

Chapter 2

Practical Calculations with Ideal Systems

2.1 The Density of States

2.1.1 Non-interacting systems

The concept of a non-interacting system is hypothetical since a system of truly non-interacting components could not achieve thermal equilibrium. Thus we are really interested in assemblies of *very weakly* interacting systems. To be precise, the interactions must be sufficient to lead to thermal equilibrium, but weak enough that these interactions have negligible effect on the energy of the individual particles. We note parenthetically, that the *rate* at which an equilibrium state is established will depend on the strength of the interactions; this is the subject of *non-equilibrium statistical mechanics*. Some aspects will be touched upon in Chapter 5.

Since the single particle states have well defined energies it follows that one can obtain full thermodynamic information about such a system once the energies of the single particle states and the mean number of particles in each state is known. Then all thermodynamic properties are found by performing sums over states and distribution functions. And for infinite or very large systems, where the spacings between the energy levels become very small, such sums may usually be converted to integrals.

2.1.2 Converting sums to integrals

In quantum statistical mechanics there are many sums over states to be evaluated. An example is the partition function we encountered in the previous

chapter

$$Z(N, V, T) = \sum_j e^{-E_j(N, V)/kT}. \quad (2.1.1)$$

It is often convenient to approximate the sums by integrals. And since the individual states are densely packed negligible error is introduced in so doing. Now if $g(\varepsilon)d\varepsilon$ is the number of states with energy between ε and $\varepsilon + d\varepsilon$ then the sum may be approximated by

$$\sum_j e^{-E_j(N, V)/kT} \rightarrow \int_0^\infty g(\varepsilon) e^{-\varepsilon/kT} d\varepsilon. \quad (2.1.2)$$

Here $g(\varepsilon)$ is referred to as the (*energy*) *density of states*. If we are studying the properties of a gas then the microstates to be considered are the quantum states of a “particle in a box”. And the density of states for a particle in a box may be evaluated in the following way.

2.1.3 Enumeration of states

We consider a cubic box of volume V . Each side has length $V^{1/3}$. Elementary quantum mechanics tells us that the wave function of a particle in the box must go to zero at the boundary walls; only standing waves are allowed. In

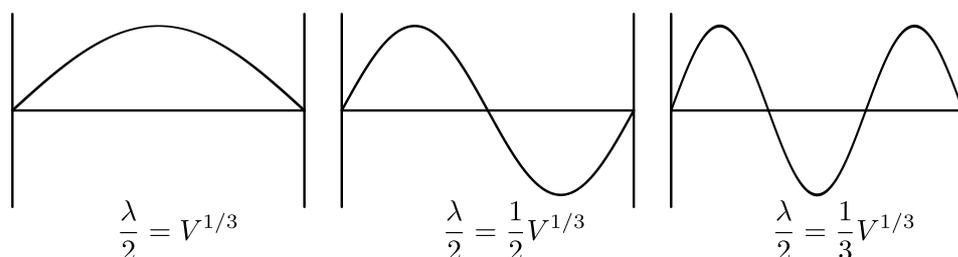


Figure 2.1: Standing waves in a box

the general case the allowed wavelengths λ satisfy $\lambda/2 = V^{1/3}/n$, that is

$$\lambda_n = \frac{2}{n} V^{1/3}, \quad n = 1, 2, 3, 4, \dots \infty. \quad (2.1.3)$$

In three dimensions there will be a λ for the x , y , and z directions:

$$\lambda_{n_x} = 2 \frac{V^{1/3}}{n_x}, \quad \lambda_{n_y} = 2 \frac{V^{1/3}}{n_y}, \quad \lambda_{n_z} = 2 \frac{V^{1/3}}{n_z}. \quad (2.1.4)$$

Or, since this corresponds to the components of the wave vector $k_x = 2\pi/\lambda_{n_x}$ etc.,

$$k_x = \frac{\pi}{V^{1/3}}n_x, \quad k_y = \frac{\pi}{V^{1/3}}n_y, \quad k_z = \frac{\pi}{V^{1/3}}n_z. \quad (2.1.5)$$

We can now use the de Broglie relation $\mathbf{p} = \hbar\mathbf{k}$ to obtain the momentum and hence the energy.

$$p_x = \frac{\pi\hbar}{V^{1/3}}n_x, \quad p_y = \frac{\pi\hbar}{V^{1/3}}n_y, \quad p_z = \frac{\pi\hbar}{V^{1/3}}n_z \quad (2.1.6)$$

And so for a free particle the energy is then

$$\varepsilon = \frac{p^2}{2m} = \frac{p_x^2 + p_y^2 + p_z^2}{2m} \quad (2.1.7)$$

which is

$$\varepsilon = \frac{\pi^2\hbar^2}{2mV^{2/3}}(n_x^2 + n_y^2 + n_z^2). \quad (2.1.8)$$

In this expression it is the triple of quantum numbers $\{n_x, n_y, n_z\}$ which specifies the quantum state. Now each triple defines a point on a cubic grid. If we put

$$R^2 = n_x^2 + n_y^2 + n_z^2 \quad (2.1.9)$$

then the energy is given by

$$\varepsilon = \frac{\pi^2\hbar^2}{2mV^{2/3}}R^2. \quad (2.1.10)$$

Observe that the energy levels depend on the size of the container. We used this fact in the considerations of Section 1.2.2 on the probabilistic interpretation of the First Law.

2.1.4 Counting states

The number of states of energy up to ε , denoted by $N(\varepsilon)$, is given by the number of points in the octant up to $\varepsilon(R)$. (An octant is used since n_x , n_y and n_z are restricted to being positive). And the number of points in the octant is approximately equal to the volume of the octant:

$$N(\varepsilon) = \frac{1}{8} \frac{4}{3} \pi R^3. \quad (2.1.11)$$

But since, from Eq. (2.1.10),

$$R = \left(\frac{2mV^{2/3}}{\pi^2\hbar^2} \right)^{1/2} \varepsilon^{1/2} \quad (2.1.12)$$

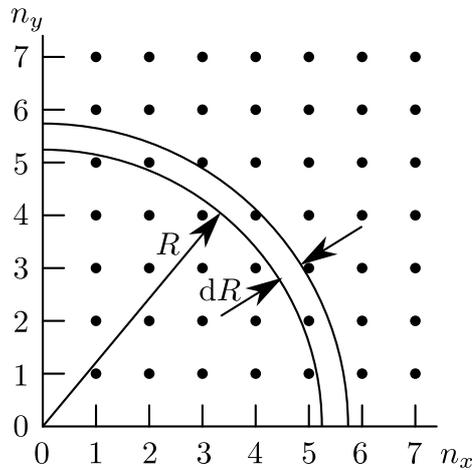


Figure 2.2: Counting of quantum states

we then obtain

$$N(\varepsilon) = \frac{1}{6} \frac{V}{\pi^2 \hbar^3} (2m\varepsilon)^{3/2}. \quad (2.1.13)$$

Recall that the density of states $g(\varepsilon)$ is defined by saying that the number of states with energy between ε and $\varepsilon + d\varepsilon$ is $g(\varepsilon)d\varepsilon$. In other words

$$g(\varepsilon)d\varepsilon = N(\varepsilon + d\varepsilon) - N(\varepsilon) \quad (2.1.14)$$

or, simply

$$g(\varepsilon) = \frac{dN(\varepsilon)}{d\varepsilon}. \quad (2.1.15)$$

So differentiating $N(\varepsilon)$ we obtain

$$g(\varepsilon) = \frac{1}{4} \frac{V}{\pi^2 \hbar^3} (2m)^{3/2} \varepsilon^{1/2} \quad (2.1.16)$$

which is the required expression for the density of states.

For completeness we shall also give the expressions for the density of states in two and in one dimension; these are found by arguments similar to those above. They will be discussed in some of the Problems. In a two-dimensional system of area A the density of states is

$$g(\varepsilon) = \frac{mA}{2\pi\hbar^2} \quad (\text{two dimensions}) \quad (2.1.17)$$

observe this is *independent of energy*. And in a one-dimensional system of length L the density of states is

$$g(\varepsilon) = \frac{L}{\pi\hbar} \left(\frac{m}{2}\right)^{1/2} \varepsilon^{-1/2} \quad (\text{one dimension}). \quad (2.1.18)$$

2.1.5 General expression for the density of states

The result of the previous section gives the (energy) density of states for free particles confined to a box of specified volume. This, we argued, was appropriate for the consideration of ideal gases. And it will indeed be quite adequate for the consideration of the ideal gas in both the classical and the quantum mechanical cases.

In order to be able to treat systems comprising elements other than free particles we need to adopt a more general approach than that of the previous section. Central to that approach was the energy-momentum relation (really the energy – wave vector relation) of the particles: $\varepsilon = p^2/2m = \hbar^2 k^2/2m$. But in the general case this expression may not be appropriate. Thus at relativistic speeds free particles would obey $\varepsilon = \sqrt{c^2 p^2 + m^2 c^4}$ and extreme-relativistic/massless particles, $\varepsilon = cp$. In these cases as well as those with other energy-momentum relations a more general approach is needed for the density of states.

The key to the general treatment is to consider the density of states in k -space. The point is that the quantisation condition discussed above applies fundamentally to the k -states: the wave function for any elements confined to a box must vanish at the walls. This means that the standing wave condition, Eq. (2.1.5) applies generally:

$$k_x = \frac{\pi}{V^{1/3}} n_x, \quad k_y = \frac{\pi}{V^{1/3}} n_y, \quad k_z = \frac{\pi}{V^{1/3}} n_z.$$

The allowed states correspond to triples of integers $\{n_x, n_y, n_z\}$; in other words, there is a uniform density of states in k -space.

The number of states up to a maximum k value is then the volume of the octant

$$N(k) = \frac{1}{8} \frac{4}{3} \pi R^3 = \frac{1}{6} \pi (n_x^2 + n_y^2 + n_z^2)^{3/2}. \quad (2.1.19)$$

And since $n_x = k_x V^{1/3}/\pi$, etc. it follows that

$$N(k) = \frac{V}{6\pi^2} k^3. \quad (2.1.20)$$

The density of states in k -space, which we shall denote by $g(k)$, is then the derivative of $N(k)$, so that

$$g(k) = \frac{V}{2\pi^2} k^2. \quad (2.1.21)$$

Recall that the energy density of states is defined as $g(\varepsilon) = dN/d\varepsilon$. And this can be expressed in terms of $g(k)$ by using the chain rule for differentiation

$$g(\varepsilon) = \frac{dN}{d\varepsilon} = \frac{dN}{dk} \frac{dk}{d\varepsilon} = g(k) \left/ \frac{d\varepsilon}{dk} \right. \quad (2.1.22)$$

Thus we have the general result

$$g(\varepsilon) = \frac{V}{2\pi^2} k^2 \left/ \frac{d\varepsilon}{dk} \right. \quad (2.1.23)$$

where we must eliminate k in favour of ε . Thus to find the energy density of states in this general case we need to know the energy-momentum (energy-wave vector) relation for the particles or excitations.

For completeness we shall also quote the corresponding expressions for the density of states in two and in one dimension. In a two-dimensional system of area A the general density of states is

$$g(\varepsilon) = \frac{A}{2\pi} k \left/ \frac{d\varepsilon}{dk} \right. \quad (\text{two dimensions}) \quad (2.1.24)$$

And in a one-dimensional system of length L the general density of states is

$$g(\varepsilon) = \frac{L}{\pi} \left/ \frac{d\varepsilon}{dk} \right. \quad (\text{one dimension}). \quad (2.1.25)$$

2.1.6 General relation between pressure and energy

It is possible to obtain a very general relation between the internal energy and the pressure of a gas of particles. Central to the argument is the understanding, discussed in Section 2.1.3 that the energy levels of a particle in a box depend on the volume of the box, Eq. (2.1.10).

From the differential expression for the First Law it follows that

$$p = - \left. \frac{\partial E}{\partial V} \right|_S. \quad (2.1.26)$$

We may write the internal energy in terms of the energy levels ε_i and the occupation numbers of these states n_i :

$$E = \sum_i n_i \varepsilon_i. \quad (2.1.27)$$

The differential of this expression is

$$dE = \sum_i n_i d\varepsilon_i + \sum_i \varepsilon_i dn_i. \quad (2.1.28)$$

These expressions should be compared with those in the discussion of the probabilistic interpretation of the First Law in Section 1.2.2. There we used

(what we now understand as) the Gibbs approach to the calculation of mean values; here we use the Boltzmann approach. Apart from that they are equivalent.

The second term of the differential expression vanishes at constant entropy. Thus we identify

$$p = - \left. \frac{\partial E}{\partial V} \right|_S = - \sum_i n_i \frac{d\varepsilon_i}{dV}. \quad (2.1.29)$$

Now we take the energy levels to depend on V as a simple power. We shall write

$$\varepsilon_i = AV^\alpha \quad (2.1.30)$$

so that

$$\frac{d\varepsilon_i}{dV} = A\alpha V^{\alpha-1} \quad (2.1.31)$$

which it is convenient to write as

$$\frac{d\varepsilon_i}{dV} = \frac{A\alpha V^\alpha}{V} = \alpha \frac{\varepsilon_i}{V}. \quad (2.1.32)$$

Thus the expression for the pressure becomes

$$p = - \sum_i n_i \frac{d\varepsilon_i}{dV} = - \frac{\alpha}{V} \sum_i n_i \varepsilon_i = -\alpha \frac{E}{V}. \quad (2.1.33)$$

For (non-relativistic) particles of mass m (where the kinetic energy is $p^2/2m$) we saw in Section 2.1.3, Eq. (2.1.10), that $\alpha = -2/3$. So in this case

$$p = \frac{2}{3} \frac{E}{V} \quad (2.1.34)$$

or

$$pV = \frac{2}{3} E. \quad (2.1.35)$$

It is important to appreciate the generality of this result. It relies only on the power law dependence of the energy levels upon volume. It applies to quantum particles irrespective of statistics and thus it applies to classical particles as well. It only holds, however, for non-interacting particles; with interactions the energy levels will depend on volume in a much more complicated way.

As a further example we can consider a gas of ultra-relativistic/massless particles. In this case the energy-momentum relation $\varepsilon = cp$ leads to the energy levels

$$\varepsilon = \frac{c\pi\hbar}{V^{1/3}} (n_x^2 + n_y^2 + n_z^2)^{1/2} \quad (2.1.36)$$

so now the index α is $-1/3$ and then

$$pV = \frac{1}{3}E. \quad (2.1.37)$$

This result applies to a gas of photons, and in that case the expression gives the radiation pressure as one third of the energy density. The identical expression for radiation pressure is conventionally derived in electromagnetism [1] – without the need for quantum arguments.

2.2 Identical Particles

2.2.1 Indistinguishability

Since the partition function is proportional to probabilities it follows that for composite systems the partition function is essentially a product of the partition functions for the individual subsystems. The free energy is proportional to the logarithm of the partition function and this leads to the extensive variables of composite systems being additive.

In this section we shall examine how the (canonical) partition function of a many-particle system is related to the partition function of a single particle.

If we had an assembly of N identical but *distinguishable* particles the resultant partition function would be the product of the N (same) partition functions of a single particle, z :

$$Z = z^N. \quad (2.2.1)$$

The key question here is that of *indistinguishability* of the atoms or molecules of a many-body system. When two identical molecules are interchanged the system is still in the same microstate, so the distinguishable particle result *overcounts* the states in this case. Now the number of ways of redistributing N particles when there are n_1 particles in the first state, n_2 particles in the second state etc. is

$$\frac{N!}{n_1! n_2! n_3! \dots} \quad (2.2.2)$$

so that for a given distribution $\{n_i\}$ the partition function for identical indistinguishable particles is

$$Z = \frac{n_1! n_2! n_3! \dots}{N!} z^N. \quad (2.2.3)$$

2.2.2 Classical approximation

The problem here is the occupation numbers $\{n_i\}$; we do not know these in advance. However at high temperatures the probability of occupancy of any state is small; the probability of multiple occupancy is then negligible. This is the classical régime, where the thermal de Broglie wavelength is very much less than the inter-particle spacing. The thermal de Broglie wavelength is the wavelength, corresponding to the momentum, corresponding to the kinetic energy corresponding to a temperature T . This will appear in Section 2.3.1. Under these circumstances the factors $n_1!, n_2!, n_3!, \dots$ can be ignored and we have a soluble problem.

In the classical case we have then

$$Z = \frac{1}{N!} z^N. \quad (2.2.4)$$

The Helmholtz free energy

$$F = -kT \ln Z \quad (2.2.5)$$

is thus

$$F = -NkT \ln z + kT \ln N!. \quad (2.2.6)$$

This is N times the Helmholtz free energy for a single particle plus an extra term depending on T and N . So the second term can be ignored so long as we differentiate with respect to something other than T or N . Specifically, when differentiating with respect to volume to find the pressure, the result is N times that for a single particle.

The structure of Eq. (2.2.6) and in particular the logical necessity for the $1/N!$ term in the classical gas partition function will be explored further in Section 2.3.4.

2.3 The Ideal Gas

2.3.1 Quantum approach

The partition function for a single particle is

$$z(V, T) = \sum_i e^{-\varepsilon_i(V)/kT} \quad (2.3.1)$$

where ε_i is the energy of the i th single-particle state; these states were enumerated in Section 2.1.3. As explained previously, the energy states are

closely packed and this allows us to replace the sum over states by an integral using the density of states $g(\varepsilon) = V(2m)^{3/2}\varepsilon^{1/2}/4\pi^2\hbar^3$:

$$\begin{aligned} z &= \int_0^{\infty} g(\varepsilon) e^{-\varepsilon/kT} d\varepsilon \\ &= \frac{1}{4} \frac{V}{\pi^2\hbar^3} (2m)^{3/2} \int_0^{\infty} \varepsilon^{1/2} e^{-\varepsilon/kT} d\varepsilon. \end{aligned} \quad (2.3.2)$$

Following a change of variable this may be expressed, in terms of a standard integral, as¹

$$z = V \left(\frac{mkT}{2\pi\hbar^2} \right)^{3/2} \frac{2}{\sqrt{\pi}} \int_0^{\infty} x^{1/2} e^{-x} dx. \quad (2.3.3)$$

The integral is $\sqrt{\pi}/2$, so that

$$z = \left(\frac{mkT}{2\pi\hbar^2} \right)^{3/2} V = \frac{V}{\Lambda^3} \quad (2.3.4)$$

where

$$\Lambda = \sqrt{\frac{2\pi\hbar^2}{mkT}}. \quad (2.3.5)$$

The parameter Λ is known as the *thermal deBroglie wavelength*; to within a numerical factor it is the wavelength corresponding to the momentum corresponding to the thermal kinetic energy of the particle. Thus, in a sense, it represents the quantum “size” of the particle.

For a gas of N particles we then have

$$Z = \frac{1}{N!} z^N = \frac{1}{N!} \left(\frac{V}{\Lambda^3} \right)^N. \quad (2.3.6)$$

We shall use Stirling’s approximation, $\ln N! = N \ln N - N = N \ln(N/e)$, when evaluating the logarithm so that

$$\ln Z = N \ln(ze/N) = N \ln \left[\left(\frac{mkT}{2\pi\hbar^2} \right)^{3/2} \frac{Ve}{N} \right] \quad (2.3.7)$$

from which all thermodynamic properties can be found, by the formulae of Section 1.4.4.

Since Stirling’s approximation becomes true in the thermodynamic limit it follows that by invoking Stirling’s approximation we are implicitly taking the thermodynamic limit.

¹Observe: the change of variable has brought the “physics” out of the integral.

2.3.2 Classical approach

It is instructive to consider the calculation of the single-particle partition function from the classical point of view. The classical partition function is given by the integral

$$\begin{aligned} z &= \frac{1}{h^3} \int e^{-\varepsilon/kT} d^3p d^3q \\ &= \frac{1}{8\pi\hbar^3} \int e^{-\varepsilon/kT} d^3p d^3q \end{aligned} \quad (2.3.8)$$

where for the ideal gas $\varepsilon = p^2/2m$. The q integrals are trivial, giving a factor V , and we have

$$z = \frac{V}{8\pi^3\hbar^3} \left[\int_{-\infty}^{\infty} e^{-p^2/2mkT} dp \right]^3. \quad (2.3.9)$$

The integral is transformed to a pure number by changing variables: $p = x\sqrt{2mkT}$ so that

$$z = V \left(\frac{mkT}{2\pi\hbar^2} \right)^{3/2} \frac{1}{\pi^{3/2}} \left[\int_{-\infty}^{\infty} e^{-x^2} dx \right]^3. \quad (2.3.10)$$

As in the quantum calculation, the physics is all outside the integral and the integral is just a pure number. The value of this integral is $\sqrt{\pi}$ so that

$$z = \left(\frac{mkT}{2\pi\hbar^2} \right)^{3/2} V = \frac{V}{\Lambda^3} \quad (2.3.11)$$

just as in the “quantum” calculation Eq. (2.3.4); we obtain the identical result. *This* justifies the use of h in the normalization factor for the classical state element of phase space.

2.3.3 Thermodynamic properties

In order to investigate the thermodynamic properties of the classical ideal gas we start from the Helmholtz free energy, Eq. (2.3.7):

$$F = -kT \ln Z = NkT \ln \left[\left(\frac{mkT}{2\pi\hbar^2} \right)^{3/2} \frac{Ve}{N} \right]. \quad (2.3.12)$$

Then upon differentiation we obtain

$$p = kT \left. \frac{\partial \ln Z}{\partial V} \right|_{T,N} = NkT \left. \frac{\partial \ln z}{\partial V} \right|_T = \frac{NkT}{V}. \quad (2.3.13)$$

This is the ideal gas equation of state, and from this we identify k as Boltzmann's constant. Furthermore we see that the ideal gas temperature thus corresponds to the “statistical” temperature introduced in the previous chapter.

The internal energy is

$$E = kT^2 \left. \frac{\partial \ln Z}{\partial T} \right|_{V,N} = NkT^2 \frac{d \ln T^{3/2}}{dT} = \frac{3}{2} NkT. \quad (2.3.14)$$

This is the result we obtained previously from equipartition. This gives another important property of an ideal gas: the internal energy depends *only* on temperature (not pressure or density). This is known as Joule's law. From the energy expression we obtain the thermal capacity

$$C_V = \left. \frac{\partial E}{\partial T} \right|_{V,N} = \frac{3}{2} Nk. \quad (2.3.15)$$

This is a constant, independent of temperature, in violation of the Third Law. This is because of the classical approximation – ignoring multiple state occupancy etc. We also find the entropy and chemical potential:

$$\begin{aligned} S &= Nk \ln \left[\left(\frac{mkT}{2\pi\hbar^2} \right)^{3/2} \frac{V}{N} e^{5/2} \right], \\ \mu &= -kT \ln \left[\left(\frac{mkT}{2\pi\hbar^2} \right)^{3/2} \frac{V}{N} \right]. \end{aligned} \quad (2.3.16)$$

The formula for the entropy is often expressed as

$$S = Nk \ln V - Nk \ln N + \frac{3}{2} Nk \ln T + Nk s_0 \quad (2.3.17)$$

where the reduced “entropy constant” s_0 is given by

$$s_0 = \frac{3}{2} \ln \left(\frac{mk}{2\pi\hbar^2} \right) + \frac{5}{2}. \quad (2.3.18)$$

The above expression for the entropy is known as the Sackur-Tetrode equation. It is often interpreted as indicating different contributions to the entropy: the volume contribution in the first term, the number contribution in the second term and the temperature contribution in the third term. Such an identification is entirely *incorrect*; this matter is explored in Problem 2.3.

The entropy constant may be determined experimentally, as explained by Guénault[2]. One measures the heat capacity of a substance as a function

of temperature from very low temperatures (essentially $T = 0$) up to a temperature sufficiently high so that the substance behaves as an ideal gas. One also needs the latent heats of melting L_m and boiling L_b . Then the entropy at temperature T is given by

$$S(T) = \int_0^T \frac{C_V(T')}{T'} dT' + \frac{L_m}{T_m} + \frac{L_b}{T_b} \quad (2.3.19)$$

where T_m and T_b are the melting and boiling temperatures. This gives the entropy of the ideal gas. By comparing this entropy with that given by Eq. (2.3.17) and subtracting off the first three terms, one obtains s_0 . When the Avogadro constant is known, then Boltzmann's constant and the atomic mass are also known. Then it follows that Planck's constant may be found by "straightforward" calorimetric measurements. This relies on using the Third Law to fix the zero-temperature entropy at zero.

2.3.4 The $1/N!$ term in the partition function

In Section 2.2.2 we used quantum arguments to justify the factor $1/N!$ in the partition function for a gas of particles. Gibbs worked before quantum mechanics, so he had a problem. He *thought* the many-particle partition function was just the product of the individual particle partition functions, Eq. (2.2.1). This would give

$$\begin{aligned} \tilde{Z} &= z^N \\ &= \left(\frac{mkT}{2\pi\hbar^2} \right)^{3N/2} V^N. \end{aligned} \quad (2.3.20)$$

I have used \tilde{Z} to indicate the erroneous partition function and I will use \tilde{F} to indicate the corresponding (erroneous) Helmholtz free energy:

$$\begin{aligned} \tilde{F} &= -kT \ln \tilde{Z} \\ &= -NkT \ln \left\{ \left(\frac{mkT}{2\pi\hbar^2} \right)^{3/2} V \right\}. \end{aligned} \quad (2.3.21)$$

You should note that this free energy will give, upon differentiation with respect to V , the correct equation of state. But, as Gibbs realized, the free energy expression is nevertheless problematic. While the argument of the logarithm is dimensionless, the V factor makes it *extensive*. In other words *the logarithm will diverge in the thermodynamic limit*. One would

have expected the argument of the logarithm to be size-independent, since then the extensivity of F is ensured by the N prefactor.

This was the problem confronted by Gibbs. He *knew* the argument of the logarithm should be independent of size and he achieved this by inserting a factor of $1/N$ “by hand”.

We know that the $1/N!$ multiplier of the partition function, required by quantum mechanics, results in a factor e/N in the logarithm, upon the use of Stirling’s approximation. So Gibbs’s paradox is resolved using quantum mechanics and the thermodynamic limit.

2.3.5 Entropy of mixing

Let us consider the mixing of two gases. Fig. 2.3 shows a container with a wall separating it into two regions. In the left hand region there are N_1 particles and in the right there are N_2 particles. We shall assume that both regions are at the same temperature and pressure. Furthermore we will assume that the number density N/V is the same on both sides.

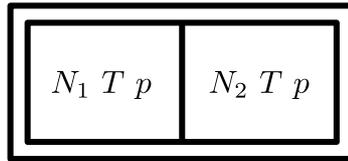


Figure 2.3: Mixing of gases

We shall investigate what happens when the wall is removed. In particular we shall consider what happens when the gases on either side are (a) different and (b) when they are the same.

When the wall is in place the partition function is simply the product of the partition functions of the two systems. We use the partition function expression of Eq. (2.1.16) so that

$$\begin{aligned} Z &= Z_1 Z_2 \\ &= \frac{1}{N_1!} \left(\frac{mkT}{2\pi\hbar^2} \right)^{3N_1/2} V_1^{N_1} \frac{1}{N_2!} \left(\frac{mkT}{2\pi\hbar^2} \right)^{3N_2/2} V_2^{N_2}. \end{aligned} \quad (2.3.22)$$

This may be simplified to

$$Z = \frac{1}{N_1! N_2!} \left(\frac{mkT}{2\pi\hbar^2} \right)^{3(N_1+N_2)/2} V_1^{N_1} V_2^{N_2}. \quad (2.3.23)$$

This is the same whether the particles are the identical or different.

Now we shall remove the separating wall and allow the gases to mix. There are two cases to consider: identical and different particles.

a) Identical particles

If the particles are identical then the new partition function is that corresponding to $N = N_1 + N_2$, $V = V_1 + V_2$. Thus the “after” partition function will be

$$Z = \frac{1}{(N_1 + N_2)!} \left(\frac{mkT}{2\pi\hbar^2} \right)^{3(N_1+N_2)/2} (V_1 + V_2)^{(N_1+N_2)}. \quad (2.3.24)$$

The ratio of the after to the before partition function is

$$\frac{Z_{\text{after}}}{Z_{\text{before}}} = \frac{N_1!N_2!}{(N_1 + N_2)!} \frac{(V_1 + V_2)^{(N_1+N_2)}}{V_1^{N_1}V_2^{N_2}}. \quad (2.3.25)$$

This may be simplified. Since $V_1/N_1 = V_2/N_2 = V/N$ it follows that $V_1 = VN_1/N$ and $V_2 = VN_2/N$ so that

$$\frac{Z_{\text{after}}}{Z_{\text{before}}} = \frac{N_1!N_2!}{N!} \frac{N^N}{N_1^{N_1}N_2^{N_2}}. \quad (2.3.26)$$

Upon using Stirling’s approximation—that is, upon taking the thermodynamic limit—this expression becomes unity. In other words, in the case of identical particles

$$Z_{\text{after}} = Z_{\text{before}}. \quad (2.3.27)$$

So for identical particles there is no effect on removing the separating wall and the original (macro-)state will be recovered if the wall is replaced. This is as expected on physical grounds, but note that the result would not have been obtained if the $1/N!$ term in the partition function had not been used.

b) Different particles

If the particles on the two sides were different then on removing the wall we have a composite system with N_1 type-1 particles in the volume $V = V_1 + V_2$ and N_2 type-2 particles in the same volume. Thus we have

$$\begin{aligned} Z &= \frac{1}{N_1!} \left(\frac{mkT}{2\pi\hbar^2} \right)^{3N_1/2} V^{N_1} \frac{1}{N_2!} \left(\frac{mkT}{2\pi\hbar^2} \right)^{3N_2/2} V^{N_2} \\ &= \frac{1}{N_1!N_2!} \left(\frac{mkT}{2\pi\hbar^2} \right)^{3N/2} V^N. \end{aligned} \quad (2.3.28)$$

The ratio of the after to the before partition function is then

$$\frac{Z_{\text{after}}}{Z_{\text{before}}} = \frac{V^N}{V_1^{N_1}V_2^{N_2}}. \quad (2.3.29)$$

In this case the “after” partition function is different to the “before”. Then, for unlike particles, the free energy and some of the other thermodynamic parameters will change when the wall is removed.

The change in the free energy is given by

$$\begin{aligned} F_{\text{after}} - F_{\text{before}} &= -kT \ln \frac{Z_{\text{after}}}{Z_{\text{before}}} \\ &= -kT \ln \left\{ \frac{V^N}{V_1^{N_1} V_2^{N_2}} \right\}. \end{aligned} \quad (2.3.30)$$

This will lead to a change of entropy. Since

$$S = - \left. \frac{\partial F}{\partial T} \right|_{V,N} \quad (2.3.31)$$

it follows that the entropy change upon removal of the wall is

$$\begin{aligned} \Delta S &= k \ln \left\{ \frac{V^N}{V_1^{N_1} V_2^{N_2}} \right\} \\ &= Nk \ln V - N_1 k \ln V_1 - N_2 k \ln V_2. \end{aligned} \quad (2.3.32)$$

This may be written as

$$\Delta S = N_1 k \ln \frac{V}{V_1} + N_2 k \ln \frac{V}{V_2} \quad (2.3.33)$$

which shows that the entropy increases when the wall is removed. This increase of entropy when two different gases are mixed is known as the *entropy of mixing*. The expression may be understood from the Boltzmann entropy expression, using simple counting arguments: the first term gives the entropy increase of the N_1 type-1 particles expanding from volume V_1 into volume V while the second term gives the entropy increase of the N_2 type-2 particles expanding from volume V_2 into volume V .

2.4 The Quantum Gas

2.4.1 Methodology for quantum gases

The Bose-Einstein and the Fermi-Dirac distribution functions give the mean number of particles in a given single particle quantum state in terms of the temperature T and the chemical potential μ . The temperature and chemical potential are the *intensive* variables that determine the equilibrium distribution $\bar{n}(\varepsilon)$. We have a good intuitive feel for the temperature of a system. But

the chemical potential is different. This determines the number of particles in a system that can exchange particles with its surrounding. In practice, however, it might be more intuitive to speak of a system containing a given number of particles. In that case it is the number of particles in the system that determines the chemical potential.

Now the number of particles in the system is given by

$$N = \sum_i \alpha \bar{n}(\varepsilon_i) \quad (2.4.1)$$

which converts to the integral

$$N = \int_0^\infty \alpha \bar{n}(\varepsilon) g(\varepsilon) d\varepsilon \quad (2.4.2)$$

where $g(\varepsilon)$ is the energy density of states and α is the factor which accounts for the degeneracy of the particles' spin states. This is 2 for electrons since there are two spin states for a spin $S = 1/2$; more generally it will be $2S + 1$, (but see Section 2.8.3 dealing with photons; massless particles are different).

The expression for N must be inverted to give μ , which can then be used in the distribution function to find the other properties of the system. For instance, the internal energy of the system would be found from

$$E = \sum_i \alpha \varepsilon_i \bar{n}(\varepsilon_i) \quad (2.4.3)$$

or, in integral form

$$E = \int_0^\infty \alpha \varepsilon \bar{n}(\varepsilon) g(\varepsilon) d\varepsilon. \quad (2.4.4)$$

More generally, the average value of a function of energy $f(\varepsilon)$ is given by

$$\bar{f} = \sum_i \alpha f(\varepsilon_i) \bar{n}(\varepsilon_i) \quad (2.4.5)$$

where the sum is taken over the single particle energy states. In integral form this is

$$\bar{f} = \int_0^\infty \alpha f(\varepsilon) g(\varepsilon) \bar{n}(\varepsilon) d\varepsilon. \quad (2.4.6)$$

Thus the methodology for treating a quantum gas starts with the expression for the number of particles N , which is inverted to find the chemical potential μ . This is substituted into the distribution function $\bar{n}(\varepsilon)$, from which all other properties may be found.

2.5 Fermi Gas at Low Temperatures

2.5.1 Ideal Fermi gas at zero temperature

The Fermi-Dirac distribution function is given by

$$n(\varepsilon) = \frac{1}{e^{(\varepsilon-\mu)/kT} + 1} \quad (2.5.1)$$

Henceforth, for notational convenience, we shall drop the bar over n . We have plotted $n(\varepsilon)$ in Fig. 2.4, where the dashed line shows the zero temperature case. At $T = 0$ the distribution becomes a box function

$$n(\varepsilon) = \begin{cases} 1 & \varepsilon < \mu \\ 0 & \varepsilon > \mu. \end{cases} \quad (2.5.2)$$

Note that in general the chemical potential depends on temperature. Its zero temperature value is called the Fermi energy

$$\varepsilon_F = \mu(T = 0). \quad (2.5.3)$$

And the temperature defined by $kT_F = \varepsilon_F$ is known as the Fermi temperature.

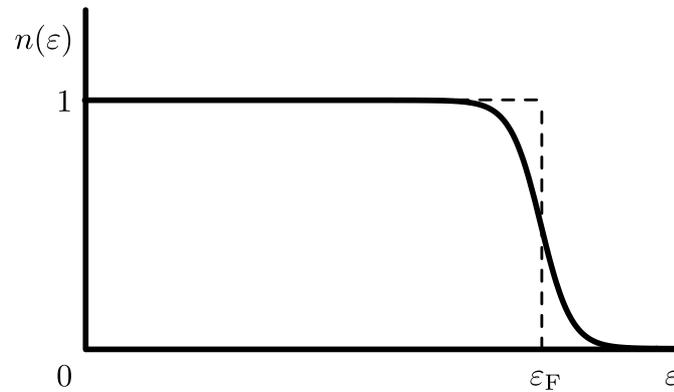


Figure 2.4: Fermi-Dirac distribution, with $T = 0$ limit

In accordance with the methodology described in the previous section, the first thing to do is to evaluate the total number of particles in the system in order to find the chemical potential – the Fermi energy in the $T = 0$ case.

The density of states is given by Eq. (2.1.16):

$$g(\varepsilon) = \frac{1}{4} \frac{V}{\pi^2 \hbar^3} (2m)^{3/2} \varepsilon^{1/2}. \quad (2.5.4)$$

The total number of particles in the system is

$$\begin{aligned} N &= \frac{\alpha V}{4\pi^2 \hbar^3} (2m)^{3/2} \int_0^{\varepsilon_F} \varepsilon^{1/2} d\varepsilon \\ &= \frac{\alpha V}{6\pi^2 \hbar^3} (2m\varepsilon_F)^{3/2}. \end{aligned} \quad (2.5.5)$$

And this may be inverted to obtain the Fermi energy

$$\varepsilon_F = \frac{\hbar^2}{2m} \left(\frac{6\pi^2 N}{\alpha V} \right)^{2/3}. \quad (2.5.6)$$

This gives the chemical potential at zero temperature. Observe that it depends on the *density* of particles in the system N/V , so the Fermi energy is, as expected, an intensive variable.

Fermi momentum and Fermi wave vector

There is a host of Fermi-related quantities. We have introduced the Fermi energy and the Fermi temperature. It will prove convenient also to mention the the Fermi velocity v_F , the Fermi momentum p_F , and the Fermi wave vector k_F . Since we are considering non-relativistic particles we define v_F and k_F through

$$\varepsilon_F = \frac{1}{2} m v_F^2 = \frac{p_F^2}{2m} \quad (2.5.7)$$

so that

$$v_F = \frac{\hbar}{m} \left(\frac{6\pi^2 N}{\alpha V} \right)^{1/3} \quad (2.5.8)$$

and

$$p_F = \hbar \left(\frac{6\pi^2 N}{\alpha V} \right)^{1/3}. \quad (2.5.9)$$

From this the Fermi wave vector follows naturally as

$$k_F = \left(\frac{6\pi^2 N}{\alpha V} \right)^{1/3}. \quad (2.5.10)$$

Observe that k_F depends only on the number density (and the spin degeneracy factor). In terms of the mean particle spacing $d = (V/N)^{1/3}$ we have

$$k_F = \left(\frac{6\pi^2}{\alpha} \right)^{1/3} \frac{1}{d} \quad (2.5.11)$$

which for spin $\frac{1}{2}$ is

$$k_F \approx \frac{3.09}{d}. \quad (2.5.12)$$

So the Fermi wave vector is essentially a measure of the inverse particle separation.

Re-expression of the density of states

We see that the Fermi energy/velocity/temperature/momentum/wave vector provide natural and useful scales for the consideration of the properties of Fermi systems. Thus it proves convenient and expedient to express the density of states in terms of the Fermi energy

$$\begin{aligned} g(\varepsilon) &= \frac{3N}{2\alpha\varepsilon_F^{3/2}}\varepsilon^{1/2} \\ &= \frac{3}{2\alpha} \frac{N}{\varepsilon_F} \left(\frac{\varepsilon}{\varepsilon_F} \right)^{1/2}. \end{aligned} \quad (2.5.13)$$

Having obtained the zero-temperature chemical potential, the Fermi-Dirac function is now completely specified at $T = 0$, and we can proceed to find the zero temperature internal energy of the system. This is given by

$$E(T = 0) = \frac{3N}{2\varepsilon_F^{3/2}} \int_0^{\varepsilon_F} \varepsilon^{3/2} d\varepsilon, \quad (2.5.14)$$

which evaluates to

$$E = \frac{3}{5} N \varepsilon_F. \quad (2.5.15)$$

The internal energy is proportional to the number of particles in the system and so it is, as expected, an extensive quantity.

Pressure is related to the internal energy. For non-relativistic particles (Eq. (2.1.35)) we have simply $pV = \frac{2}{3}E$. So the zero-temperature pressure of a Fermi gas is

$$p(T = 0) = \frac{2}{5} \frac{N}{V} \varepsilon_F. \quad (2.5.16)$$

The zero-temperature pressure of a classical gas is zero. By contrast the pressure of a Fermi gas at $T = 0$ is finite; it corresponds to the pressure of a classical gas at a temperature $T = \frac{2}{3}T_F$.

The considerable ground state energy and zero-temperature pressure of a Fermi gas are a consequence of the Pauli exclusion principle.

2.5.2 Fermi gas at low temperatures – simple model

The effect of a small finite temperature may be modelled very simply by approximating the Fermi-Dirac distribution by a piecewise linear function, Fig. 2.5. This must match the slope of the curve at $\varepsilon = \mu$, and the derivative is found to be

$$\left. \frac{dn(\varepsilon)}{d\varepsilon} \right|_{\varepsilon=\mu} = -\frac{1}{4kT}. \quad (2.5.17)$$

This indicates that the energy width of the transition region is $\Delta\varepsilon \sim kT$ so that only a fraction kT/ε_F of the particles, in the vicinity of the Fermi energy are “excitable”. In other words, in many respects a degenerate gas of N fermions at a temperature T is “like” a classical gas of $N\frac{T}{T_F}$ particles.

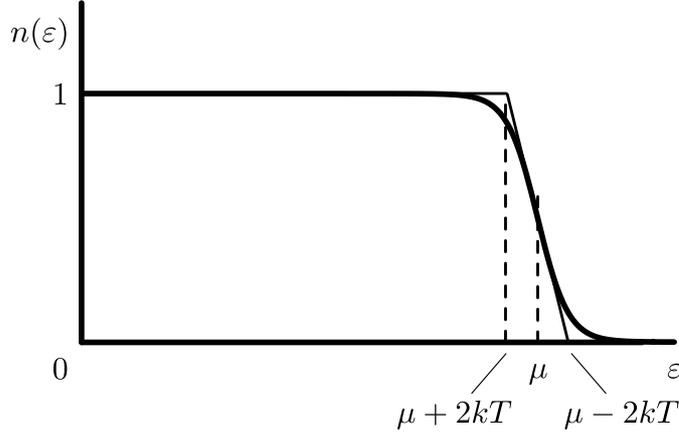


Figure 2.5: Simple modelling of Fermi-Dirac distribution

The distribution function, in this approximation, is then

$$n(\varepsilon) = \begin{cases} 1 & 0 < \varepsilon < \mu - 2kT \\ 1 - (\varepsilon - \mu + 2kT)/4kT & \mu - 2kT < \varepsilon < \mu + 2kT \\ 0 & \mu + 2kT < \varepsilon \end{cases} \quad (2.5.18)$$

from which the thermodynamic properties may be calculated.

The chemical potential is found by considering the total number of particles in the system:

$$\begin{aligned} N &= \alpha \int_0^{\infty} n(\varepsilon)g(\varepsilon)d\varepsilon \\ &= \frac{3N}{2\varepsilon_F^{3/2}} \int_0^{\infty} n(\varepsilon)\varepsilon^{1/2}d\varepsilon. \end{aligned} \quad (2.5.19)$$

Observe that here the number N appears on both sides and so it cancels. The reason for this is that we have chosen to express the density of states in terms of the Fermi energy. Thus while the N cancels from both sides the number (density) is contained in the Fermi energy. So in this approach we are really expressing the Fermi energy in terms of the chemical potential:

$$\varepsilon_{\text{F}}^{3/2} = \frac{3}{2} \int_0^{\infty} n(\varepsilon) \varepsilon^{1/2} d\varepsilon \quad (2.5.20)$$

and we wish to invert this relation to give the chemical potential in terms of the Fermi energy (and temperature).

We use the approximate form for $n(\varepsilon)$. Upon integration, this gives

$$\varepsilon_{\text{F}}^{3/2} = \mu^{3/2} \frac{1}{10} \left\{ \sqrt{1 + 2 \frac{kT}{\mu}} \left[4 \frac{kT}{\mu} + 4 + \frac{\mu}{kT} \right] - \sqrt{1 - 2 \frac{kT}{\mu}} \left[4 \frac{kT}{\mu} - 4 + \frac{\mu}{kT} \right] \right\}. \quad (2.5.21)$$

As we are interested specifically in the low temperature behaviour we shall expand as a series in powers of kT/μ

$$\varepsilon_{\text{F}}^{3/2} = \mu^{3/2} \left\{ 1 + \frac{1}{2} \left(\frac{kT}{\mu} \right)^2 + \frac{3}{40} \left(\frac{kT}{\mu} \right)^4 \dots \right\}. \quad (2.5.22)$$

The Fermi energy is then the 2/3 power of this, which, by the binomial theorem, is

$$\begin{aligned} \varepsilon_{\text{F}} &= \mu \left\{ 1 + \frac{1}{3} \left(\frac{kT}{\mu} \right)^2 + \frac{1}{45} \left(\frac{kT}{\mu} \right)^4 + \dots \right\} \\ &= \mu + \frac{1}{3} \frac{(kT)^2}{\mu} + \frac{1}{45} \frac{(kT)^4}{\mu^3} + \dots \end{aligned} \quad (2.5.23)$$

This series may be inverted to give μ in terms of ε_{F} :

$$\mu = \varepsilon_{\text{F}} \left\{ 1 - \frac{1}{3} \left(\frac{kT}{\varepsilon_{\text{F}}} \right)^2 - \frac{2}{15} \left(\frac{kT}{\varepsilon_{\text{F}}} \right)^4 + \dots \right\}. \quad (2.5.24)$$

This shows that as the temperature is increased from $T = 0$ the chemical potential decreases from its zero temperature value, and the first term is proportional to T^2 .

In a similar way the internal energy is found to be

$$E = E_0 \left\{ 1 + \frac{5}{3} \left(\frac{kT}{\varepsilon_F} \right)^2 - \frac{2}{3} \left(\frac{kT}{\varepsilon_F} \right)^4 + \dots \right\} \quad (2.5.25)$$

up to the term in T^4 .

We should note that the approximation of the Fermi-Dirac distribution used in this section is only a model that allows the simple calculation of properties of the Fermi gas, indicating the general behaviour at low temperatures. But the coefficients of the powers of kT/ε_F are incorrect; this is simply a model that permits demonstration of the *qualitative* low temperature behaviour.

2.5.3 Fermi gas at low temperatures – series expansion

We have formal expressions for the thermodynamic behaviour of a gas of fermions: expressions like Eqs. (2.4.2) and (2.4.4). In the previous section a model was described which treated the deviations from $T = 0$ behaviour in a simplistic and qualitative way. What is required is a systematic procedure for calculating finite (but low) temperature behaviour. We shall see that such a procedure is possible based on the special shape of the Fermi-Dirac distribution function; this approach was pioneered by Arnold Sommerfeld [3].

Very generally, one requires to evaluate integrals of the form

$$I = \int_0^\infty n(\varepsilon) \varphi(\varepsilon) d\varepsilon \quad (2.5.26)$$

where $n(\varepsilon)$ is the Fermi-Dirac distribution function and $\varphi(\varepsilon)$ is the function to be integrated over, including the density of states. Eqs. (2.4.2) and (2.4.4) for N and E are of this form. If we define $\psi(\varepsilon)$, the integral of $\varphi(\varepsilon)$, by

$$\psi(\varepsilon) = \int_0^\varepsilon \varphi(\varepsilon') d\varepsilon' \quad (2.5.27)$$

then the expression for I may be integrated by parts to give

$$I = n(\varepsilon) \psi(\varepsilon) \Big|_0^\infty - \int_0^\infty n'(\varepsilon) \psi(\varepsilon) d\varepsilon. \quad (2.5.28)$$

Now since $n(\infty) = 0$ from the form of the Fermi-Dirac function, and $\psi(0) = 0$ from its definition, the first term vanishes and one is left with

$$I = - \int_0^\infty n'(\varepsilon) \psi(\varepsilon) d\varepsilon, \quad (2.5.29)$$

an integral over $n'(\varepsilon)$. But $n'(\varepsilon)$ has an important shape (Fig. 2.6): it is sharply peaked at $\varepsilon = \mu$, particularly at the lowest of temperatures; this was Sommerfeld's key point. It means that in the integral for I the behaviour of $\psi(\varepsilon)$ only in the vicinity of $\varepsilon = \mu$ is important.

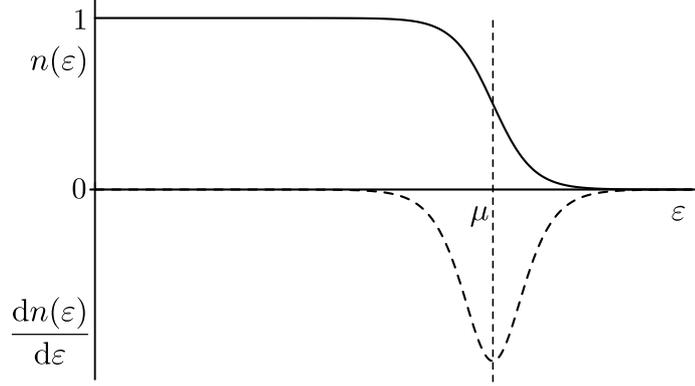


Figure 2.6: Fermi-Dirac distribution and its derivative

It then follows that a convenient series for I may be obtained by expanding $\psi(\varepsilon)$ about $\varepsilon = \mu$ and integrating Eq. (2.5.29) term by term. The Taylor expansion is

$$\psi(\varepsilon) = \sum_{n=0}^{\infty} \frac{1}{n!} \left. \frac{d^n \psi}{d\varepsilon^n} \right|_{\varepsilon=\mu} (\varepsilon - \mu)^n \quad (2.5.30)$$

so that

$$I = - \sum_{n=0}^{\infty} \frac{1}{n!} \left. \frac{d^n \psi}{d\varepsilon^n} \right|_{\varepsilon=\mu} \int_0^{\infty} n'(\varepsilon) (\varepsilon - \mu)^n d\varepsilon. \quad (2.5.31)$$

The integral is simplified through the substitution $x = (\varepsilon - \mu)/kT$, and since $n'(\varepsilon)$ goes to zero away from $\varepsilon = \mu$ the lower limit of the integral can be extended to $-\infty$ without introducing significant error. Then

$$\int_0^{\infty} n'(\varepsilon) (\varepsilon - \mu)^n d\varepsilon = - (kT)^n \mathcal{I}_n \quad (2.5.32)$$

where the \mathcal{I}_n are just numbers:

$$\begin{aligned} \mathcal{I}_n &= \int_{-\infty}^{\infty} \frac{e^x}{(e^x + 1)^2} x^n dx \\ &= \int_{-\infty}^{\infty} \frac{x^n}{4 \cosh^2(x/2)} dx. \end{aligned} \quad (2.5.33)$$

Since $\cosh^2(x/2)$ is an even function, the \mathcal{I}_n for odd n vanish. We then find

$$I = \sum_{\substack{n=0 \\ \text{(even } n)}}^{\infty} \mathcal{I}_n \frac{(kT)^n}{n!} \left. \frac{d^n \psi}{d\varepsilon^n} \right|_{\varepsilon=\mu} \quad (2.5.34)$$

which is a series expansion for the quantity I in powers of temperature. This thus provides our *low temperature* expansion. By contrast, the high temperature behaviour will be treated in Section 2.7.1.

The general expression for the integrals is (even n)

$$\mathcal{I}_n = (2 - 2^{2-n}) \zeta(n) n! \quad (2.5.35)$$

where $\zeta(n)$ is Riemann's zeta function². So we may write I as

$$I = \sum_{\substack{n=0 \\ \text{(even } n)}}^{\infty} (2 - 2^{2-n}) \zeta(n) (kT)^n \left. \frac{d^n \psi}{d\varepsilon^n} \right|_{\varepsilon=\mu}. \quad (2.5.36)$$

The first few \mathcal{I}_n values are

$$\begin{aligned} \mathcal{I}_0 &= 1 \\ \mathcal{I}_2 &= \pi^2/3 \\ \mathcal{I}_4 &= 7\pi^4/15 \\ \mathcal{I}_6 &= 31\pi^6/21 \\ \mathcal{I}_8 &= 127\pi^8/15 \\ \mathcal{I}_{10} &= 2555\pi^{10}/33 \end{aligned} \quad (2.5.37)$$

so that

$$I = \psi(\mu) + \frac{\pi^2}{6} (kT)^2 \left. \frac{d^2 \psi}{d\varepsilon^2} \right|_{\varepsilon=\mu} + \frac{7\pi^4}{360} (kT)^4 \left. \frac{d^4 \psi}{d\varepsilon^4} \right|_{\varepsilon=\mu} + \dots \quad (2.5.38)$$

or, in terms of the original function $\varphi(\varepsilon)$,

$$I = \int_0^\mu \varphi(\varepsilon) d\varepsilon + \frac{\pi^2}{6} (kT)^2 \left. \frac{d\varphi}{d\varepsilon} \right|_{\varepsilon=\mu} + \frac{7\pi^4}{360} (kT)^4 \left. \frac{d^3 \varphi}{d\varepsilon^3} \right|_{\varepsilon=\mu} + \dots \quad (2.5.39)$$

Note this is not *quite* the simple power series it appears since the chemical potential μ also depends upon temperature. Thus chemical potential must always be found before proceeding to the other thermodynamic quantities.

²The Riemann zeta function $\zeta(n)$ is defined as the infinite series $\zeta(n) = \frac{1}{1^n} + \frac{1}{2^n} + \frac{1}{3^n} + \dots$. *Mathematica* provides this function as `Zeta[n]`.

We should also point out that in extending the lower limit of the integral in Eq. (2.5.33) to minus infinity, we are neglecting exponentially small terms. Landau and Lifshitz [4] point out that the resultant expansion is thus an *asymptotic* and not a convergent series. This is dramatically illustrated in the two dimensional case, considered in Problem 2.6.

These series expansions are conveniently evaluated using a computer symbolic mathematics system such as *Mathematica*. It is then expedient to recast the expression for I of Eq. (2.5.29) as

$$\begin{aligned} I &= - \int_0^\infty n'(\varepsilon) \psi(\varepsilon) d\varepsilon \\ &= \frac{1}{kT} \int_0^\infty \frac{e^{(\varepsilon-\mu)/kT}}{(e^{(\varepsilon-\mu)/kT} + 1)^2} \psi(\varepsilon) d\varepsilon. \end{aligned} \quad (2.5.40)$$

Then making the substitution $x = (\varepsilon - \mu)/kT$, and extending the lower limit of the integral to $-\infty$ as explained above,

$$I = \int_{-\infty}^\infty \frac{e^x}{(e^x + 1)^2} \psi(kTx + \mu) dx. \quad (2.5.41)$$

We shall call this a Sommerfeld integral. The procedure for evaluating the low temperature series for I then comprises expanding ψ in powers of x before integrating term by term.

Chemical potential

The chemical potential is found by considering the total number of particles in the system:

$$\begin{aligned} N &= \alpha \int_0^\infty n(\varepsilon) g(\varepsilon) d\varepsilon \\ &= \frac{3N}{2\varepsilon_F^{3/2}} \int_0^\infty n(\varepsilon) \varepsilon^{1/2} d\varepsilon. \end{aligned} \quad (2.5.42)$$

Observe that here the number N appears on both sides and so it cancels. The reason for this is that we have chosen to express the density of states in terms of the Fermi energy. Thus while the N cancels from both sides the number (density) is contained in the Fermi energy. So in this approach we are really expressing the Fermi energy in terms of the chemical potential

$$\varepsilon_F^{3/2} = \frac{3}{2} \int_0^\infty n(\varepsilon) \varepsilon^{1/2} d\varepsilon \quad (2.5.43)$$

and we wish to invert this relation to give the chemical potential in terms of the Fermi energy (and temperature).

In this case

$$\varphi(\varepsilon) = \frac{3N}{2\varepsilon_{\text{F}}^{3/2}}\varepsilon^{1/2} \quad (2.5.44)$$

so that

$$\psi(\varepsilon) = \frac{N}{\varepsilon_{\text{F}}^{3/2}}\varepsilon^{3/2}. \quad (2.5.45)$$

Then using the above result in Eq. (2.5.39) or using the *Mathematica* procedure in the Appendix, we find

$$\varepsilon_{\text{F}}^{3/2} = \mu^{3/2} \left\{ 1 + \frac{\pi^2}{6} \frac{3}{4} \left(\frac{kT}{\mu} \right)^2 + \frac{7\pi^4}{360} \frac{9}{16} \left(\frac{kT}{\mu} \right)^4 + \dots \right\}, \quad (2.5.46)$$

or, upon simplification:

$$\varepsilon_{\text{F}}^{3/2} = \mu^{3/2} \left\{ 1 + \frac{1}{8}\pi^2 \left(\frac{kT}{\mu} \right)^2 + \frac{7}{640}\pi^4 \left(\frac{kT}{\mu} \right)^4 + \dots \right\}. \quad (2.5.47)$$

The Fermi energy is then the 2/3 power of this which, by the binomial theorem, gives ε_{F} as

$$\begin{aligned} \varepsilon_{\text{F}} &= \mu \left\{ 1 + \frac{2}{3} \frac{1}{8}\pi^2 \left(\frac{kT}{\mu} \right)^2 + \frac{1}{180}\pi^4 \left(\frac{kT}{\mu} \right)^4 + \dots \right\} \\ &= \mu + \frac{\pi^2}{12} \frac{(kT)^2}{\mu} + \frac{\pi^4}{180} \frac{(kT)^4}{\mu^3} \dots \end{aligned} \quad (2.5.48)$$

and to the same order this may be inverted to give

$$\mu = \varepsilon_{\text{F}} \left\{ 1 - \frac{\pi^2}{12} \left(\frac{kT}{\varepsilon_{\text{F}}} \right)^2 - \frac{\pi^4}{80} \left(\frac{kT}{\varepsilon_{\text{F}}} \right)^4 + \dots \right\}. \quad (2.5.49)$$

This shows that as the temperature is increased from $T = 0$ the chemical potential decreases from its zero temperature value, and the first term is in T^2 . The result is similar to the qualitative approximation of the previous section, Eq. (2.5.24), but now the coefficients of the series are correct.

The procedure can be extended easily to find higher powers of T in the expansion; indeed the *Mathematica* code in Appendix C can do this automatically. The starting function in this case is the Sommerfeld integral:

$$\varepsilon_{\text{F}}^{3/2} = \int_{-\infty}^{\infty} \frac{e^x (kTx + \mu)^{3/2}}{(e^x + 1)^2} dx. \quad (2.5.50)$$

The series for ε_{F} in powers of μ is inverted to give a series for μ in powers of ε_{F} .

Internal energy

The internal energy for the gas of Fermions is given by:

$$\begin{aligned} E &= \alpha \int_0^\infty \varepsilon n(\varepsilon) g(\varepsilon) d\varepsilon \\ &= \frac{3N}{2\varepsilon_F^{3/2}} \int_0^\infty n(\varepsilon) \varepsilon^{3/2} d\varepsilon, \end{aligned} \quad (2.5.51)$$

so that in this case

$$\varphi(\varepsilon) = \frac{3N}{2\varepsilon_F^{3/2}} \varepsilon^{3/2} \quad (2.5.52)$$

and

$$\psi(\varepsilon) = \frac{3}{5} \frac{N}{\varepsilon_F^{3/2}} \varepsilon^{5/2}. \quad (2.5.53)$$

Then using the above result in Eq. (2.5.39) or using the *Mathematica* procedure in Appendix C, we find

$$E = \frac{3}{5} \frac{N\mu^{5/2}}{\varepsilon_F^{3/2}} + \frac{\pi^2}{6} (kT)^2 \frac{9}{4} \frac{N\mu^{1/2}}{\varepsilon_F^{3/2}} - \frac{7\pi^4}{360} (kT)^4 \frac{9}{16} \frac{N\mu^{-3/2}}{\varepsilon_F^{3/2}} + \dots \quad (2.5.54)$$

This, however, gives the energy in terms of μ , which has a temperature dependence of its own. So we must substitute for μ , from Eq. (2.5.49). This will then give the temperature dependence of the internal energy. Up to the term in T^4 this is:

$$\begin{aligned} E &= \frac{3}{5} N\varepsilon_F + \frac{\pi^2}{4} N\varepsilon_F \left(\frac{kT}{\varepsilon_F} \right)^2 - \frac{3\pi^4}{80} N\varepsilon_F \left(\frac{kT}{\varepsilon_F} \right)^4 + \dots \\ &= E_0 \left\{ 1 + \frac{5\pi^2}{12} \left(\frac{kT}{\varepsilon_F} \right)^2 - \frac{5\pi^4}{80} \left(\frac{kT}{\varepsilon_F} \right)^4 + \dots \right\}. \end{aligned} \quad (2.5.55)$$

This procedure can be extended easily to find higher powers of T in the expansion; indeed the *Mathematica* code in Appendix C can do this automatically. The starting function in this case is the Sommerfeld integral

$$E = \frac{3}{5} \frac{N}{\varepsilon_F^{3/2}} \int_{-\infty}^{\infty} \frac{e^x (kTx + \mu)^{5/2}}{(e^x + 1)^2} dx. \quad (2.5.56)$$

Equation of state

Since we know that $pV = \frac{2}{3}E$ for classical (non-relativistic) particles we obtain the low temperature equation of state for fermions

$$pV = \frac{2}{5} N\varepsilon_F + \frac{\pi^2}{6} N\varepsilon_F \left(\frac{kT}{\varepsilon_F} \right)^2 - \frac{\pi^4}{40} N\varepsilon_F \left(\frac{kT}{\varepsilon_F} \right)^4 + \dots \quad (2.5.57)$$

Thermal capacity

The thermal capacity is found by differentiating the internal energy with respect to temperature:

$$C_V = \left. \frac{\partial E}{\partial T} \right|_V \quad (2.5.58)$$

so that

$$C_V = Nk \left\{ \frac{\pi^2 kT}{2 \varepsilon_F} - \frac{3\pi^4}{20} \left(\frac{kT}{\varepsilon_F} \right)^3 + \dots \right\}. \quad (2.5.59)$$

We see that the heat capacity goes to zero with temperature, in agreement with the Third Law.

At low temperatures it decreases linearly

$$C_V = Nk \frac{\pi^2 kT}{2 \varepsilon_F} \quad (2.5.60)$$

and we observe that in this limit C_V is $\frac{\pi^2}{3} \frac{kT}{\varepsilon_F}$ times the classical value. This is in accordance with the idea that in a degenerate gas of fermions, only a fraction kT/ε_F of the particles, in the vicinity of the Fermi energy are “excitable”.

We may substitute for ε_F to write the linear heat capacity as

$$\begin{aligned} C_V &= N \frac{m\pi^2}{\hbar^2 k_F^2} k^2 T \\ &= N \frac{m}{\hbar^2} \left(\frac{\pi \alpha V}{6N} \right)^{2/3} k^2 T. \end{aligned} \quad (2.5.61)$$

2.5.4 More general treatment of low temperature heat capacity

The low temperature heat capacity of real fermions, such as electrons or liquid ^3He , is observed to follow the linear temperature behaviour above, but the coefficient can be different from that of the free particle expression, Eq. (2.5.61). The linearity of the heat capacity is interpreted as indicating that while the free-particle picture is inappropriate, the excitations in the system are nevertheless “particle-like”. The dispersion (energy–momentum) may not be that of free particles and, correspondingly, the density of states may not correspond to that for free particles.

We shall approach this issue by considering the heat capacity of a system of fermions where the form for the density of states function is not assumed. This means we are no longer considering non-interacting fermions particles;

instead we are considering a gas of non-interacting (weakly interacting) Fermi *quasiparticles*. In this sense the discussion is appropriate for this chapter. We shall utilise a generalisation of the Sommerfeld expansion method. Our treatment was inspired by the discussion of Reif [5].

In accordance with our general procedures, the first thing to do is to obtain a suitable expression for the chemical potential for the system. Since we are considering low temperatures, we know that μ will be close to the Fermi energy, but we will require the small deviation from this value.

The number of particles in the system is given by

$$N = \alpha \int_0^{\infty} n(\varepsilon)g(\varepsilon) d\varepsilon \quad (2.5.62)$$

where here $g(\varepsilon)$ is our general expression for the density of states. In terms of the Sommerfeld expansion, Eq. (2.5.39), here

$$\varphi(\varepsilon) = \alpha g(\varepsilon) \quad (2.5.63)$$

so that up to second order in T

$$N = \alpha \int_0^{\mu} g(\varepsilon)d\varepsilon + \alpha \frac{\pi^2}{6} (kT)^2 g'(\varepsilon). \quad (2.5.64)$$

In this expression we shall split the integral in the first term into the range from 0 to ε_F and from ε_F to μ :

$$N = \alpha \int_0^{\varepsilon_F} g(\varepsilon)d\varepsilon + \alpha \int_{\varepsilon_F}^{\mu} g(\varepsilon)d\varepsilon + \alpha \frac{\pi^2}{6} (kT)^2 g'(\mu). \quad (2.5.65)$$

Here the first integral is simply the total number of particles N . In the second integral we note that ε_F is close to μ and that over this small range the argument of the integral, $g(\varepsilon)$ will hardly change. Thus the second term may be approximated by

$$\alpha(\mu - \varepsilon_F)g(\varepsilon_F). \quad (2.5.66)$$

Since the third term already has a T^2 factor we introduce negligible error here by replacing μ by ε_F . Then we have

$$(\mu - \varepsilon_F)g(\varepsilon_F) + \frac{\pi^2}{6} (kT)^2 g'(\varepsilon_F) = 0 \quad (2.5.67)$$

so that to this order of approximation

$$\mu = \varepsilon_F - \frac{\pi^2}{6} (kT)^2 \frac{g'(\varepsilon_F)}{g(\varepsilon_F)}. \quad (2.5.68)$$

This gives the leading order deviation of the chemical potential from the zero-temperature value of the Fermi energy. We see the leading order deviation goes as T^2 , as we found for the free particle case, Eq. (2.5.49).

Now moving to the calculation of the internal energy, in this case we have

$$\varphi(\varepsilon) = \alpha\varepsilon g(\varepsilon). \quad (2.5.69)$$

Then the series for the energy may be written in a similar way as

$$E = \alpha \int_0^{\varepsilon_F} \varepsilon g(\varepsilon) d\varepsilon + \alpha \int_{\varepsilon_F}^{\mu} \varepsilon g(\varepsilon) d\varepsilon + \alpha \frac{\pi^2}{6} (kT)^2 \{g(\mu) + \mu g'(\mu)\}. \quad (2.5.70)$$

Here the first term is the ground state energy E_0 . In the second term ε_F is again close to μ and over this small range the argument of the integral, $\varepsilon g(\varepsilon)$ will hardly change. Thus the second term may be approximated by

$$\alpha(\mu - \varepsilon_F)\varepsilon_F g(\varepsilon_F). \quad (2.5.71)$$

But now we have an expression for μ in Eq. (2.5.68). Thus the second term may be written as

$$-\alpha \frac{\pi^2}{6} (kT)^2 g'(\varepsilon_F)\varepsilon_F. \quad (2.5.72)$$

And since the third term already has a T^2 factor we introduce negligible error by replacing μ by ε_F . Then we have

$$E = E_0 - \alpha \frac{\pi^2}{6} (kT)^2 g'(\varepsilon_F)\varepsilon_F + \alpha \frac{\pi^2}{6} (kT)^2 \{g(\varepsilon_F) + \varepsilon_F g'(\varepsilon_F)\} \quad (2.5.73)$$

which simplifies to

$$E = E_0 + \alpha \frac{\pi^2}{6} (kT)^2 g(\varepsilon_F) \quad (2.5.74)$$

as the derivative terms cancel. This result shows that the internal energy depends on the density of states only at the Fermi surface.

The heat capacity is found by differentiating the internal energy. So in the low temperature limit the heat capacity of an assembly of Fermions with arbitrary dispersion relation and thus arbitrary density of states is

$$C_V = \frac{1}{3} \alpha \pi^2 g(\varepsilon_F) k^2 T. \quad (2.5.75)$$

We see that the low temperature heat capacity remains linear in temperature, and we see that the coefficient is determined by the density of states at the Fermi surface. The general form for $g(\varepsilon)$ is unimportant; only its value at the Fermi level is required.

Effective mass

The quasiparticle excitations giving rise to the heat capacity above may be regarded as having an effective mass m^* such that the free fermion low temperature heat capacity, Eq. (2.5.61)

$$C_V = N \frac{m\pi^2}{\hbar^2 k_F^2} k^2 T$$

is rehabilitated by the replacement $m \rightarrow m^*$ where

$$\begin{aligned} m^* &= \frac{\alpha}{3} \hbar^2 k_F^2 \frac{g(\varepsilon_F)}{N} \\ &= 2\pi^2 \frac{\hbar^2}{k_F} \frac{g(\varepsilon_F)}{V}. \end{aligned} \tag{2.5.76}$$

It is possible that the effective mass enhancement ratio m^*/m can be as high as 1000 in some compounds. These are referred to as *heavy fermion* compounds.

2.6 Bose Gas at Low Temperatures

There is no restriction on the number of bosons occupying a single state. This means that at low temperatures there will be a substantial occupation of the low-energy states. This is in contrast to the Fermi case where the Pauli exclusion principle restricts the state occupation. Thus the behaviour of the Bose gas and the Fermi gas will be particularly different at low temperatures. Indeed the zero-temperature states are very different. The Fermi gas has all states up to the Fermi level occupied, with a resultant significant internal energy. Since there is no restriction on occupation, the ground state of the Bose gas will have all particles occupying the same lowest energy single particle state. This macroscopic occupation of the lowest energy state is known as Bose-Einstein condensation; its possibility was predicted by Einstein in 1925. The early treatment of this phenomenon by London [7] is still one of the clearest.

2.6.1 General procedure for treating the Bose gas

The Bose Einstein distribution is

$$n(\varepsilon) = \frac{1}{e^{(\varepsilon-\mu)/kT} - 1}, \tag{2.6.1}$$

which gives the mean number of bosons in the state of energy ε in a system at temperature T and chemical potential μ . As with the Fermi case, the average value of a general function of energy $f(\varepsilon)$ is given by

$$\bar{f} = \sum_i \alpha f(\varepsilon_i) n(\varepsilon_i) \quad (2.6.2)$$

where the sum is taken over the single particle energy states. Conventionally this sum is transformed to an integral over energy states using the density of states function $g(\varepsilon)$ as:

$$\bar{f} = \int_0^\infty \alpha f(\varepsilon) g(\varepsilon) n(\varepsilon) d\varepsilon, \quad (2.6.3)$$

where $g(\varepsilon)$ is given by Eq. (2.1.16):

$$g(\varepsilon) = \frac{V}{4\pi^2 \hbar^3} (2m)^{3/2} \varepsilon^{1/2}. \quad (2.6.4)$$

The procedure, as described, will give the expression for \bar{f} in terms of the system's characterising intensive parameters T and μ . But, as we have seen already, the chemical potential is best eliminated in terms of the total number of particles in the system. Thus the first task must be to consider the expression for the number of particles. But since we know that the number of particles in the ground state can be significant at low temperatures, let us start by looking specifically at the ground state occupation.

2.6.2 Ground state occupation

The number of particles in the ground state N_0 is given by

$$N_0 = \frac{\alpha}{e^{(\varepsilon_0 - \mu)/kT} - 1} \quad (2.6.5)$$

where α is the spin degeneracy factor; this will be unity for $S = 0$ particles. Here ε_0 is the ground state energy. In the thermodynamic limit ($V \rightarrow \infty$) the ground state energy will vanish: $\varepsilon_0 \rightarrow 0$. In this case we have

$$N_0 = \frac{1}{e^{-\mu/kT} - 1}. \quad (2.6.6)$$

If the ground state occupation is significant: above a few hundred, for instance, then the denominator will be small, which means that the exponential will differ only slightly from unity. Then μ must be very small (and negative) so that

$$N_0 = \frac{1}{1 - \mu/kT - \dots - 1} \sim -kT/\mu \quad (2.6.7)$$

or

$$\mu \sim -kT/N_0. \quad (2.6.8)$$

We conclude that a macroscopic occupation of the ground state is associated with a vanishingly small chemical potential; indeed in the thermodynamic limit it will be zero.

It must also be noted that the chemical potential cannot be positive as this would give a negative number of particles in the ground state. For bosons μ is always negative.

2.6.3 Number of particles – chemical potential

One is inclined to write the expression for the number of particles in the system by following the recipe of (2.6.3) by integrating over the number of particles in each quantum state:

$$N = \sum_i n_i \rightarrow \int_0^\infty g(\varepsilon) n(\varepsilon) d\varepsilon. \quad (2.6.9)$$

However there is a problem with this. We know that at low enough temperatures, for bosons, there will be a large number of particles in the ground state, of energy $\varepsilon = 0$. But the density of states $g(\varepsilon)$ is proportional to $\varepsilon^{1/2}$ (in three dimensions). This means that it gives *zero weight* to the ground state. There is an error introduced in transforming from a sum over states to an integral using the density of states. Ordinarily there will be no problem with the neglect of a single state. But if there is an appreciable occupation of this state then the error becomes serious. Since the $\varepsilon^{1/2}$ factor neglects completely the ground state we must add this “by hand” to the calculation for N . Thus we write (using a spin degeneracy factor α of unity):

$$N = N_0 + \frac{V}{4\pi^2\hbar^3} (2m)^{3/2} \int_0^\infty \frac{\varepsilon^{1/2}}{e^{(\varepsilon-\mu)/kT} - 1} d\varepsilon \quad (2.6.10)$$

where N_0 is the number of particles in the ground state. We should note that while N_0 may be a large number, the *fraction* of particles in the ground state N_0/N may be small.

2.6.4 Low temperature behaviour of Bose gas

At low temperatures, when N_0 is appreciable, the chemical potential is very small and it can be ignored. Then, within this approximation, the expression for N becomes

$$N = N_0 + \frac{V}{4\pi^2\hbar^3} (2m)^{3/2} \int_0^\infty \frac{\varepsilon^{1/2}}{e^{\varepsilon/kT} - 1} d\varepsilon. \quad (2.6.11)$$

The integral may be “tidied” by the substitution $x = \varepsilon/kT$ whereupon³

$$N = N_0 + V \left(\frac{mkT}{2\pi\hbar^2} \right)^{3/2} \frac{2}{\sqrt{\pi}} \int_0^\infty \frac{x^{1/2}}{e^x - 1} dx. \quad (2.6.12)$$

The integral in this expression is a pure number. Let’s just denote it by $\mathcal{B}_{1/2}$ for the moment, and consider its actual value later. Then the number of excited particles in the system is given by

$$N_{\text{ex}} = V \left(\frac{mkT}{2\pi\hbar^2} \right)^{3/2} \frac{2}{\sqrt{\pi}} \mathcal{B}_{1/2}. \quad (2.6.13)$$

As the temperature increases the number of excited particles increases. There will be a certain temperature when N_{ex} will be equal to the total number of particles in the system N — at least according to this equation. In reality the expression will become invalid when N_0 becomes *too* small, but let us just use this as a mathematical definition of a characteristic temperature T_c ; that is, let us define T_c by

$$N = V \left(\frac{mkT_c}{2\pi\hbar^2} \right)^{3/2} \frac{2}{\sqrt{\pi}} \mathcal{B}_{1/2}. \quad (2.6.14)$$

Then the expression for N becomes

$$N = N_0 + N \left(\frac{T}{T_c} \right)^{3/2} \quad (2.6.15)$$

which may be inverted to give the number of particles in the ground state as

$$N_0 = N \left\{ 1 - \left(\frac{T}{T_c} \right)^{3/2} \right\}. \quad (2.6.16)$$

This expression is valid for very low temperatures; clearly we must have $T < T_c$, but how close to T_c can one go? In fact one can go very close indeed since we require the *absolute* value of N_0 to be large. And as one has $N \sim 10^{23}$ it follows that the *fractional* value N_0/N may be very small while N_0 will still be *enormous*. So we can use the above expression for N_0 for temperatures $T < T_c$ to within a whisker of T_c ; indeed in the thermodynamic limit we can go right up to T_c . Then we can identify the temperature T_c as the transition temperature, below which there will be a *macroscopic* occupation of the ground state. This is known as the *Bose-Einstein condensation* and

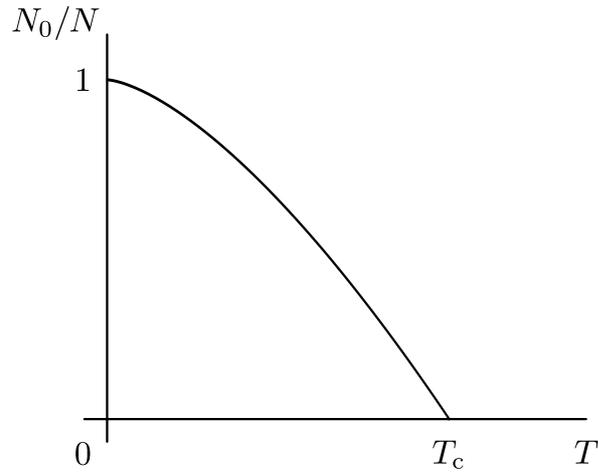


Figure 2.7: Ground state occupation for Bose gas

it happens at the temperature T_c . It is the only phase transition in nature that happens in the absence of any interactions.

The transition temperature is given, from Eq. (2.6.14), by

$$T_c = \frac{2\pi^2\hbar^2}{mk} \left\{ \frac{N}{2\pi\mathcal{B}_{1/2}V} \right\}^{2/3}. \quad (2.6.17)$$

Now $\mathcal{B}_{1/2}$ is a particular case of the integral

$$\mathcal{B}_n = \int_0^\infty \frac{x^n}{e^x - 1} dx. \quad (2.6.18)$$

These integrals may be expressed as

$$\mathcal{B}_n = \Gamma(n+1)\zeta(n+1) \quad (2.6.19)$$

where $\Gamma()$ is Euler's gamma function⁴ and $\zeta()$ is Riemann's zeta function (see Footnote 2 on p. 81). So in our present case

$$\mathcal{B}_{1/2} = \Gamma(3/2)\zeta(3/2) \quad (2.6.20)$$

³Here and below I have used the bracket $(mkT/2\pi\hbar^2)$ since this is Λ^{-2} , where Λ is the thermal de Broglie wavelength, Eq. (2.3.5).

⁴The gamma function $\Gamma(z)$ was introduced by Euler in order to extend the factorial function to non-integer arguments. It may be specified by an integral: $\Gamma(z) = \int_0^\infty t^{z-1}e^{-t}dt$ since when z is a positive integer then $\Gamma(z) = (z-1)!$. However the recursion relation $\Gamma(z+1) = z\Gamma(z)$ holds for non-integer z as well. Another useful property is the reflection relation $\Gamma(z)\Gamma(1-z) = \pi/\sin(\pi z)$. The gamma function has the *Mathematica* symbol `Gamma[z]`.

and these have values

$$\begin{aligned}\Gamma(3/2) &= \sqrt{\pi}/2 \\ \zeta(3/2) &= 2.612\dots\end{aligned}\tag{2.6.21}$$

From these we may write T_c as

$$\begin{aligned}T_c &= \frac{2\pi\hbar^2}{mk} \left\{ \frac{N}{2.612V} \right\}^{2/3} \\ &= 3.313 \frac{\hbar^2}{mk} \left\{ \frac{N}{V} \right\}^{2/3}.\end{aligned}\tag{2.6.22}$$

2.6.5 Thermal capacity of Bose gas – below T_c

To find the thermal capacity of the Bose gas we must first obtain an expression for the internal energy. We shall do this all within the approximation of neglecting the chemical potential. In other words, our results will be valid for temperatures *below* the Bose-Einstein condensation temperature.

The internal energy is given by

$$E = \int_0^\infty \varepsilon g(\varepsilon) n(\varepsilon) d\varepsilon.\tag{2.6.23}$$

Here we do not need to worry about the ground state occupation since it contributes nothing to the internal energy. The expression for E is then

$$E = \frac{V}{4\pi^2\hbar^3} (2m)^{3/2} \int_0^\infty \frac{\varepsilon^{3/2}}{e^{\varepsilon/kT} - 1} d\varepsilon,\tag{2.6.24}$$

and as in the previous case the integral may be “tidied” by the substitution $x = \varepsilon/kT$ whereupon

$$E = \frac{V}{4\pi^2\hbar^3} (2m)^{3/2} (kT)^{5/2} \int_0^\infty \frac{x^{3/2}}{e^x - 1} dx.\tag{2.6.25}$$

The integral in this expression is a pure number; we recognize it as $\mathcal{B}_{3/2}$ from Eq. (2.6.18). Then the internal energy of the assembly of Bosons below T_c is

$$E = V \left(\frac{mkT}{2\pi\hbar^2} \right)^{3/2} (kT) \frac{2}{\sqrt{\pi}} \mathcal{B}_{3/2}.\tag{2.6.26}$$

But since the number of particles in the system is given by Eq. (2.6.14)

$$N = V \left(\frac{mkT_c}{2\pi\hbar^2} \right)^{3/2} \frac{2}{\sqrt{\pi}} \mathcal{B}_{1/2}$$

then we may write the internal energy as

$$E = Nk \frac{\mathcal{B}_{3/2} T^{5/2}}{\mathcal{B}_{1/2} T_c^{3/2}}. \quad (2.6.27)$$

Upon differentiation the thermal capacity (at constant volume) is

$$C_V = \frac{5}{2} Nk \frac{\mathcal{B}_{3/2}}{\mathcal{B}_{1/2}} \left(\frac{T}{T_c} \right)^{3/2}. \quad (2.6.28)$$

We already have the value of the integral $\mathcal{B}_{1/2}$; it remains then, to find the value of the integral $\mathcal{B}_{3/2}$. From Eq. (2.6.19) we have

$$\mathcal{B}_{3/2} = \Gamma(5/2) \zeta(5/2). \quad (2.6.29)$$

These have values

$$\begin{aligned} \Gamma(5/2) &= 3\sqrt{\pi}/4 \\ \zeta(3/2) &= 1.342\dots \end{aligned} \quad (2.6.30)$$

so that below T_c the thermal capacity is given by

$$\begin{aligned} C_V &= \frac{15}{4} Nk \left(\frac{T}{T_c} \right)^{3/2} \times \frac{1.342}{2.612} \\ &= 1.926 Nk \left(\frac{T}{T_c} \right)^{3/2}. \end{aligned} \quad (2.6.31)$$

This should be compared with the classical value of $\frac{3}{2}Nk$.

Above the transition temperature C_V will fall, gradually, to the classical value as shown in Fig. 2.8.

2.6.6 Comparison with Superfluid ^4He and other systems

In 1995 Bose-Einstein condensation was observed in rubidium vapour [8] and in lithium vapour [9]. An accessible account of these discoveries is given in the article by Meacher and Ruprecht [10]. In order to have very small inter-particle interactions, the density of these gases was kept very low. The

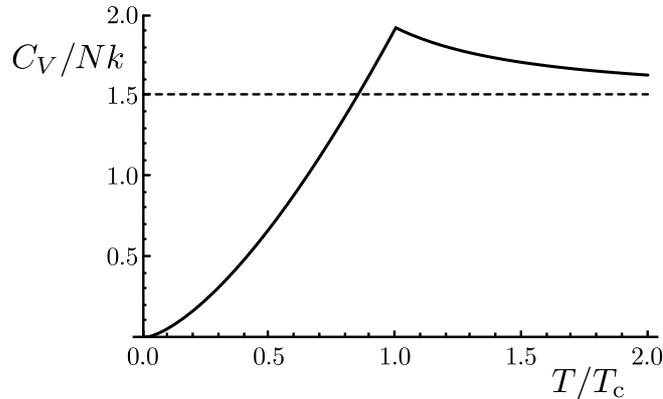


Figure 2.8: Thermal capacity of a Bose gas. The dashed line shows the classical value.

condensation temperature was, correspondingly very low and temperatures in the nanokelvin range were required, achieved by laser confinement and laser cooling of the trapped vapour cloud.

The Bose-Einstein condensation was observed in rubidium vapour by imaging the density and momentum distribution of the atoms. Fig. 2.9 [11] shows the velocity distribution of rubidium atoms at three different temperatures. The left frame shows the velocity distribution at 400 nK, just before the appearance of the Bose-Einstein condensate. The centre frame is at 200 nK, just after the appearance of the condensate. And the right frame is at 50 nK, after further evaporation leaves a sample of nearly pure condensate. The area of view of each image is 200 mm by 270 mm. The appearance of the peak indicates the existence of a significant number of atoms in the ground state.

The interest in the two different materials was because rubidium has a remnant repulsive interaction while the remnant interaction in lithium is attractive; in both these cases the Bose-Einstein condensation was observed. However in both these cases the amount of material involved precluded the measurement of any thermodynamic properties. The case is different for liquid helium.

The common isotope of helium, ^4He , is found to go superfluid at a temperature of 2.172 K. In 1924, Kamerlingh Onnes observed that *something* strange happened to liquid ^4He at this temperature and in 1932 Keesom and Clusius observed a cusp in the heat capacity, indicative of a phase transition. Subsequently the low-temperature phase was observed to flow with no viscosity – superfluid behaviour. The calculated Bose-Einstein condensation transition temperature for particles whose mass and density corresponds to

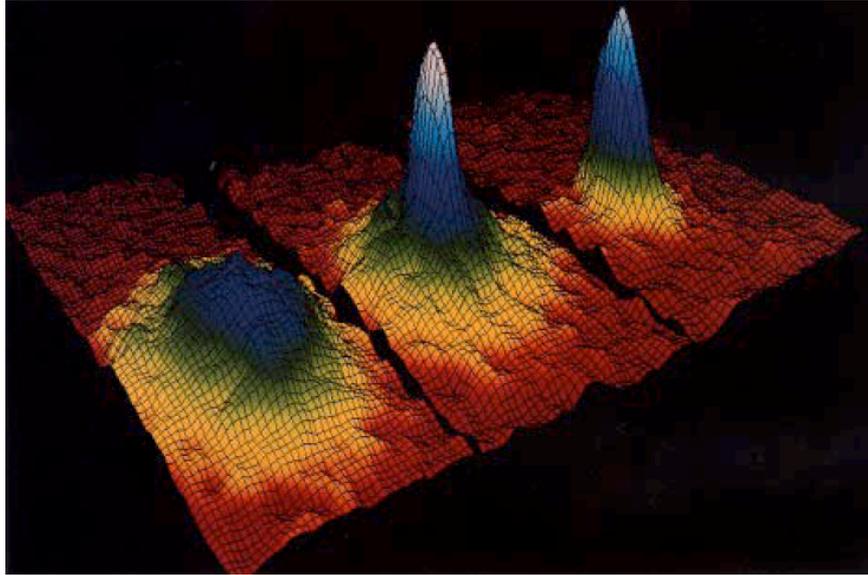


Figure 2.9: Bose-Einstein condensation in rubidium vapour. Three velocity distributions of the rubidium atoms at three different temperatures.

those of liquid ^4He is 3.13 K. Since these temperatures are similar it is possible that the superfluidity is related to the Bose-Einstein condensation. This was first suggested in 1938 by London [12] and by Tisza [13]. The possibility is supported by the fact that at these temperatures ^3He , a fermion, does not become superfluid; there is no such transition. The small difference in transition temperatures is ascribed to the interatomic interactions in liquid ^4He , which are neglected in the Bose gas model.

The following discussions will consider *interacting* bosons, so strictly this is a topic for the next chapter. However we shall place the discussion here as it follows naturally from our previous considerations.

2.6.7 Two-fluid model of superfluid ^4He

The two fluid model is a very successful thermodynamic/macroscopic model of superfluid helium. It was proposed by Tiza in 1938. The Bose-Einstein condensation gives a microscopic *motivation* for the model, but it cannot be regarded as a microscopic *justification* – as we shall see.

According to the two fluid model the superfluid comprises mixture of two interpenetrating fluids. One is the *normal* component and the other is the *superfluid* component. The density of the liquid is then expressed as the sum

$$\rho = \rho_s + \rho_n. \quad (2.6.32)$$

The normal component is assumed to have properties similar to the fluid above the transition. The superfluid component is assumed to have *zero entropy*. As the temperature is lowered below the transition temperature the superfluid fraction grows at the expense of the normal fraction. And at $T = 0$ the normal component has reduced to zero.

Originally, as proposed by Tisza, the connection with Bose-Einstein condensation was made by identifying the superfluid component with the macroscopically occupied ground state of the Bose gas. Since these particles are all in the same single-particle state there is only one microstate corresponding to this and its entropy is thus zero. However subsequently Landau proposed that the normal component should be associated with the elementary excitations of the system.

An experiment by Andronikashvili [14] measured the normal component of superfluid helium using a stack of discs oscillating in the liquid.

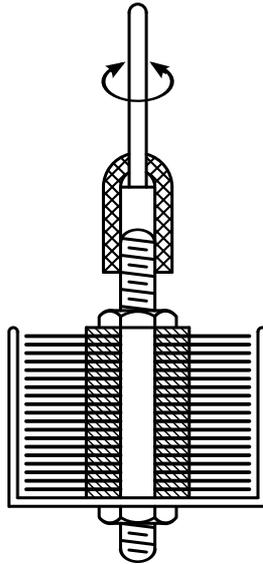


Figure 2.10: Andronikashvili's experiment

The normal component will move with the discs while the superfluid component will be decoupled. The resonant frequency of the disc assembly will depend on its effective mass. Thus the normal component can be measured through the resonant frequency of the discs. The normal fraction, as measured by Andronikashvili, is compared with the fractional ground state occupation for the Bose-Einstein condensation in Fig. 2.11. There is a *qualitative* similarity, but the discrepancy is serious.

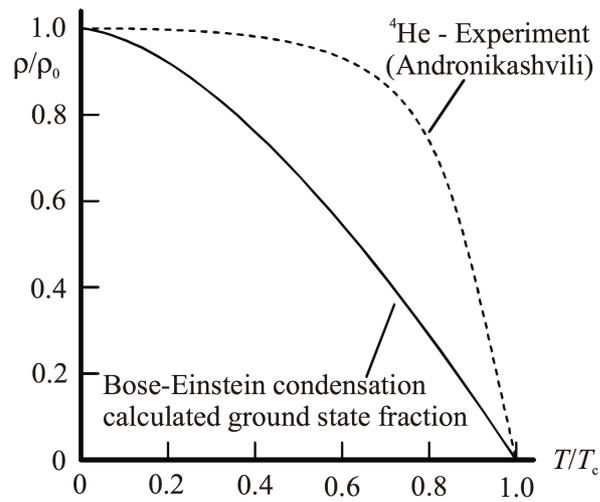


Figure 2.11: Ground state fraction

2.6.8 Elementary excitations

The difference between superfluid helium and the Bose-Einstein condensed fluid is made more apparent by measurements of thermal capacity.

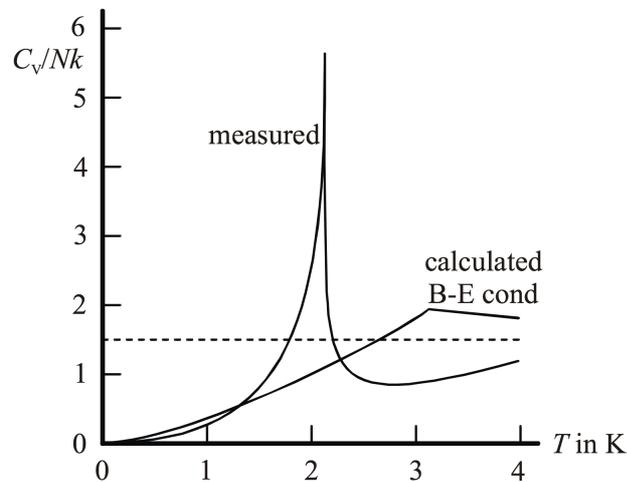


Figure 2.12: Thermal capacity of liquid helium

In Fig. 2.12 we show C_V as measured in liquid helium compared with that calculated for an ideal Bose gas. (Most books compare the calculated C_V with the observed thermal capacity under the liquid's saturated vapour pressure. This has a qualitatively different behaviour so the comparison is invalid.)

The low temperature behaviour of these two are different. The calculated C_V increases with temperature as $T^{3/2}$, but the observed thermal capacity varies as T^3 . Now a T^3 thermal capacity indicates *phonon excitations*. Thus the interactions between the particles seem to quench the single-particle behaviour and leads to collective motion of the particles. This is supported by calculations of Bogoliubov [15], who showed that even very weak repulsive interactions change the elementary excitations of the system from free particle motion to phonon-like collective motion.

The conclusion is that the interactions cannot be regarded as causing a slight change to the properties of the Bose-Einstein condensate; the two fluid model cannot be built on the Bose-Einstein condensate idea. In reality the normal component comprises the elementary excitations in the system. The spectrum of elementary excitations is more complex than just phonons, but that is another story. A good account of the properties of superfluid helium-4 and their understanding is given in the book by Khalatnikov [16]. This book also contains translated reprints of the original papers by Landau on the subject.

2.7 Quantum Gas at High Temperatures – the Classical Limit

2.7.1 General treatment for Fermi, Bose and Maxwell Cases

At high temperatures we shall see that the difference between Fermi and Bose gases disappears; the quantum distinction becomes negligible. It will therefore prove sensible to consider the Fermi and Bose cases together.

When the temperature is high, the probability of occupation of the individual single-particle states becomes significantly less than unity. Then in the Fermi and Bose distribution functions

$$n(\varepsilon) = \frac{1}{e^{(\varepsilon-\mu)/kT} \pm 1}, \quad (2.7.1)$$

$n(\varepsilon)$ is much smaller than unity; the denominator is much greater than unity; the exponential is then large compared with the ± 1 . So in that limit the ± 1 in the denominator becomes negligible. Thus the distinction between fermions and bosons disappears. Indeed the classical case corresponds to dropping the ± 1 : setting it to zero. The (hypothetical) classical particles, obeying such a distribution function are called *maxwellons*. You should recall our discussion

in Section 2.2.2, where we argued that quantum effects become insignificant when the probability of occupation of the states is small.

Mathematica Notebooks for the following calculations are given in Appendix C.

In this limit we treat the Fermi, Bose and Maxwell/classical cases together, by writing the distribution function as

$$n(\varepsilon) = \frac{1}{e^{(\varepsilon-\mu)/kT} + a} \quad (2.7.2)$$

where

$$a = \begin{cases} +1 & \text{for fermions} \\ 0 & \text{for maxwellons} \\ -1 & \text{for bosons} \end{cases} \quad (2.7.3)$$

and the exponential is much greater than unity. We then re-express $n(\varepsilon)$ as

$$n(\varepsilon) = \frac{e^{(\mu-\varepsilon)/kT}}{1 + ae^{(\mu-\varepsilon)/kT}} \quad (2.7.4)$$

so that the exponential in the denominator is now small and we can then perform a binomial expansion:

$$\begin{aligned} n(\varepsilon) &= e^{(\mu-\varepsilon)/kT} \{1 + ae^{(\mu-\varepsilon)/kT}\}^{-1} \\ &= e^{(\mu-\varepsilon)/kT} \{1 - ae^{(\mu-\varepsilon)/kT} + a^2 e^{2(\mu-\varepsilon)/kT} - \dots\} \end{aligned} \quad (2.7.5)$$

2.7.2 Quantum energy parameter

Recall that for fermions we introduced the idea of Fermi energy. In order to treat the Bose, Fermi and indeed Maxwell cases in a parallel fashion we shall introduce a “quantum energy” ε_q ; this is identical to the Fermi energy of the Fermi case, Eq. (2.5.6), but it is now extended to the Bose and Maxwell cases as well. Of course for bosons and maxwellons it doesn’t have the interpretation as a maximum filled energy state at $T = 0$, but it does provide a convenient energy scale. However the the analogue of the Fermi wave vector Eq. (2.5.10) is more intuitive; the “quantum wave vector” k_q is still essentially the inverse particle spacing:

$$k_q = \left(\frac{6\pi^2 N}{\alpha V} \right)^{1/3}. \quad (2.7.6)$$

So in *this* spirit we shall use the quantum energy parameter

$$\varepsilon_q = \frac{\hbar^2 k_q^2}{2m} = \frac{\hbar^2}{2m} \left(\frac{6\pi^2 N}{\alpha V} \right)^{2/3}. \quad (2.7.7)$$

In effect we are using ε_q simply as a characteristic energy that conveniently parameterises the number density N/V .

Note that the dimensionless ratio ε_q/kT is related simply to the thermal deBroglie wavelength Λ (Eq. (2.3.5)):

$$\frac{\varepsilon_q}{kT} = \Lambda^2 \left(\frac{3\sqrt{\pi} N}{4\alpha V} \right)^{2/3}. \quad (2.7.8)$$

2.7.3 Chemical potential

In order to find the chemical potential we must invert (the analogue of) Eq. (2.5.43),

$$\varepsilon_q^{3/2} = \frac{3}{2} \int_0^\infty n(\varepsilon) \varepsilon^{1/2} d\varepsilon \quad (2.7.9)$$

which we shall do in terms of the above series expansion, Eq. (2.7.5), for $n(\varepsilon)$

$$\varepsilon_q^{3/2} = \frac{3}{2} \int_0^\infty \left\{ e^{(\mu-\varepsilon)/kT} - a e^{2(\mu-\varepsilon)/kT} + a^2 e^{3(\mu-\varepsilon)/kT} - \dots \right\} \varepsilon^{1/2} d\varepsilon \quad (2.7.10)$$

This can be integrated term by term. It will be convenient, in the first instance, to work in terms of the *fugacity* $z = e^{\mu/kT}$ rather than the chemical potential. Then upon integrating term by term we obtain $\varepsilon_q^{3/2}$ as a power series in z :

$$\varepsilon_q^{3/2} = (kT)^{3/2} \left\{ \frac{3}{4} \sqrt{\pi} z - a \frac{3}{8} \sqrt{\frac{\pi}{2}} z^2 + a^2 \frac{1}{4} \sqrt{\frac{\pi}{3}} z^3 + \dots \right\}. \quad (2.7.11)$$

And then ε_q is obtained by taking the 2/3 power, which is sensibly written as

$$\frac{\varepsilon_q}{kT} = \frac{1}{2} 3^{2/3} \left(\frac{\pi}{2} \right)^{1/3} z^{2/3} - a \frac{1}{2 \times 2^{5/6}} \left(\frac{\pi}{3} \right)^{1/3} z^{5/3} + a^2 \frac{16\sqrt{3} - 3}{144} \left(\frac{\pi}{6} \right)^{1/3} z^{8/3} + \dots \quad (2.7.12)$$

This is an expression for ε_q/kT as a power series in z . We invert this to give the fugacity z as a power series in ε_q/kT :

$$z = e^{\mu/kT} = \frac{4}{3\sqrt{\pi}} \left(\frac{\varepsilon_q}{kT} \right)^{3/2} + a \frac{4\sqrt{2}}{9\pi} \left(\frac{\varepsilon_q}{kT} \right)^3 + a^2 \frac{16(9 - 4\sqrt{3})}{243\pi^{3/2}} \left(\frac{\varepsilon_q}{kT} \right)^{9/2} + \dots \quad (2.7.13)$$

In the classical case we take $a = 0$, whereupon

$$z_c = e^{\mu_c/kT} = \frac{4}{3\sqrt{\pi}} \left(\frac{\varepsilon_q}{kT} \right)^{3/2} \quad (2.7.14)$$

or

$$\mu_c = kT \ln \left[\frac{4}{3\sqrt{\pi}} \left(\frac{\varepsilon_q}{kT} \right)^{3/2} \right]. \quad (2.7.15)$$

Upon substituting for ε_q we obtain the classical ideal gas chemical potential as

$$\mu_c = -kT \ln \left[\alpha \left(\frac{mkT}{2\pi\hbar^2} \right)^{3/2} \frac{V}{N} \right] \quad (2.7.16)$$

in agreement with Eq. (2.3.16) in Section 2.3.3.

We can express the series for the fugacity, Eq. (2.7.13) as

$$z = z_c \left\{ 1 + a \frac{1}{3} \sqrt{\frac{2}{\pi}} \left(\frac{\varepsilon_q}{kT} \right)^{3/2} + a^2 \frac{4(9 - 4\sqrt{3})}{81\pi} \left(\frac{\varepsilon_q}{kT} \right)^3 + \dots \right\}. \quad (2.7.17)$$

Then, upon taking the logarithm, we can write the high temperature/low density chemical potential in terms of its classical value plus a series of correction terms

$$\mu = \mu_c + kT \left\{ a \frac{1}{3} \sqrt{\frac{2}{\pi}} \left(\frac{\varepsilon_q}{kT} \right)^{3/2} - a^2 \frac{16\sqrt{3} - 27}{81\pi} \left(\frac{\varepsilon_q}{kT} \right)^3 + \dots \right\}. \quad (2.7.18)$$

In the Fermi case ($a = +1$) the chemical potential is above the classical value while in the Bose case ($a = -1$) the chemical potential falls below the classical value.

Observe that μ/ε_q may be written as a function of the single variable kT/ε_q . In particular, the classical/maxwellon chemical potential is

$$\frac{\mu_c}{\varepsilon_q} = \frac{kT}{\varepsilon_q} \ln \left[\frac{4}{3\sqrt{\pi}} \left(\frac{\varepsilon_q}{kT} \right)^{3/2} \right]. \quad (2.7.19)$$

2.7.4 Internal energy

The internal energy of a quantum gas is

$$E = \alpha \int_0^\infty \varepsilon n(\varepsilon) g(\varepsilon) d\varepsilon. \quad (2.7.20)$$

We follow the procedure of the previous section. We write $n(\varepsilon)$ for the general Fermi/Maxwell/Bose case as in Eq. (2.7.2)/Eq. (2.7.4), so that E is given by

$$\begin{aligned} E &= \frac{3N}{2\varepsilon_q^{3/2}} \int_0^\infty \frac{\varepsilon^{3/2}}{e^{(\varepsilon-\mu)/kT} + a} d\varepsilon \\ &= \frac{3N}{2\varepsilon_q^{3/2}} \int_0^\infty \frac{\varepsilon^{3/2} e^{(\mu-\varepsilon)/kT}}{1 + a e^{(\mu-\varepsilon)/kT}} d\varepsilon. \end{aligned} \quad (2.7.21)$$

We perform the binomial expansion and integrate term by term, as in the previous section, giving E as a power series in $x = e^{\mu/kt}$:

$$E = NkT \left(\frac{kT}{\varepsilon_q} \right)^{3/2} \left\{ \frac{9\sqrt{\pi}}{8} z - a \frac{9}{32} \sqrt{\frac{\pi}{2}} z^2 + a^2 \frac{1}{8} \sqrt{\frac{\pi}{3}} z^3 + \dots \right\}. \quad (2.7.22)$$

We need the expansion for z from Eq. (2.7.13), which we substitute into the above series. This gives

$$E = \frac{3}{2} NkT \left\{ 1 + a \frac{1}{3\sqrt{2\pi}} \left(\frac{\varepsilon_q}{kT} \right)^{3/2} - a^2 \frac{2(16\sqrt{3} - 27)}{243\pi} \left(\frac{\varepsilon_q}{kT} \right)^3 + \dots \right\}. \quad (2.7.23)$$

2.7.5 Equation of state

From the general relation, Eq. (2.1.35), $pV = \frac{2}{3}E$ we obtain the equation of state for the gases as

$$pV = NkT \left\{ 1 + a \frac{1}{3\sqrt{2\pi}} \left(\frac{\varepsilon_q}{kT} \right)^{3/2} - a^2 \frac{2(16\sqrt{3} - 27)}{243\pi} \left(\frac{\varepsilon_q}{kT} \right)^3 + \dots \right\}. \quad (2.7.24)$$

Or, substituting for ε_q :

$$pV = NkT \left\{ 1 + a \frac{\pi^{3/2}}{2\alpha} \frac{N}{V} \frac{\hbar^3}{(mkT)^{3/2}} - a^2 \frac{\pi^3}{\alpha^2} \frac{16\sqrt{3} - 27}{27} \left(\frac{N}{V} \right)^2 \frac{\hbar^6}{(mkT)^3} + \dots \right\}. \quad (2.7.25)$$

When $a = 0$ we have the conventional ideal gas equation of state. The pressure of the fermion gas is increased over that of the classical gas, while the pressure of the boson gas is decreased.

Some tables and series expressions for the thermodynamic properties of Fermi gases are given by Ebner and Fu [6] (beware of some errors) and references therein.

2.8 Black body radiation – the photon gas

2.8.1 Photons as quantized electromagnetic waves

The harmonic oscillator has the very important property that its energy eigenvalues are equally spaced:

$$\varepsilon_n = n\hbar\omega + \text{zero point energy} \quad n = 0, 1, 2, \dots \quad (2.8.1)$$

You will have calculated the internal energy of the harmonic oscillator in Problem 1.16. We shall write this result here as

$$E = \frac{\hbar\omega}{e^{\hbar\omega/kT} - 1} + \text{zero point contribution.} \quad (2.8.2)$$

And we shall, in the following sections, ignore the (constant) zero point energy contribution. This is acceptable since the zero of energy is, to a certain extent, arbitrary.

We now see that the expression for E can be reinterpreted in terms of the Bose distribution. The internal energy has the form

$$E = \bar{n}\hbar\omega + \text{zero point contribution} \quad (2.8.3)$$

where \bar{n} is the Bose distribution, the mean number of bosons of energy $\hbar\omega$. But here we observe in the Bose distribution that the chemical potential is zero.

The conclusion is that we can regard a harmonic oscillator of (angular) frequency ω as a collection of bosons of energy $\hbar\omega$, having zero chemical potential.

The fact that we can regard the harmonic oscillator as a collection of bosons is a consequence of the equal spacing of the oscillator energy levels. The vanishing of the chemical potential is due to the fact that the number of these bosons is not conserved.

We shall explore this by considering an isolated system of particles. If N is conserved then the number is determined – it is given and it will remain constant for the system. On the other hand if the number of particles is not conserved then one must determine the equilibrium number by maximising the entropy:

$$\left. \frac{\partial S}{\partial N} \right|_{E,V} = 0, \quad (2.8.4)$$

where we note that E and V are constant since the system is isolated. From the differential expression for the first law we see that

$$dS = \frac{1}{T} (dE + pdV - \mu dN). \quad (2.8.5)$$

So the entropy derivative is

$$\left. \frac{\partial S}{\partial N} \right|_{E,V} = -\frac{\mu}{T} \quad (2.8.6)$$

and we conclude that the equilibrium condition for this system, at finite temperatures, is simply

$$\mu = 0. \quad (2.8.7)$$

In other words $\mu = 0$ for non-conserved particles.

2.8.2 Photons in thermal equilibrium – black body radiation

It is known that bodies glow and emit light when heated sufficiently. In 1859 Kirchhoff laid down a challenge: to derive the mathematical formula for the radiation spectrum. This challenge was one of the key factors in the development of quantum theory.

The spectrum of radiation emitted by a body depends on its temperature. The spectrum also depends on the nature of its surface – to a more or lesser extent. However Kirchhoff appreciated that there was an idealisation that could be considered, when the surface absorbs all the radiation that falls upon it. Such a surface, when cold, appears to be black and Kirchhoff speculated on the spectrum of the radiation emitted by such a black body. He appreciated that the radiation was in thermal equilibrium with the body and that therefore the spectrum depended only on the temperature. The intensity of the spectrum was thus some function $U(\omega, T)$ and Kirchhoff's challenge was to find the form of this function.

The spectrum is then a property of the radiation and not of the body under consideration. Thus we can make a model system, an idealisation of the situation which retains the important features of the problem, but which is possible to solve.

Our model is simply a cavity, which is connected to the outside world by a small hole. We shall look through the hole, at the spectrum of the radiation in the cavity.

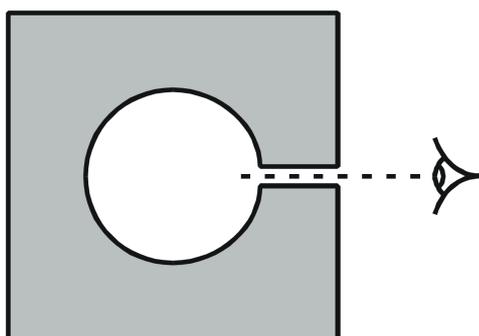


Figure 2.13: Radiation from a cavity

We consider the electromagnetic waves to be in thermal equilibrium with the walls. The photons will have a distribution given by the Bose-Einstein formula, but with zero chemical potential. And we then calculate the properties of this photon gas by the methods of statistical mechanics.

2.8.3 Planck's formula

In Section 2.1.5 we saw that the general expression for the energy density of states in three dimensions is given by Eq. (2.1.23):

$$g(\varepsilon) = \frac{V}{2\pi^2} k^2 \left/ \frac{d\varepsilon}{dk} \right. \quad (2.8.8)$$

where k is to be eliminated in terms of ε . For photons there is a linear relation between ε and k :

$$\varepsilon = \hbar ck \quad (2.8.9)$$

where c is the speed of light. Thus the density of states is

$$g(\varepsilon) = \frac{1}{2} \frac{V \varepsilon^2}{c^3 \pi^2 \hbar^3}. \quad (2.8.10)$$

Now although photons have a spin $S = 1$, they have zero mass. Quantum-mechanically this means that only the $S_z = -1$ and $+1$ orientations occur; the $S_z = 0$ orientation is suppressed. Classically this is understood because electromagnetic waves propagate as transverse disturbances; there is no longitudinal mode. The photons' two quantum states correspond to the two polarisation states of the electromagnetic waves. This means that we must take a degeneracy factor α for photons to be 2. And so the internal energy for the photon gas in thermal equilibrium is given by

$$\begin{aligned} E &= 2 \int_0^\infty \frac{g(\varepsilon) \varepsilon d\varepsilon}{e^{\varepsilon/kT} - 1} \\ &= \frac{V}{c^3 \pi^2 \hbar^3} \int_0^\infty \frac{\varepsilon^3 d\varepsilon}{e^{\varepsilon/kT} - 1}. \end{aligned} \quad (2.8.11)$$

Before we evaluate this integral we shall make connection with Kirchhoff's $U(\omega, T)$ introduced in Section 2.8.2. To this end we shall change variables to $\omega = \varepsilon/\hbar$ so that

$$E = \frac{V \hbar}{c^3 \pi^2} \int_0^\infty \frac{\omega^3 d\omega}{e^{\hbar\omega/kT} - 1}. \quad (2.8.12)$$

Now the energy can be expressed in terms of the spectrum $U(\omega, T)$ by integrating over all frequencies

$$E = \int_0^\infty U(\omega, T) d\omega. \quad (2.8.13)$$

And from these two expressions we can then identify

$$U(\omega, T) = \frac{V \hbar}{c^3 \pi^2} \frac{\omega^3}{e^{\hbar\omega/kT} - 1}. \quad (2.8.14)$$

This is Planck’s formula for black body radiation. Some examples are shown in Fig. 2.14, but plotted as a function of wavelength, which is more popular with spectroscopists.

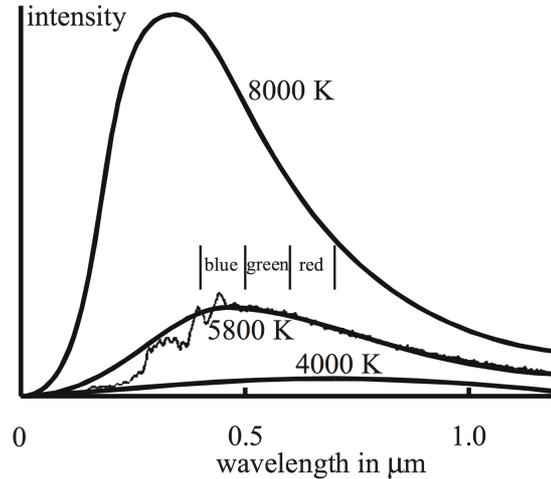


Figure 2.14: Black body radiation at three different temperatures; the wiggly line is the spectrum from the sun

The spectrum from the sun indicates that its temperature is about 5800 K. It is also of interest to note that the peak of the sun’s spectrum corresponds to the visible spectrum, that is the region of greatest sensitivity of the human eye.

A remarkable example of black body radiation is the spectrum of electromagnetic radiation arriving from outer space. It is found that when looking into space with radio telescopes, a uniform background electromagnetic “noise” is seen. The spectrum of this is found to fit the black body curve – for a temperature of approximately 2.7 K. The conclusion is that the equilibrium temperature of the universe is 2.7 K, which is understood as the remnant “glow” from the Big Bang. The data shown in Fig. 2.15 comes from the COBE satellite and it fits the Planck black body curve for a temperature of 2.74 K. The quality of the fit of the data to the theoretical curve is quite remarkable.

2.8.4 Internal energy and heat capacity

We now integrate the expression for the photon free energy in the previous section, Eq. (2.8.11)

$$E = \frac{V}{c^3 \pi^2 \hbar^3} \int_0^\infty \frac{\varepsilon^3 d\varepsilon}{e^{\varepsilon/kT} - 1}. \quad (2.8.15)$$

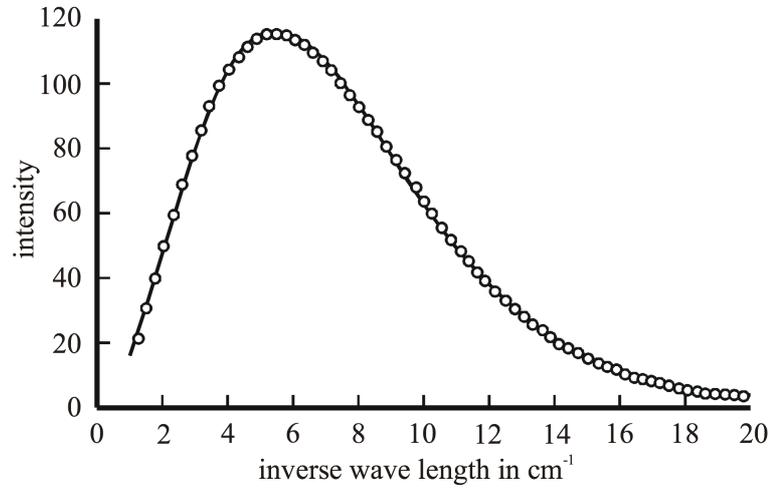


Figure 2.15: Cosmic background radiation plotted on 2.74 K black body curve

By changing the variable of integration to $x = \hbar\omega/kT$ the integral becomes a dimensionless number

$$E = \frac{V\hbar}{\pi^2 c^3} \left(\frac{kT}{\hbar} \right)^4 \int_0^{\infty} \frac{x^3}{e^x - 1} dx. \quad (2.8.16)$$

The integral is \mathcal{B}_3 from the definition Eq. (2.6.18), so that

$$E = \frac{V\hbar}{\pi^2 c^3} \left(\frac{kT}{\hbar} \right)^4 \mathcal{B}_3 \quad (2.8.17)$$

and

$$\mathcal{B}_3 = \Gamma(4)\zeta(4). \quad (2.8.18)$$

These have values

$$\begin{aligned} \Gamma(4) &= 6 \\ \zeta(4) &= \pi^4/90 \end{aligned} \quad (2.8.19)$$

so that

$$\mathcal{B}_3 = \pi^4/15. \quad (2.8.20)$$

Then the internal energy is

$$E = \frac{\pi^2 V \hbar}{15 c^3} \left(\frac{kT}{\hbar} \right)^4. \quad (2.8.21)$$

The heat capacity is found by differentiating the internal energy

$$C_V = \left. \frac{\partial E}{\partial T} \right|_V, \quad (2.8.22)$$

giving

$$C_V = \frac{4\pi^2 V k^4}{15\hbar^3 c^3} T^3. \quad (2.8.23)$$

We see that the photon heat capacity is proportional to T^3 . Also note that the heat capacity goes to zero as $T \rightarrow 0$ in conformity with the Third Law.

2.8.5 Black body radiation in one dimension – Johnson noise

We shall see that by considering black body radiation in one dimension, we can make an important connection with electrical noise, a topic that will be treated again in Chapter 5. We may regard a waveguide as a one-dimensional black body cavity, and to start with we shall imagine this waveguide to connect black body cavities at either end. We imagine the cavities and the waveguide to be at a common temperature T and we consider the equilibrium thermal radiation in the waveguide.

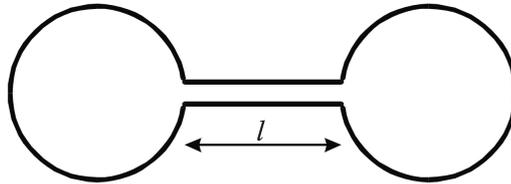


Figure 2.16: Waveguide joining two black body cavities

In a one-dimensional cavity of length l the energy density of states is given by Eq. (2.1.25):

$$g(\varepsilon) = \frac{l}{\pi} \left/ \frac{d\varepsilon}{dk} \right., \quad (2.8.24)$$

where $\varepsilon = c\hbar k$ for photons. Then the density of states is

$$g(\varepsilon) = \frac{l}{\pi c\hbar}, \quad (2.8.25)$$

independent of energy. The internal energy is then found by integrating:

$$\begin{aligned} E &= 2 \int_0^\infty \frac{\varepsilon g(\varepsilon)}{e^{\varepsilon/kT} - 1} d\varepsilon \\ &= \frac{2l}{\pi c\hbar} \int_0^\infty \frac{\varepsilon}{e^{\varepsilon/kT} - 1} d\varepsilon. \end{aligned} \quad (2.8.26)$$

We substitute $x = \varepsilon/kT$ to obtain the integral in terms of the \mathcal{B}_n integrals, Eq. (2.6.18):

$$\begin{aligned} E &= \frac{2lk^2T^2}{\pi c\hbar} \int_0^\infty \frac{x}{e^x - 1} dx \\ &= \frac{2lk^2T^2}{\pi c\hbar} \mathcal{B}_1 \end{aligned} \quad (2.8.27)$$

and since, from Eq. (2.6.19), $\mathcal{B}_1 = \Gamma(2)\zeta(2) = 1 \times \pi^2/6$ it follows that

$$E = \frac{\pi}{3} \frac{l}{c\hbar} k^2 T^2. \quad (2.8.28)$$

In the three-dimensional case we made connection with the radiation spectrum by changing variables to *angular* frequency $\omega = \varepsilon/\hbar$. However in the electrical case it is conventional to work in terms of *cyclic* frequency f ; we change variables in Eq. (2.8.26) to $f = \varepsilon/2\pi\hbar = \varepsilon/h$ so that

$$E = \frac{4lh}{c} \int_0^\infty \frac{f df}{e^{2\pi hf/kT} - 1}. \quad (2.8.29)$$

This enables us to identify the (one-dimensional) radiation spectrum $U(f, T)$ as

$$U(f, T) = \frac{4l}{c} \frac{hf}{e^{hf/kT} - 1}. \quad (2.8.30)$$

From the electrical point of view an infinitely long transmission line is equivalent to a finite transmission line terminated with its characteristic resistance. In this case the spectrum of radiation in the transmission line will

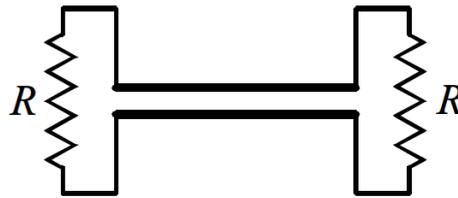


Figure 2.17: Transmission line terminated with its characteristic resistance

be the same. Thus the resistors may be regarded as emitting and absorbing the radiation. The time for the radiation to propagate along the waveguide is l/c . Thus the rate of energy flow, the power, in a frequency range Δf is given by

$$P_{\Delta f} = 4 \frac{hf}{e^{hf/kT} - 1} \Delta f. \quad (2.8.31)$$

This may be interpreted as a random current or voltage in the resistors, in a frequency range Δf , of mean square value

$$\begin{aligned}\langle V^2 \rangle_{\Delta f} &= 4R \frac{hf}{e^{hf/kT} - 1} \Delta f \\ \langle I^2 \rangle_{\Delta f} &= \frac{4}{R} \frac{hf}{e^{hf/kT} - 1} \Delta f.\end{aligned}\tag{2.8.32}$$

In the high-temperature/equipartition limit these expressions become

$$\begin{aligned}\langle V^2 \rangle_{\Delta f} &= 4kTR\Delta f \\ \langle I^2 \rangle_{\Delta f} &= \frac{4}{R}kT\Delta f,\end{aligned}\tag{2.8.33}$$

independent of h and frequency. These random voltage/current fluctuations are a consequence of the thermal motion of the current-carriers in the resistors. As we shall see in Chapter 5, this phenomenon was predicted by Einstein in 1906, observed by Johnson in 1927. The spectrum of the fluctuations was explained theoretically by Nyquist in the same year.

2.9 Ideal Paramagnet

2.9.1 Partition function and free energy

Our treatment of the ferromagnet and the paramagnet-ferromagnet transition in Chapter 4 will be based upon an extension of the conventional model for the paramagnet—that is, an assembly of non-interacting, stationary magnetic moments. For this reason we shall present, in the following few sections, a summary of the properties of the ideal paramagnet. For convenience we shall consider magnetic moments of spin $\frac{1}{2}$. This will correspond to electrons, and the treatment is simplified in that case. In a magnetic field \mathbf{B} a magnetic moment $\boldsymbol{\mu}$ will have an energy $-\boldsymbol{\mu} \cdot \mathbf{B}$. Now a spin $\frac{1}{2}$ may point either parallel or antiparallel to the applied magnetic field. Then the energy of these states will be

$$\begin{aligned}\varepsilon_{\uparrow} &= -\mu B = -\gamma \hbar B / 2 \\ \varepsilon_{\downarrow} &= +\mu B = +\gamma \hbar B / 2\end{aligned}\tag{2.9.1}$$

where γ is the magnetogyric (gyromagnetic) ratio of the moments.

The partition function Z for the entire system is

$$Z = z^N\tag{2.9.2}$$

where z is the partition function for a single one of the N spins. This is the expression for a collection of *distinguishable* identical subsystems. Although the spins themselves are certainly indistinguishable, we are considering a solid assembly where the subsystems can be distinguished by their positions. Now z is the sum over the two states

$$\begin{aligned} z &= \sum_{i=\uparrow,\downarrow} e^{-\varepsilon_i/kT} \\ &= e^{\varepsilon/kT} + e^{-\varepsilon/kT} \\ &= 2 \cosh(\varepsilon/kT) \end{aligned} \quad (2.9.3)$$

where we denote $\varepsilon = \mu B$. Then

$$Z = [2 \cosh(\varepsilon/kT)]^N \quad (2.9.4)$$

and the connection with thermodynamics is made through the expression for the (magnetic) free energy

$$F = -kT \ln Z. \quad (2.9.5)$$

Thus we have

$$F = -NkT \ln [2 \cosh(\varepsilon/kT)]. \quad (2.9.6)$$

2.9.2 Thermodynamic properties

The various thermodynamic properties are found through differentiation. The differential of F , in the magnetic case, is

$$dF = -SdT - MdB. \quad (2.9.7)$$

Magnetization and Curie's law

The magnetic moment M is given by

$$M = \left. \frac{\partial F}{\partial B} \right|_T = N\mu \tanh\left(\frac{\varepsilon}{kT}\right) \quad (2.9.8)$$

or

$$M = N\mu \tanh\left(\frac{\mu B}{kT}\right); \quad (2.9.9)$$

this is the equation of state for the paramagnet.

Fig. 2.18 shows the magnetization as a function of $\varepsilon/kT = \mu B/kT$. At small fields B we have linear behaviour but saturation sets in at higher

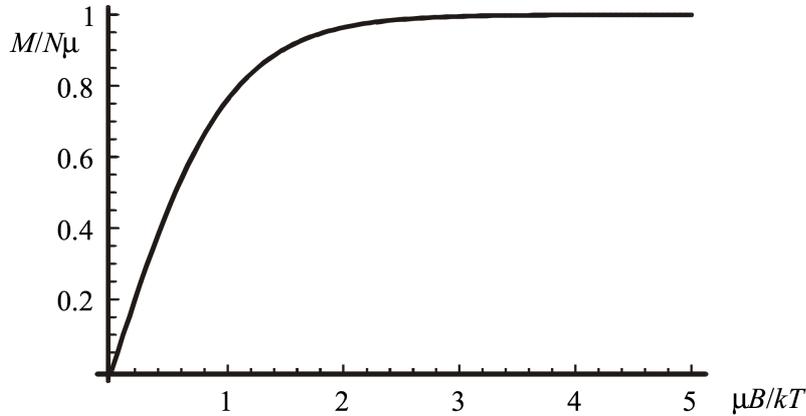


Figure 2.18: Magnetization of a paramagnet

fields/lower temperatures when the dipoles are all aligned along the field so that no more magnetisation can be created.

In the low field/high temperature limit the tanh may be expanded to first order: $\tanh x \sim x$. Then

$$M = N\mu^2 \frac{B}{kT}. \quad (2.9.10)$$

In this limit we have M proportional to B and inversely proportional to T ; this result is known as Curie's law. The magnetic susceptibility χ is

$$\chi = \frac{\mu_0 M}{V B} \quad (2.9.11)$$

(this ensures that χ is dimensionless and intensive) and then

$$\chi = \mu_0 \frac{N \mu^2}{V kT}. \quad (2.9.12)$$

One conventionally writes

$$M = C \frac{B}{T}, \quad \chi = \frac{\mu_0 C}{V} \frac{1}{T} \quad (2.9.13)$$

where C is known as the Curie constant.

Observe that Curie's law is like the ideal gas equation of state:

$$M = \text{const} \times \frac{B}{T} \quad \text{is like} \quad \frac{1}{V} = \text{const} \times \frac{p}{T}. \quad (2.9.14)$$

In this respect we may regard Curie's law as the equation of state of the ideal paramagnet.

Entropy

The other variable we find from dF is the entropy:

$$\begin{aligned} S &= - \left. \frac{\partial F}{\partial T} \right|_B \\ &= Nk \left[\ln \left\{ 2 \cosh \left(\frac{\varepsilon}{kT} \right) \right\} - \frac{\varepsilon}{kT} \tanh \left(\frac{\varepsilon}{kT} \right) \right]. \end{aligned} \quad (2.9.15)$$

This is shown as a function of temperature (kT/B). At high temperatures the entropy approaches $k \ln 2$ per particle as each moment has a choice of two states (two orientations).

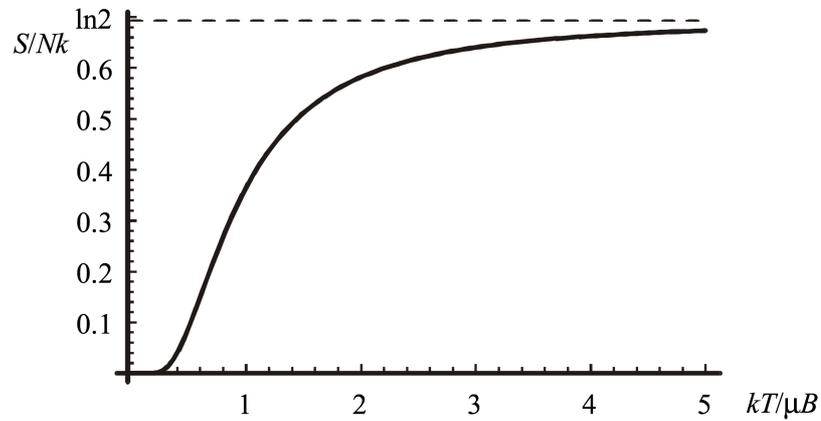


Figure 2.19: Entropy of a paramagnet

We observe that the entropy tends to zero as T/B tends to zero. When the field B is finite this indicates behaviour in accord with the Third Law. The case of zero external fields must be treated carefully, as discussed in Section 1.7.6. The reality is that there will always be internal magnetic fields present: those produced by the dipoles themselves. Thus the Third Law is safe.

Internal energy and heat capacity

The internal energy is found as

$$E = F + TS = -N\mu B \tanh \left(\frac{\mu B}{kT} \right), \quad (2.9.16)$$

which, we see, corresponds to $-MB$.

The heat capacity is given by:

$$\begin{aligned} C_B &= \left. \frac{\partial E}{\partial T} \right|_B \\ &= Nk \left(\frac{\mu B}{kT} \right)^2 \operatorname{sech}^2 \left(\frac{\mu B}{kT} \right), \end{aligned} \quad (2.9.17)$$

which we plot in Fig. 2.20.

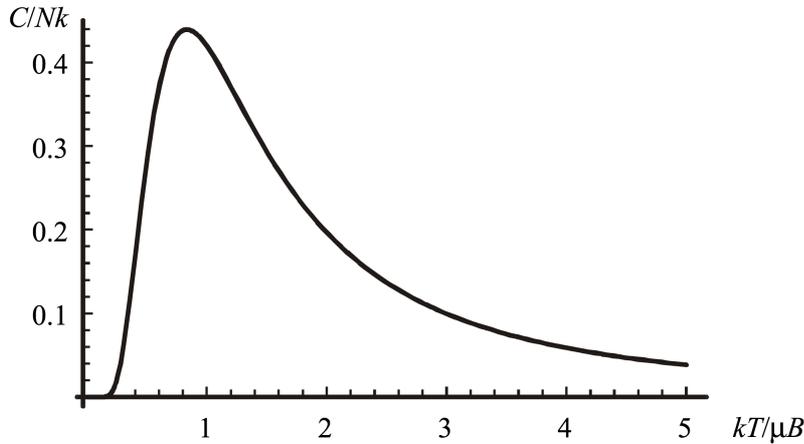


Figure 2.20: Thermal capacity of a paramagnet

The thermal capacity of the paramagnet has a characteristic peak at $kT = \mu B$. The peak is a consequence of the magnetic energy being bounded from above (unlike mechanical energy). This is known as the Schottky peak.

We conclude this section by considering the equilibrium fluctuations in the magnetisation of a paramagnet. The magnetic moment of each spin $\frac{1}{2}$ particle is plus or minus μ . The square of the magnetic moment of each particle is then μ^2 , so that the mean square magnetisation for the assembly of N particles is then

$$\langle M^2 \rangle = N\mu^2. \quad (2.9.18)$$

This may be regarded as the mean square of the fluctuations in the magnetisation from its mean value of zero. This may be related to the Curie law susceptibility in Eq. (2.9.12), thus

$$\chi = \mu_0 \frac{1}{VkT} \langle M^2 \rangle. \quad (2.9.19)$$

Here we see how the magnetisation response function, the magnetic susceptibility, is related to the equilibrium fluctuations in the magnetisation. This

is analogous to our result of Section 1.4.6 where we saw that the heat capacity (energy response function) was related to the equilibrium fluctuations in the energy. Indeed these are both special cases of the *fluctuation-dissipation* theorem, which we will encounter in Chapter 5.

2.9.3 Negative temperatures

The occupation of the up state and the down state are given by the appropriate Boltzmann factors. Since, as we have seen the energies of the two states are

$$\begin{aligned}\varepsilon_{\uparrow} &= -\mu B \\ \varepsilon_{\downarrow} &= +\mu B\end{aligned}\tag{2.9.20}$$

it follows that since

$$p_{\uparrow} = e^{-\varepsilon_{\uparrow}/kT} / z \quad p_{\downarrow} = e^{-\varepsilon_{\downarrow}/kT} / z,\tag{2.9.21}$$

then the number of spins in the up and the down state are

$$N_{\uparrow} = N e^{-\varepsilon_{\uparrow}/kT} / z \quad N_{\downarrow} = N e^{-\varepsilon_{\downarrow}/kT} / z.\tag{2.9.22}$$

And then we see that the ratio of occupation of the up and down states is

$$\frac{N_{\uparrow}}{N_{\downarrow}} = e^{2\mu B/kT}.\tag{2.9.23}$$

Thus ordinarily there will be more spins in the up state than the down state; this follows since the up state has a lower energy than the down state.

It is clear that by pumping energy into this system, we will flip spins from the lower energy “up” state to the higher energy “down” state. And we can conceive of pumping energy in, in this way until the populations of the two states becomes equalised. Moreover we could continue to pump even more energy into the system so that there are more spins in the (higher energy) down state than the (lower energy) up state. This would be a strange configuration for our system, but in the interests of simplicity we could still apply Eq. (2.9.23) to describe it. In particular we could use this equation to specify the temperature of our system. Then we would reach the following conclusions:

1. The “normal” situation, where the occupation of the lower energy state is higher than the occupation of the upper energy state corresponds to a situation where the temperature is a positive quantity.

2. When the populations of the two states are equalised, this corresponds to an *infinite* temperature.
3. When the occupation of the higher energy state is higher than the occupation of the lower energy state the system would have a *negative* temperature.

Things become clearer when we plot the resultant temperature against the population ratio. We observe that there is a linear relation between *inverse* temperature and the logarithm of the population ratios. So in this context the inverse temperature is a more natural variable to use. In the figure we see that starting at large occupation of the up state corresponds to a low (positive) temperature — far right hand side. Then feeding energy in, so that the up state occupation decreases, the temperature increases — moving to the left. The temperature diverges to plus infinity as the populations equalise. And then with greater occupation of the down state, the temperature returns from minus infinity and then it increases towards zero from the negative side.

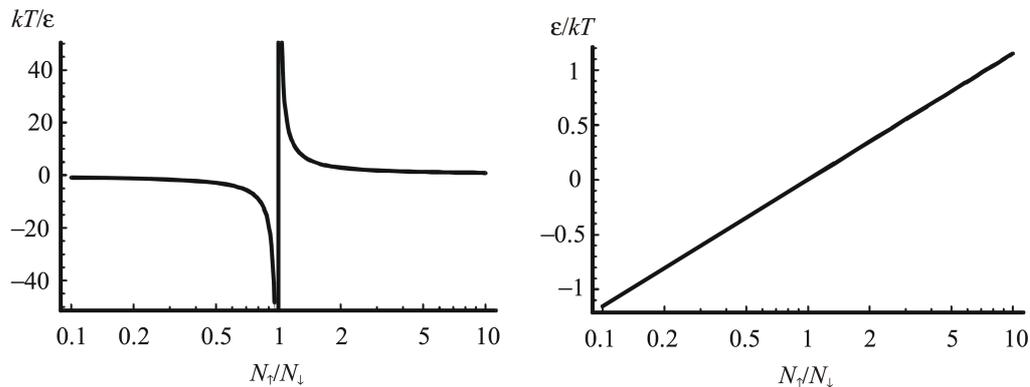


Figure 2.21: Temperature and inverse temperature as a function of population ratio

It may be argued that the discussion justifying the concept of negative temperatures is somewhat artificial. It relies upon inversion of the Boltzmann factor expression for the population probabilities. Now the Boltzmann factor $\exp -\epsilon/kT$ gives the population probabilities for a system in thermal equilibrium at a temperature T . But to what extent can we regard the states discussed in the section above as being in thermal equilibrium?

We were able to sidestep this question in the introductory discussion through restricting the consideration to spin $\frac{1}{2}$ particles where each has the

choice of two orientations. Then any values for N_{\uparrow} and N_{\downarrow} will give a temperature value through Eq. (2.9.12). The situation is different, however, for spins $S > 1/2$. If there are more than two possible spin states then only specific numbers of particles occupying the different states will correspond to the Boltzmann distribution and thus to states of thermal equilibrium.

As an example, consider the case of $S = 1$, where there are three spin orientations: $S_z = -1, 0$ and $+1$. The energies of these states, in a magnetic field B , are

$$\begin{aligned}\varepsilon_1 &= -\mu B \\ \varepsilon_0 &= 0 \\ \varepsilon_{-1} &= +\mu B\end{aligned}\tag{2.9.24}$$

so that the populations of the three states will be

$$\begin{aligned}N_1 &= Ne^{\mu B/kT}/z \\ N_0 &= N/z \\ N_{-1} &= Ne^{-\mu B/kT}/z.\end{aligned}\tag{2.9.25}$$

And only when the populations obey a relation such as this, can one ascribe a temperature to the system.

If we use the ratio N_1/N_{-1} as the independent variable (by analogy with the spin $1/2$ case) then in this case we have the supplementary condition $N_0 = \sqrt{N_1 N_{-1}}$. Only when this is satisfied, will the system be in thermal equilibrium and we can ascribe a temperature to it. In real systems the (small) interactions between the spins will be such to establish this thermal equilibrium. We will return to this point at the end of the next section.

2.9.4 Thermodynamics of negative temperatures

The thermodynamic definition of temperature, from the First Law, is given by

$$\frac{1}{T} = \frac{\partial S}{\partial E}.\tag{2.9.26}$$

Now in “normal” systems, the entropy is a monotonically increasing function of the energy. In this case the derivative will be positive and so negative temperatures will not arise. We see that to have a negative temperature the entropy must be a *decreasing* function of the energy. This is possible with a spin system.

At the lowest energy all spins will be in their lowest energy state; all spins in the same state then means low (zero) entropy. Then as the energy increases, an increasing number of spins will be promoted to the higher state.

Here the disorder is increasing and so the entropy is increasing. With sufficient energy the populations will become equalised; this corresponds to the maximum entropy possible. And then as the energy continues to increase, an increasing number of spins will find themselves in the higher energy state. Finally, at the maximal energy, all spins will be in the higher energy state and the entropy once again will become zero. This behaviour is shown in Fig. 2.22; we now calculate this.

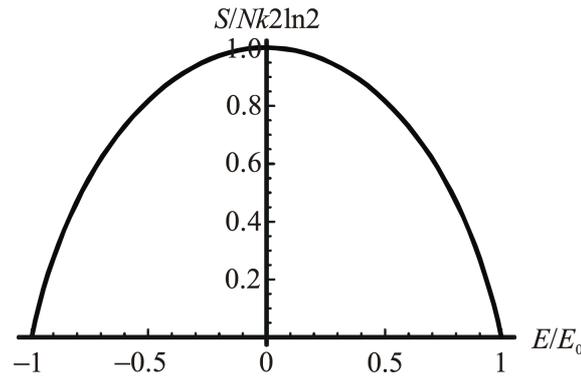


Figure 2.22: Entropy of a spin $\frac{1}{2}$ paramagnet as a function of energy

The entropy is most conveniently expressed in terms of the Gibbs expression

$$S = -Nk \sum_j p_j \ln p_j \quad (2.9.27)$$

where the p_j are the probabilities of the single-particle states. Restricting our discussion to the spin $\frac{1}{2}$ case, there are two states to consider:

$$S = -Nk \{p_{\uparrow} \ln p_{\uparrow} + p_{\downarrow} \ln p_{\downarrow}\}. \quad (2.9.28)$$

These probabilities may be expressed in terms of the magnetisation as

$$p_{\uparrow} = \frac{1 + M/N\mu}{2}, \quad p_{\downarrow} = \frac{1 - M/N\mu}{2}, \quad (2.9.29)$$

or, since the energy is given by $E = -MB$,

$$p_{\uparrow} = \frac{1 - E/E_0}{2}, \quad p_{\downarrow} = \frac{1 + E/E_0}{2} \quad (2.9.30)$$

where E_0 is the energy corresponding to the saturation magnetisation: $E_0 = N\mu B$. Thus the entropy is given by

$$S = \frac{Nk}{2} \left\{ 2 \ln 2 - \left(1 + \frac{E}{E_0}\right) \ln \left(1 + \frac{E}{E_0}\right) - \left(1 - \frac{E}{E_0}\right) \ln \left(1 - \frac{E}{E_0}\right) \right\}. \quad (2.9.31)$$

This is shown in Fig. 2.22. For $-E_0 < E < 0$ we have $\partial S/\partial E > 0$ so the temperature is positive. When $E = E_0$ we have $\partial S/\partial E = 0$ so here the temperature is infinite. And when $0 < E < E_0$ we have $\partial S/\partial E < 0$ so now the temperature is negative.

It should be appreciated that a fundamental requirement for the existence of negative temperatures is that the system's energy must be bounded from above.

In the previous section we showed the heat capacity of the paramagnet for positive temperatures. The same expression holds for negative temperatures. Thus we obtain the heat capacity shown in Fig. 2.23. Note that the heat capacity remains positive at negative temperatures. This ensures stability of the system.

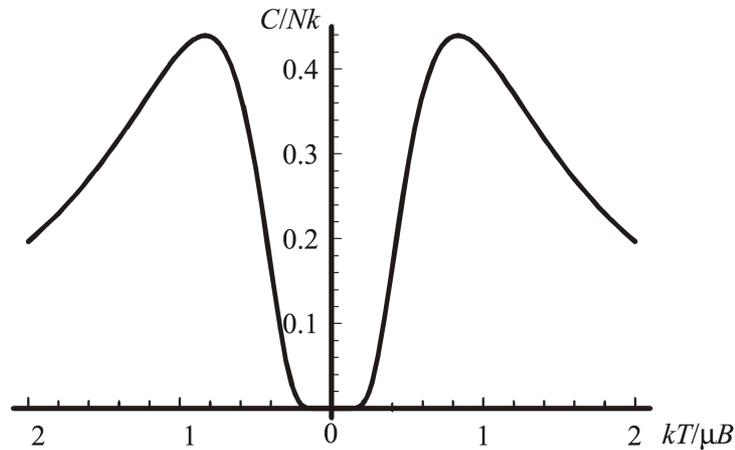


Figure 2.23: Heat capacity of a paramagnet at positive and negative temperatures

We finish this section with some general comments about negative temperature states. Since a fundamental requirement for states of negative temperature is that the energy must be bounded from above, this means that in any real system the degree of freedom with such bounded energy states must be thermally isolated from the normal (unbounded) degrees of freedom. Then the negative temperature applies to the subsystem and it is, in reality, quasi-equilibrium state.

Such quasi-equilibrium states are of interest only to the extent that they are reasonably long-lived. And they are only meaningful to the extent that the quasi-equilibrium state is established on a timescale much shorter than this. The first observations of negative temperatures were in the nuclear spins of lithium in LiF crystals [17]. There the relaxation time for the interaction between the spin degrees of freedom and the normal degrees of freedom was

of the order of five minutes while the internal equilibrium of the Li nuclear spins was established in less than 10^{-5} second.

2.10 Fermi gas magnetic susceptibility

Not sure if this will be included – but certainly not *here*.

The number of particles in a Fermi gas is given by Eq. (2.4.2)

$$N = \int_0^\infty \alpha n(\varepsilon)g(\varepsilon)d\varepsilon \quad (2.10.1)$$

where α is the spin degeneracy factor.

For spins $1/2$ there are two spin orientations, which we denote by \uparrow and \downarrow . Then if we count the number of up and down spins separately we will have

$$\begin{aligned} N_\uparrow &= \int_0^\infty n(\varepsilon)g(\varepsilon)d\varepsilon \\ N_\downarrow &= \int_0^\infty n(\varepsilon)g(\varepsilon)d\varepsilon \end{aligned} \quad (2.10.2)$$

where here $\alpha = 1$ as in each case we consider a *single* spin species. This is done in the absence of a magnetic field so the energy states do not depend on spin orientation: thus $N_\uparrow = N_\downarrow$. Note $N_\uparrow + N_\downarrow = N$ as required.

Now if we apply a magnetic field the energy states *will* depend on spin orientation. Then N_\uparrow will be different from N_\downarrow and there will be a resultant magnetization.

2.10.1 Magnetization at zero temperature

At zero temperature the Fermi-Dirac distribution $n(\varepsilon)$ is a box function cutting off at $\varepsilon = \varepsilon_F$ (Fig. 2.4). In zero magnetic field Eq. (2.10.2) becomes

$$\begin{aligned} N_\uparrow &= \int_0^{\varepsilon_F} g(\varepsilon)d\varepsilon \\ N_\downarrow &= \int_0^{\varepsilon_F} g(\varepsilon)d\varepsilon. \end{aligned} \quad (2.10.3)$$

But in an applied field the Fermi levels of the up and down spins will be shifted, up and down by mB (Use m for magnetic moment – makes more sense). Let us use ε_F to denote the Fermi energy in the absence of a magnetic

field. Then in the presence of a magnetic field Eq. (2.10.3) becomes

$$\begin{aligned} N_{\uparrow} &= \int_0^{\varepsilon_F + mB} g(\varepsilon) d\varepsilon \\ N_{\downarrow} &= \int_0^{\varepsilon_F - mB} g(\varepsilon) d\varepsilon. \end{aligned} \quad (2.10.4)$$

So now $N_{\uparrow} \neq N_{\downarrow}$ and there will be a net magnetization.

We shall split the integrals into two parts: the integral from $\varepsilon = 0$ to $\varepsilon = \varepsilon_F$ and that from $\varepsilon = \varepsilon_F$ to $\varepsilon = \varepsilon_F \pm mB$. And then since $mB \ll \varepsilon_F$ we can approximate this part by $\pm mB g(\varepsilon_F)$ so that

$$\begin{aligned} N_{\uparrow} &= \int_0^{\varepsilon_F} g(\varepsilon) d\varepsilon + mB g(\varepsilon_F) \\ N_{\downarrow} &= \int_0^{\varepsilon_F} g(\varepsilon) d\varepsilon - mB g(\varepsilon_F). \end{aligned} \quad (2.10.5)$$

There is an excess of up spins:

$$N_{\uparrow} - N_{\downarrow} = 2mB g(\varepsilon_F) \quad (2.10.6)$$

giving a magnetization

$$M = 2m^2 B g(\varepsilon_F) \quad (2.10.7)$$

corresponding to a magnetic susceptibility (Eq. (2.9.11)) of

$$\chi = \frac{\mu_0}{V} 2m^2 g(\varepsilon_F). \quad (2.10.8)$$

For non-interacting spin $\frac{1}{2}$ fermions $g(\varepsilon_F) = 3N/4\varepsilon_F$ so in the free-particle case we find

$$\chi = \mu_0 \frac{N}{V} \frac{3}{2} \frac{m^2}{\varepsilon_F}. \quad (2.10.9)$$

This corresponds to the classical (Curie law) susceptibility, Eq. (2.9.12) at a temperature $T = \frac{2}{3} T_F$.

2.11 Atoms in a harmonic trap

Some introductory text

2.11.1 Enumeration and counting of states

The energy states of a one-dimensional harmonic oscillator are given by

$$\varepsilon = (n + \frac{1}{2})\hbar\omega \quad (2.11.1)$$

where ω is the (angular) frequency of the oscillator and the quantum number n takes integer values

$$n = 0, 1, 2, \dots \quad (2.11.2)$$

We note that when $n = 0$ the oscillator is in its ground state with ground state energy $\hbar\omega/2$.

In three dimensions we will need three quantum numbers and we write the energy states of the 3d isotropic oscillator as

$$\varepsilon = (n_x + n_y + n_z + \frac{3}{2})\hbar\omega. \quad (2.11.3)$$

In this expression it is the triple of quantum numbers $\{n_x, n_y, n_z\}$ which specifies the quantum state. Now each triple defines a point on a cubic grid as in Fig. 2.24. If we put

$$n = n_x + n_y + n_z \quad (2.11.4)$$

then the energy is given by

$$\varepsilon = (n + \frac{3}{2})\hbar\omega. \quad (2.11.5)$$

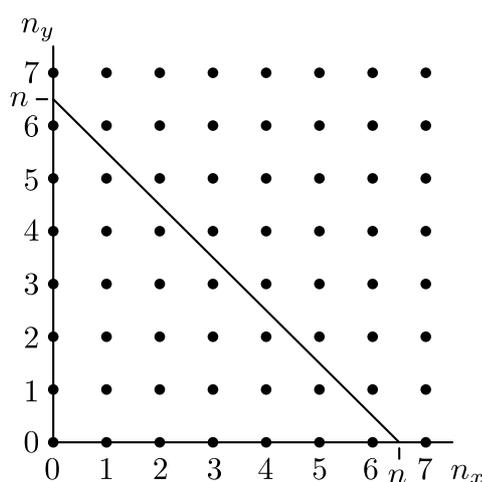


Figure 2.24: Counting of quantum states

The number of states of energy up to $\varepsilon = (n + \frac{3}{2})\hbar\omega$, denoted by $\mathcal{N}(\varepsilon)$ is given by the number of points $\{n_x, n_y, n_z\}$ satisfying

$$n_x + n_y + n_z < n. \quad (2.11.6)$$

In the 2d case this is the number of points below the sloping line. In the 3d case it will be the number of points within the oblique pyramid bounded by the x axis, the y axis, the z axis and the plane, Fig. 2.25. This is (approximately) the volume of the pyramid.

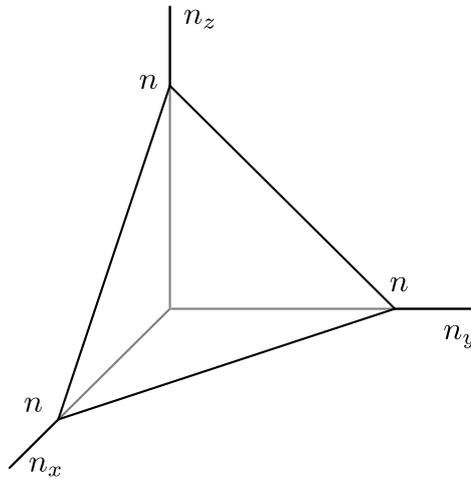


Figure 2.25: Counting of quantum states

The volume of a pyramid is given by $\frac{1}{3}$ base \times height $= \frac{1}{6}n^3$ thus

$$\begin{aligned} \mathcal{N}(\varepsilon) &= \frac{1}{6}n^3 \\ &= \frac{1}{6} \left(\frac{\varepsilon}{\hbar\omega} \right)^3. \end{aligned} \quad (2.11.7)$$

Have neglected ground state energy

The density of states $g(\varepsilon)$ is the derivative of $d\mathcal{N}/d\varepsilon$ so

$$g(\varepsilon) = \frac{1}{2} \frac{\varepsilon^2}{(\hbar\omega)^3}. \quad (2.11.8)$$

Similar calculations for 2d and 1d give

$$\begin{aligned} g(\varepsilon) &= \frac{\varepsilon}{(\hbar\omega)^2} \quad (\text{two dimensions}) \\ &= \frac{1}{\hbar\omega} \quad (\text{one dimension}). \end{aligned} \quad (2.11.9)$$

2.11.2 Fermi energy – fermions

At $T = 0$ fermions will fill up the lowest-lying energy states. So for N fermions with degeneracy factor α the highest filled state will have an energy, which we denote by ε_q , satisfying

$$N = \alpha \mathcal{N}(\varepsilon_q) \quad (2.11.10)$$

so that

$$\varepsilon_q = \left(\frac{6N}{\alpha} \right)^{1/3} \hbar\omega. \quad (2.11.11)$$

Thermodynamic limit - a bit of an idealization.