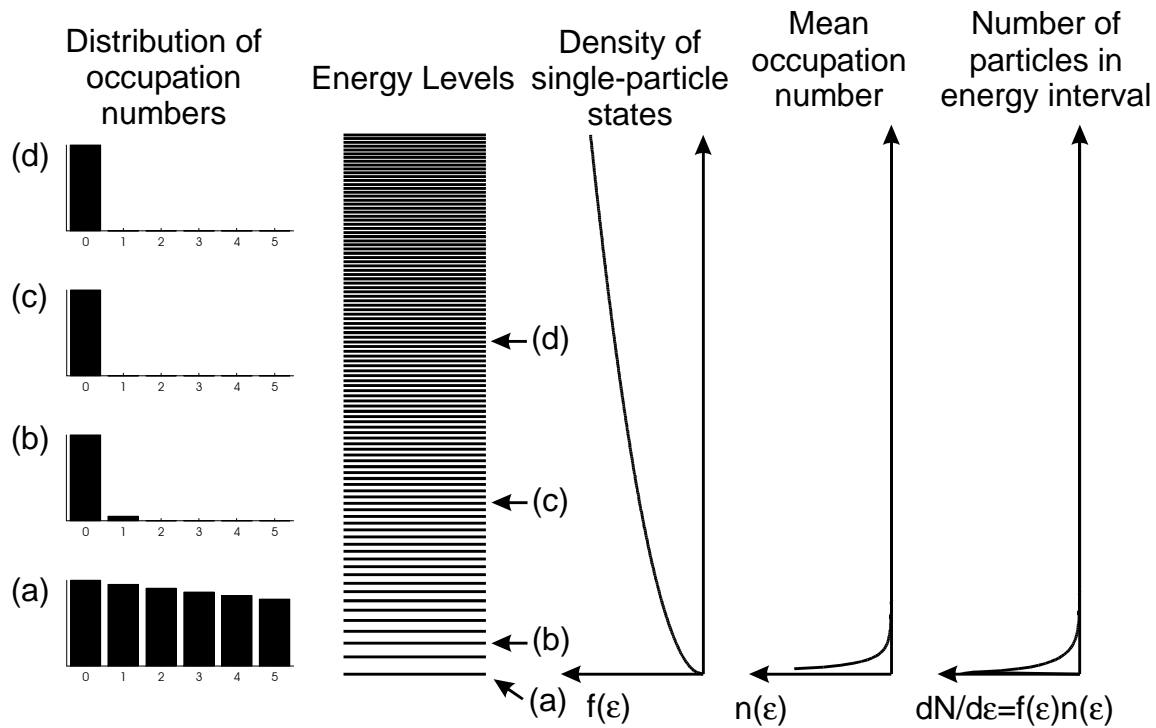


Figure 5.8 Summary diagram showing distribution of energies for bosons in a box just below the condensation temperature. The distributions of occupation numbers on the left are for the four single-particle energy eigenstates indicated.

Figure 5.8 summarizes the calculation for the system of bosons. The temperature is just below the condensation temperature and so many of the particles are in the ground state as shown by the occupancy number distribution of the ground state compared to those of the others.

Below the critical temperature, the energy of the system is due only to the particles in levels above the single-particle ground state since we have taken the ground state energy to be zero. Using the approximation that $\mu = 0$ in the integral, we see that

$$E = \int_0^{\infty} \varepsilon f(\varepsilon) \bar{n}(\varepsilon) d\varepsilon \quad (5.135)$$

$$= 2\pi V \left(\frac{2m}{h^2}\right)^{3/2} \left[\int_0^{\infty} \frac{\varepsilon^{3/2}}{\exp[\beta(\varepsilon - \mu)] - 1} d\varepsilon \right]_{\mu=0} \quad (5.136)$$

$$= 2\pi V \left(\frac{2m}{h^2}\right)^{3/2} (kT)^{5/2} \int_0^{\infty} \frac{z^{3/2}}{e^z - 1} dz \quad (5.137)$$

where we have put $z = \beta\varepsilon$. The integral can be evaluated in terms of the gamma function and the Riemann zeta function, since

$$\int_0^{\infty} \frac{z^x}{e^z - 1} dz = \Gamma(x+1) \zeta(x+1) \quad (5.138)$$

Here $\Gamma(5/2) \zeta(5/2) = 1.7833$ and so

$$E = 0.77Nk \left(\frac{T^{5/2}}{T_c^{3/2}}\right) \quad (5.139)$$

The heat capacity at constant volume is given by $(\partial E/\partial T)_V$ or

$$C = 1.93Nk \left(\frac{T}{T_c}\right)^{3/2} \quad \text{for } T < T_c \quad (5.140)$$

At temperatures above the condensation temperature, the calculation of E is complicated by the fact that μ varies with T . At high temperatures, we expect the result to tend to that for a classical monatomic ideal

gas for which $C = \frac{3}{2}Nk$. From the expression for the heat capacity for $T < T_c$, we see that $\lim_{T \rightarrow T_c^-} C = 1.93Nk > 1.5Nk$. A numerical calculation (the dashed line in Figure 5.7) shows that there is in fact a continuous but non-differentiable cusp in the heat capacity at $T = T_c$ which shows that this is a different type of phase transition to the usual liquid-gas transition for which the heat capacity becomes infinite.