

PHYS393 – Statistical Physics

Part 5: The Bose-Einstein Distribution

Distinguishable and indistinguishable particles

In the previous parts of this course, we derived the Boltzmann distribution, which described how the number of *distinguishable* particles in different energy states varied with the energy of those states, at different temperatures:

$$n_j = \frac{N}{Z} e^{-\frac{\varepsilon_j}{kT}}. \quad (1)$$

However, in systems consisting of collections of identical fermions or identical bosons, the wave function of the system has to be either antisymmetric (for fermions) or symmetric (for bosons) under interchange of any two particles. With the allowed wave functions, it is no longer possible to identify a particular particle with a particular energy state. Instead, all the particles are “shared” between the occupied states. The particles are said to be *indistinguishable*.

In the case of indistinguishable fermions, the wave function for the overall system must be antisymmetric under the interchange of any two particles. One consequence of this is the Pauli exclusion principle: any given state can be occupied by at most one particle (though we can't say which particle!)

For example, for a system of two fermions, a possible wave function might be:

$$\psi(x_1, x_2) = \frac{1}{\sqrt{2}} [\psi_A(x_1)\psi_B(x_2) - \psi_A(x_2)\psi_B(x_1)]. \quad (2)$$

Here, x_1 and x_2 are the coordinates of the two particles, and A and B are the two occupied states. If we try to put the two particles into the same state, then the wave function vanishes.

Finding the distribution with the maximum number of microstates for a system of identical fermions leads to the Fermi-Dirac distribution:

$$n_i = \frac{g_i}{e^{\frac{\varepsilon_i - \mu}{kT}} + 1}. \quad (3)$$

Here, n_i is the number of particles with energy ε_i ; g_i is the degeneracy of the energy level (i.e. the number of distinct states with energy ε_i); k is Boltzmann's constant; and T is the thermodynamic temperature. The function $\mu(T)$ is known as the chemical potential, and is determined from the condition:

$$\sum_i n_i = N, \quad (4)$$

where N is the total number of fermions in the system.

Since $e^x \geq 0$ (for real values of the variable x), we find that for all values of ε_i and T :

$$\frac{n_i}{g_i} = \frac{1}{e^{\frac{\varepsilon_i - \mu}{kT}} + 1} \leq 1, \quad (5)$$

This tells us that the number of fermions with energy ε_i must be less than or equal to the number of states g_i with that energy. This is another statement of the Pauli exclusion principle.

Indistinguishable bosons

The wave function for a system of identical bosons must be symmetric with respect to the interchange of any two of the bosons. For example, with two bosons, a possible wave function might be:

$$\psi(x_1, x_2) = \frac{1}{\sqrt{2}} [\psi_A(x_1)\psi_B(x_2) + \psi_A(x_2)\psi_B(x_1)]. \quad (6)$$

This time, if we put two particles into the same state, the wave function does not vanish: there is no limit on the number of particles we can put into any given state.

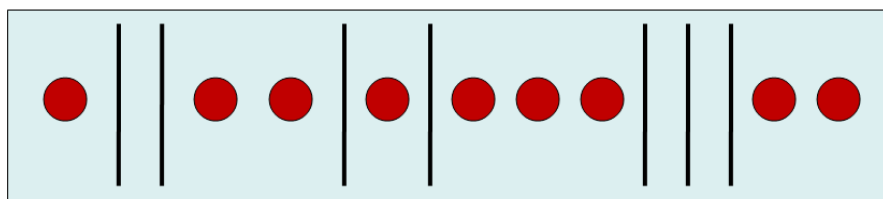
The Pauli exclusion principle does not apply to bosons: and this implies that the Fermi-Dirac distribution does not apply either, since the Pauli exclusion principle follows from the Fermi-Dirac distribution.

In this part of the lecture course, we shall derive the Bose-Einstein distribution for a system of indistinguishable bosons, and apply the distribution to three cases:

- the Bose-Einstein gas;
- a collection of photons;
- the vibrations of particles in a solid.

To find a distribution function to describe systems of bosons, we shall follow the same procedure that we did for distinguishable particles, and for indistinguishable fermions. That is, we write down the number of microstates for the possible distributions, subject to constraints determined by the macrostate specifications. Then we look for the distribution with the largest number of microstates: applying the principle of equal a priori probabilities, this distribution is more likely to occur than any other.

Consider an energy level ε_i with degeneracy g_i , containing n_i bosons. The states may be represented by $g_i - 1$ lines, and the bosons by n_i circles; distinguishable microstates correspond to different orderings of the lines and circles. For example, with 9 particles in 8 states corresponding to a particular energy, a particular microstate might be:



The number of *distinct* orderings of lines and circles is:

$$t_i = \frac{(n_i + g_i - 1)!}{n_i!(g_i - 1)!}. \quad (7)$$

A particular distribution has a specified number of particles n_i within each of the possible energy levels ε_i . The total number of microstates for a given distribution is therefore:

$$t(\{n_i\}) = \prod_i \frac{(n_i + g_i - 1)!}{n_i!(g_i - 1)!}. \quad (8)$$

Let us assume that each state has a high degeneracy, i.e. $g_i \gg 1$. Then we can make the approximation:

$$t(\{n_i\}) \approx \prod_i \frac{(n_i + g_i)!}{n_i!g_i!}. \quad (9)$$

To find the most probable distribution, we follow the same procedure as for the Boltzmann and the Fermi-Dirac distributions. That is, we maximise (9):

$$t(\{n_i\}) = \prod_i \frac{(n_i + g_i)!}{n_i!g_i!},$$

subject to the constraint on the total number of particles:

$$\sum_i n_i = N, \quad (10)$$

and the constraint on the total energy:

$$\sum_i \varepsilon_i n_i = U. \quad (11)$$

As usual, rather than maximise t directly, we maximise $\ln t$. If we assume that both g_i and n_i are large enough for Stirling's approximation to hold for $\ln g_i!$ and $\ln n_i!$, we find that $\ln t$ is given by:

$$\ln t \approx \sum_i [(n_i + g_i) \ln (n_i + g_i) - g_i \ln g_i - n_i \ln n_i]. \quad (12)$$

The change in $\ln t$ resulting from changes dn_i in each of the populations n_i is then:

$$d \ln t \approx \sum_i [\ln(n_i + g_i) dn_i - \ln n_i dn_i]. \quad (13)$$

From the constraints (10) and (11), we find:

$$\sum_i dn_i = 0, \quad \sum_i \varepsilon_i dn_i = 0. \quad (14)$$

Combining (13) and (14) with Lagrange multipliers α and β , we have:

$$d \ln t \approx \sum_i \left[\ln \left(\frac{n_i + g_i}{n_i} \right) + \alpha + \beta \varepsilon_i \right] dn_i. \quad (15)$$

For appropriate values of α and β , equation (15) is true for all dn_i , hence:

$$\ln \left(\frac{n_i + g_i}{n_i} \right) + \alpha + \beta \varepsilon_i = 0. \quad (16)$$

We then find that the most probable distribution can be written:

$$n_i = \frac{g_i}{e^{-\alpha - \beta \varepsilon_i} - 1}. \quad (17)$$

Equation (17) is the Bose-Einstein distribution. It gives the population of an energy level that has energy ε_i and degeneracy g_i . The constants α and β are determined from the constraints (10) and (11) on the total number of particles and the total energy. β can, as usual, be related to the thermodynamic temperature, so that the Bose-Einstein distribution takes the form:

$$n_i = \frac{g_i}{Be^{\frac{\varepsilon_i}{kT}} - 1}. \quad (18)$$

We have now completed our collection of three distributions. First, a collection of distinguishable particles follows the Boltzmann distribution:

$$n_j = \frac{N}{Z} e^{-\frac{\varepsilon_j}{kT}}. \quad (19)$$

Note that j indexes particle *states*, not energy levels.

Then, for a collection of indistinguishable fermions, we found the Fermi-Dirac distribution:

$$n_i = \frac{g_i}{e^{\frac{\varepsilon_i - \mu}{kT}} + 1}. \quad (20)$$

In this case, i indexes energy *levels*, not individual states.

Finally, we found the Bose-Einstein distribution for a collection of indistinguishable bosons (18):

$$n_i = \frac{g_i}{Be^{\frac{\varepsilon_i}{kT}} - 1}.$$

Fermions and bosons

The formulas for the Fermi-Dirac distribution (20):

$$n_i = \frac{g_i}{e^{\frac{\varepsilon_i - \mu}{kT}} + 1}$$

and the Bose-Einstein distribution (18):

$$n_i = \frac{g_i}{Be^{\frac{\varepsilon_i}{kT}} - 1}.$$

appear very similar. However, the difference in sign in the denominator is critical. Since $e^x > 0$ for all x , for the Fermi-Dirac distribution, we always have $n_i < g_i$; in other words, fermions always obey the Pauli exclusion principle.

But for bosons, it is possible to have $n_i \gg g_i$, if $\varepsilon_i \ll kT$, and $B \approx 1$. In other words, it is possible for many identical bosons to exist in the same state.

When we derived the Fermi-Dirac distribution, we showed that for systems with low density, the distribution could be closely approximated by the Boltzmann distribution. Using the same reasoning, we can show that this is also the case for the Bose-Einstein distribution.

We write the Bose-Einstein distribution (18) in the form:

$$\frac{n_i}{g_i} = \frac{1}{Be^{\frac{\epsilon_i}{kT}} - 1}. \quad (21)$$

If $n_i \ll g_i$, then $n_i/g_i \ll 1$, which implies that:

$$Be^{\frac{\epsilon_i}{kT}} - 1 \gg 1, \quad (22)$$

so we can approximate:

$$Be^{\frac{\epsilon_i}{kT}} - 1 \approx Be^{\frac{\epsilon_i}{kT}}. \quad (23)$$

We then have:

$$n_i \approx \frac{g_i}{B} e^{-\frac{\epsilon_i}{kT}}. \quad (24)$$

The Bose-Einstein gas

As an example of the Bose-Einstein distribution, let us consider a boson gas. This consists of a large number of identical bosons in a box with rigid walls and fixed volume. The bosons are free to move within the box, but cannot move beyond its walls. Bosons exchange energy in occasional collisions with each other. For simplicity, we assume that the bosons have spin zero, so there is no degeneracy associated with different spin states.

Let us first consider the behaviour of the constant B that appears in the expression for the Bose-Einstein distribution. This quantity corresponds to the partition function in the Boltzmann distribution, or the chemical potential in the Fermi-Dirac distribution. B is determined by the constraint:

$$\sum_i n_i = N, \quad (25)$$

where N is the total number of particles. Let us find how B depends on temperature.

From our previous analysis of the Maxwell-Boltzmann gas and the Fermi gas, the density of states for spin-0 particles moving freely in a box of volume V is:

$$g(\varepsilon) = \frac{V}{4\pi^2} \left(\frac{2m}{\hbar^2} \right)^{\frac{3}{2}} \sqrt{\varepsilon}. \quad (26)$$

Let us assume that we can replace a summation over discrete energy levels by an integration over a continuum of energy levels. Then the constraint (25) becomes:

$$\sum_i n_i \approx \int_0^\infty n(\varepsilon) d\varepsilon = N. \quad (27)$$

Using the Bose-Einstein distribution (18) and the density of states (26), this becomes:

$$\frac{V}{4\pi^2} \left(\frac{2m}{\hbar^2} \right)^{\frac{3}{2}} \int_0^\infty \frac{\sqrt{\varepsilon}}{Be^{\frac{\varepsilon}{kT}} - 1} d\varepsilon = N. \quad (28)$$

The Bose-Einstein gas

To simplify things a little, we define a new variable, y , such that:

$$y = \frac{\varepsilon}{kT}. \quad (29)$$

In terms of y , the equation for B becomes:

$$\frac{V}{4\pi^2} \left(\frac{2mkT}{\hbar^2} \right)^{\frac{3}{2}} \int_0^\infty \frac{\sqrt{y} dy}{Be^y - 1} = N. \quad (30)$$

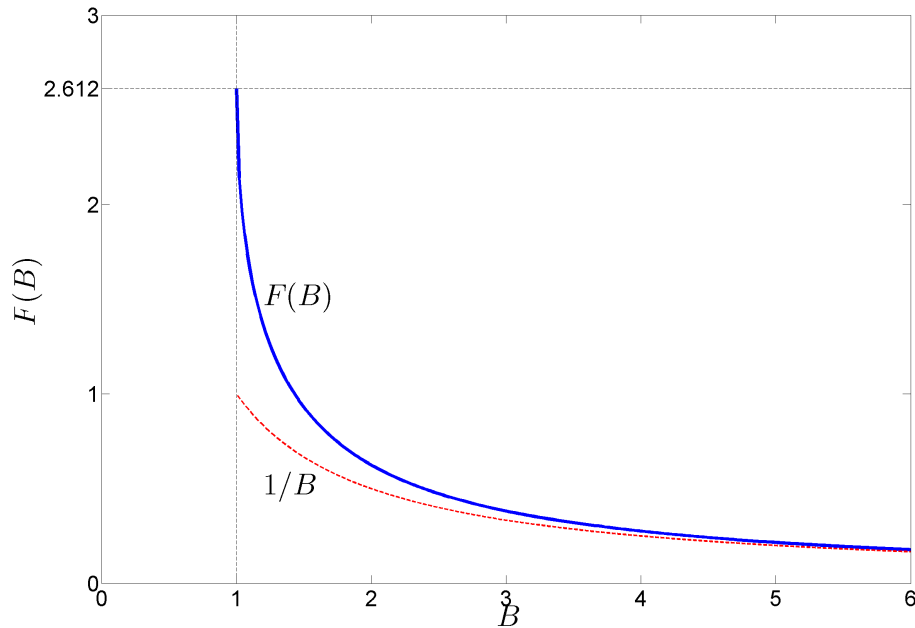
We define the function $F(B)$:

$$F(B) = \frac{2}{\sqrt{\pi}} \int_0^\infty \frac{\sqrt{y} dy}{Be^y - 1}. \quad (31)$$

In terms of $F(B)$, the equation for B becomes:

$$V \left(\frac{mkT}{2\pi\hbar^2} \right)^{\frac{3}{2}} F(B) = N. \quad (32)$$

To understand the function $F(B)$, let us draw a graph of it:



For large B , we see that $F(B) \approx 1/B$. This is because, for $B \gg 1$, we can write:

$$\frac{2}{\sqrt{\pi}} \int_0^\infty \frac{\sqrt{y} dy}{Be^y - 1} \approx \frac{2}{\sqrt{\pi}} \int_0^\infty \frac{\sqrt{y} dy}{Be^y} = \frac{1}{B}. \quad (33)$$

Thus, from equation (32):

$$V \left(\frac{mkT}{2\pi\hbar^2} \right)^{\frac{3}{2}} F(B) = N,$$

we find that, for large B (or, equivalently, for high temperature):

$$B \approx \frac{V}{N} \left(\frac{mkT}{2\pi\hbar^2} \right)^{\frac{3}{2}}. \quad (34)$$

However, we find that the integral cannot be evaluated below $B = 1$, because there is a singularity at this point. Physically, this is significant. The Bose-Einstein distribution (18) is:

$$n_i = \frac{g_i}{B e^{\frac{\varepsilon_i}{kT}} - 1}.$$

If $B < 1$, there is the possibility of an energy level ε_i such that $n_i < 0$. Clearly, we cannot have a negative number of particles in any energy level, so we expect $B \geq 1$.

We see that $F(B)$ takes a maximum value, at $B = 1$. The maximum value of $F(B)$ is given by:

$$F(1) = \frac{2}{\sqrt{\pi}} \int_0^{\infty} \frac{\sqrt{y} dy}{e^y - 1} = \zeta\left(\frac{3}{2}\right) \approx 2.612. \quad (35)$$

Here, $\zeta(x)$ is the Riemann zeta function, defined by:

$$\zeta(x) = \sum_{n=1}^{\infty} \frac{1}{n^x}. \quad (36)$$

The fact that $F(B)$ has a maximum value of $F(1) \approx 2.612$ is somewhat disturbing. It is disturbing because, since N is constant, we expect from equation (32):

$$V \left(\frac{mkT}{2\pi\hbar^2} \right)^{\frac{3}{2}} F(B) = N,$$

that as the temperature goes down, $F(B)$ has to go up.

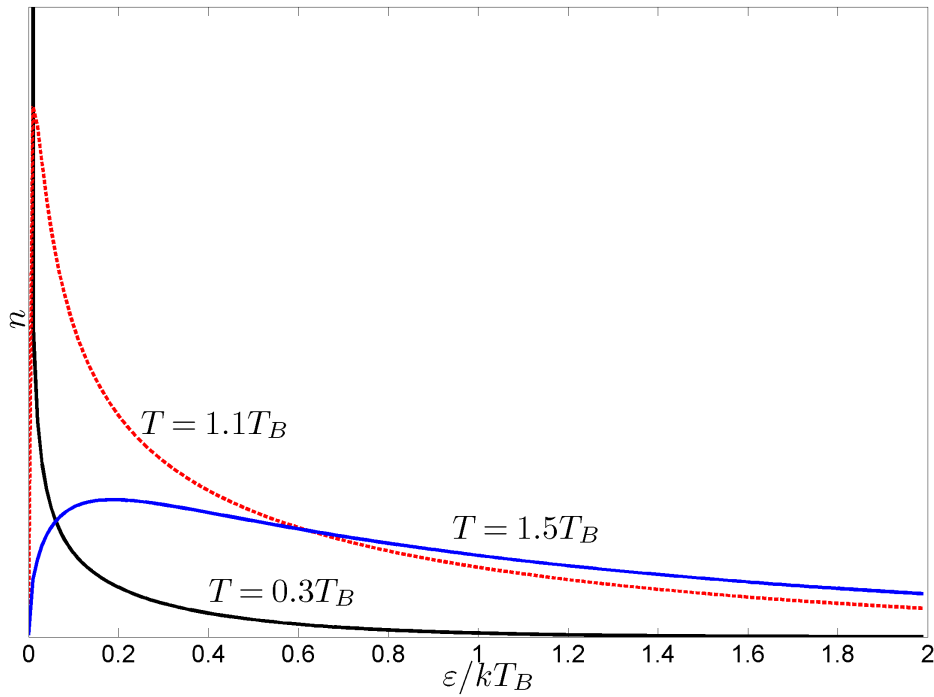
But if $F(B)$ has a finite maximum, then below some temperature T_B , the number of particles we find by integrating the Bose-Einstein distribution over all energies is less than N , the number of particles in the system:

$$\text{if } T < T_B, \text{ then } \frac{V}{4\pi^2} \left(\frac{2mkT}{\hbar^2} \right)^{\frac{3}{2}} \int_0^\infty \frac{\sqrt{y} dy}{Be^y - 1} < N \quad \text{for all } B.$$

The situation becomes clear if we plot the population density $n(\varepsilon)$ as a function of energy ε , for several different temperatures.

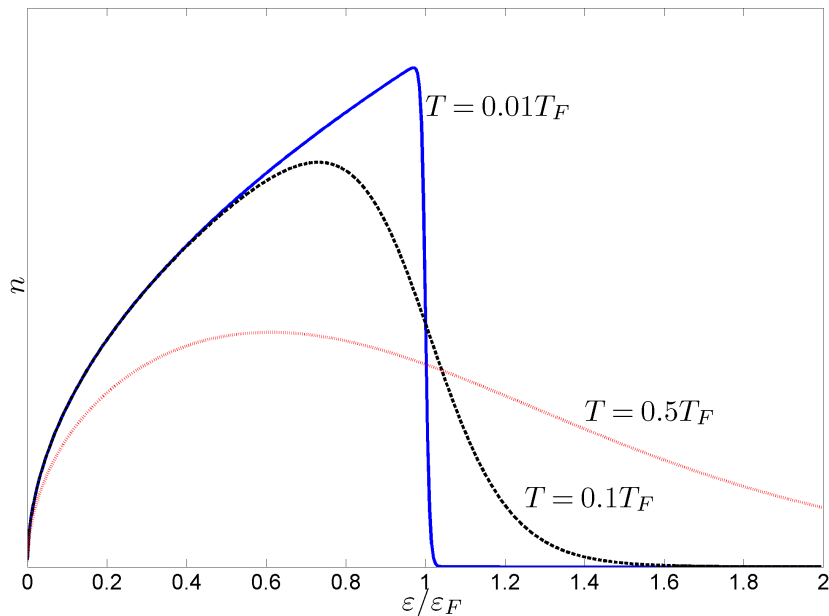
For $T > T_B$, we see a smooth distribution curve that, for high temperatures, approaches the distribution expected for a Maxwell-Boltzmann gas. The area under the curves for $T > T_B$ are independent of the temperature T .

For $T < T_B$, strictly speaking we cannot evaluate the population density, since we don't have a solution for the parameter B . If we do the best we can, and set $B = 1$ for $T < T_B$, we find a distribution that is sharply peaked at low energy: but the peak is not high enough for the area under the curve to give the correct result for the number of particles in the system.



Reminder: the Fermi gas population distribution

Compare the population distribution for the Bose-Einstein gas with that for a Fermi gas. The population distribution for a Fermi gas is well-behaved even in the limit of low temperature, $T \rightarrow 0$.



The temperature T_B at which particles start to “disappear” is given by:

$$V \left(\frac{mkT_B}{2\pi\hbar^2} \right)^{\frac{3}{2}} \zeta\left(\frac{3}{2}\right) = N, \quad (37)$$

that is:

$$T_B = \frac{2\pi\hbar^2}{mk} \left(\frac{N}{\zeta\left(\frac{3}{2}\right)V} \right)^{\frac{2}{3}}. \quad (38)$$

The natural question is, where are the “missing” particles for $T < T_B$?

The answer is: in the ground state!

The problem, which we now need to rectify, is that when we replaced the summation over discrete energy levels by an integral over a continuum of energies in equation (27):

$$\sum_i n_i \approx \int_0^\infty n(\varepsilon) d\varepsilon = N.$$

we omitted the particles in the ground state.

Since the lower limit of the integral is zero, we should assume (for consistency) that the ground state has zero energy. But the distribution function $g(\varepsilon) \propto \sqrt{\varepsilon}$; so at zero energy, the density of states is zero, and the population (in the small energy range 0 to $d\varepsilon$) is also zero.

In other words, the integral in equation (27) only counts particles in the excited states, and ignores those in the ground state.

We made the same mistake when we considered the Fermi gas: but in that case, there could only be two particles in the ground state (assuming degeneracy two, for spin- $\frac{1}{2}$ particles). In other words, we omitted two particles out of a large number N , and this did not affect our conclusions. But for a Bose-Einstein gas, there is no limit to the number of particles that can fall into the ground state. So if we omit the ground state from the sum, we risk making a large error.

Our reasoning implies that at temperatures $T > T_B$, all particles are in excited states, and the ground state is essentially unoccupied. But at temperatures $T < T_B$, particles gradually fall into the ground state, which eventually, in the limit $T \rightarrow 0$, contains all the particles in the system.

The particles in the ground state for $T < T_B$ constitute a *Bose-Einstein condensation*. The temperature T_B is known as the *Bose temperature*.

Below a critical temperature T_B in a system of indistinguishable bosons, the population of the ground state in a series of quantised states becomes very large, and discontinuous with the populations of the excited states. The extra population of the ground state is the Bose-Einstein condensation.

The existence of the Bose-Einstein condensation leads to dramatic effects in systems of bosons at temperatures below the Bose temperature. These are discussed further in the part of this course covering low-temperature physics.

The population density in the *excited states* (i.e. excluding the ground state) in a Bose-Einstein gas is given by:

$$n_{ex}(\varepsilon) = \frac{V}{4\pi^2} \left(\frac{2m}{\hbar^2} \right)^{\frac{3}{2}} \frac{\sqrt{\varepsilon}}{B e^{\frac{\varepsilon}{kT}} - 1}. \quad (39)$$

The function $B(T)$ plays the role for the Bose-Einstein distribution that the chemical potential did for the Fermi-Dirac distribution. For a Bose-Einstein gas, $B(T)$ is given by:

$$B(T) = \begin{cases} 1 & \text{for } T < T_B, \\ F^{-1} \left[\zeta\left(\frac{3}{2}\right) \left(\frac{T_B}{T}\right)^{\frac{3}{2}} \right] & \text{for } T \geq T_B. \end{cases} \quad (40)$$

The function F^{-1} is the inverse of F , given by (31):

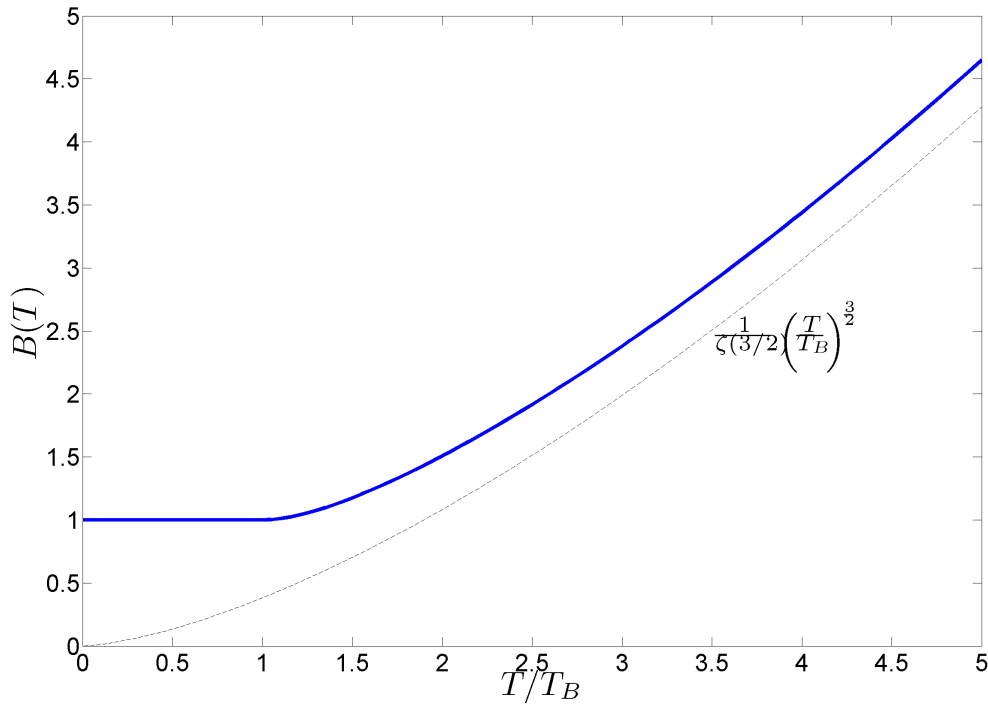
$$F(B) = \frac{2}{\sqrt{\pi}} \int_0^\infty \frac{\sqrt{y} dy}{B e^y - 1}.$$

The Bose temperature T_B is given by (38):

$$T_B = \frac{2\pi\hbar^2}{mk} \left(\frac{N}{\zeta\left(\frac{3}{2}\right) V} \right)^{\frac{2}{3}}.$$

Note that, since $F(B) \rightarrow 1/B$ as $B \rightarrow \infty$, we have:

$$B \approx \frac{1}{\zeta\left(\frac{3}{2}\right)} \left(\frac{T}{T_B} \right)^{\frac{3}{2}} \quad \text{for } T \gg T_B. \quad (41)$$



The Bose-Einstein gas: excited and ground states population

The total population N_{ex} in the excited states is, for $T < T_B$:

$$N_{ex} = \frac{V}{4\pi^2} \left(\frac{2m}{\hbar^2} \right)^{\frac{3}{2}} \int_0^\infty \frac{\sqrt{\varepsilon} d\varepsilon}{e^{\frac{\varepsilon}{kT}} - 1} \quad (42)$$

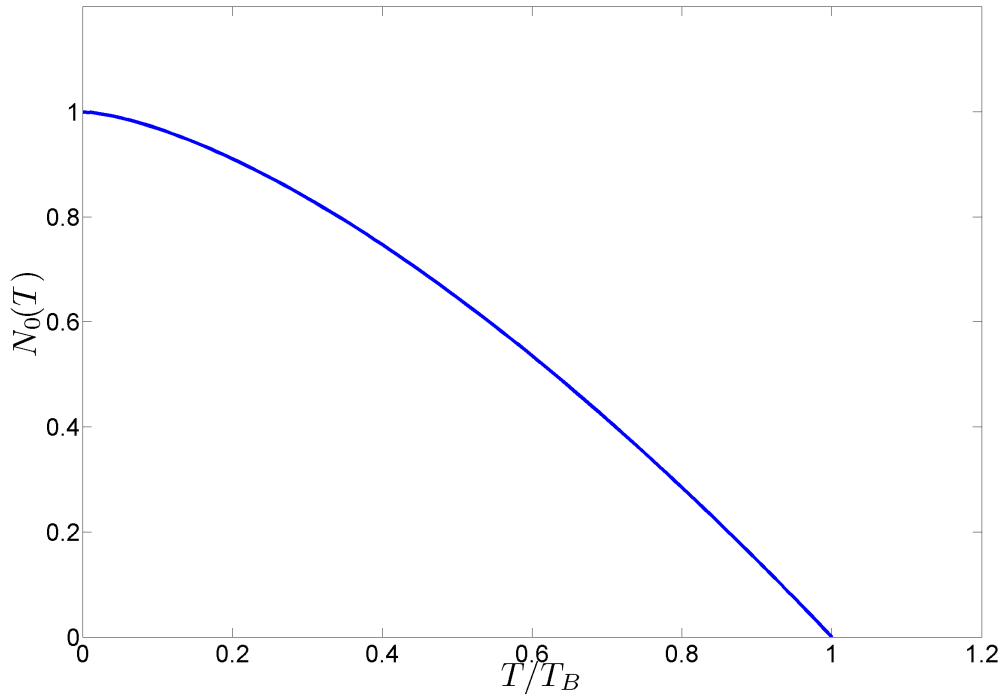
$$= \frac{V}{4\pi^2} \left(\frac{2mkT}{\hbar^2} \right)^{\frac{3}{2}} \int_0^\infty \frac{\sqrt{y} dy}{e^y - 1} \quad (43)$$

$$= V \left(\frac{mkT}{2\pi\hbar^2} \right)^{\frac{3}{2}} \zeta\left(\frac{3}{2}\right) \quad (44)$$

$$= N \left(\frac{T}{T_B} \right)^{\frac{3}{2}}. \quad (45)$$

This leaves the remaining population N_0 in the ground state:

$$N_0 = N \left[1 - \left(\frac{T}{T_B} \right)^{\frac{3}{2}} \right] \quad \text{for } T < T_B. \quad (46)$$



The Bose-Einstein gas: total energy

If we assume that the ground state is a state of zero energy, then particles in the Bose-Einstein condensation make no contribution to the total energy of the Bose-Einstein gas. The total energy U can then be written:

$$U = \int_0^\infty \varepsilon n_{ex}(\varepsilon) d\varepsilon = \frac{V}{4\pi^2} \left(\frac{2m}{\hbar^2}\right)^{\frac{3}{2}} \int_0^\infty \frac{\varepsilon^{\frac{3}{2}} d\varepsilon}{B e^{\frac{\varepsilon}{kT}} - 1}, \quad (47)$$

where we have used equation (39) for the density of particles in excited states n_{ex} . Changing the variable of integration, the total energy can be written:

$$U = \frac{V}{4\pi^2} \left(\frac{2m}{\hbar^2}\right)^{\frac{3}{2}} (kT)^{\frac{5}{2}} \int_0^\infty \frac{y^{\frac{3}{2}} dy}{B e^y - 1}. \quad (48)$$

Finally, using equation (38) for T_B , we can express the total energy as:

$$U = \frac{2}{\sqrt{\pi} \zeta\left(\frac{3}{2}\right)} N k T \left(\frac{T}{T_B}\right)^{\frac{3}{2}} \int_0^\infty \frac{y^{\frac{3}{2}} dy}{B e^y - 1}. \quad (49)$$

At low temperature ($T < T_B$), we can take $B = 1$, and the total energy becomes:

$$\begin{aligned}
 U &= \frac{2}{\sqrt{\pi}\zeta\left(\frac{3}{2}\right)} NkT \left(\frac{T}{T_B}\right)^{\frac{3}{2}} \int_0^\infty \frac{y^{\frac{3}{2}} dy}{e^y - 1}, \\
 &= \frac{3\zeta\left(\frac{5}{2}\right)}{2\zeta\left(\frac{3}{2}\right)} NkT \left(\frac{T}{T_B}\right)^{\frac{3}{2}}, \\
 &\approx 0.770 NkT \left(\frac{T}{T_B}\right)^{\frac{3}{2}}. \tag{50}
 \end{aligned}$$

We see that at low temperature ($T < T_B$):

$$U \propto T^{\frac{5}{2}}. \tag{51}$$

At high temperatures, $B \gg 1$, we can make the approximation $B e^y - 1 \approx B e^y$:

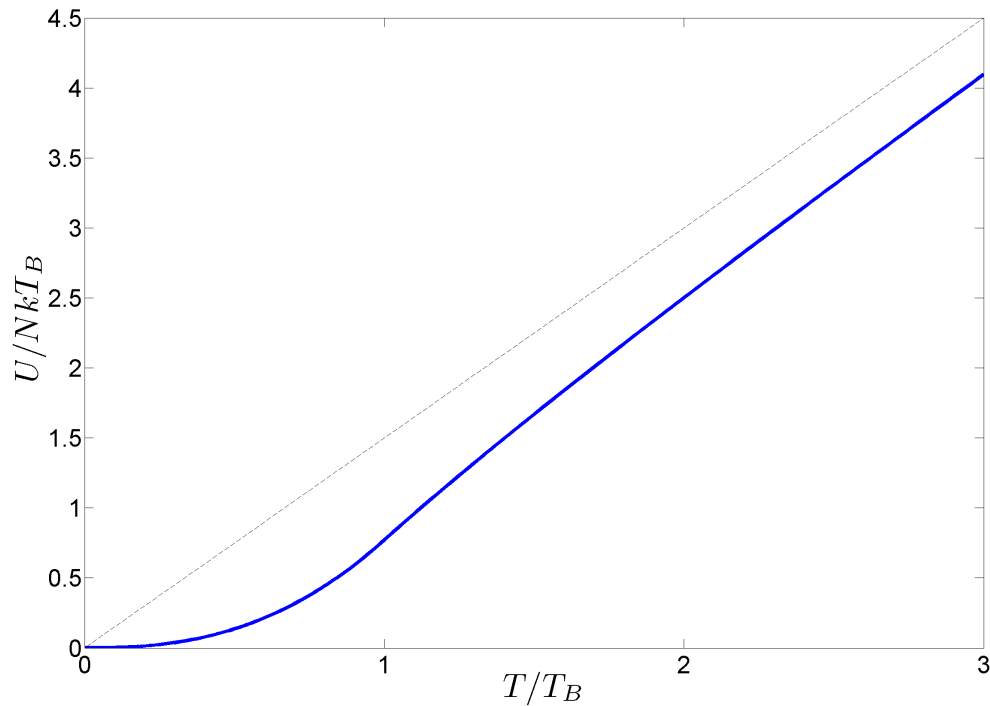
$$\begin{aligned}
 U &\approx \frac{2}{\sqrt{\pi}\zeta\left(\frac{3}{2}\right)} NkT \left(\frac{T}{T_B}\right)^{\frac{3}{2}} \frac{1}{B} \int_0^\infty \frac{y^{\frac{3}{2}} dy}{e^y}, \\
 &\approx \frac{3}{2\zeta\left(\frac{3}{2}\right)} NkT \left(\frac{T}{T_B}\right)^{\frac{3}{2}} \frac{1}{B}. \tag{52}
 \end{aligned}$$

Using (41) for B , we find:

$$U \approx \frac{3}{2} NkT. \tag{53}$$

Note that this is the same result as for the Maxwell-Boltzmann gas: as we might expect, since the Boltzmann distribution approximates the Bose-Einstein distribution at high temperature.

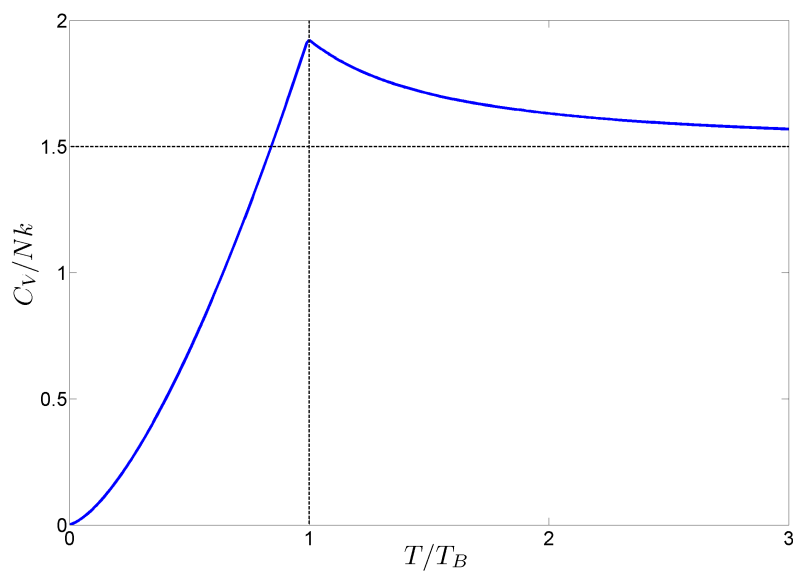
The Bose-Einstein gas: total energy



The Bose-Einstein gas: heat capacity

The heat capacity is given, as usual, by the derivative of the total energy with respect to temperature:

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V. \quad (54)$$



We turn now to the next system we shall analyse using Bose-Einstein statistics: a “gas” of photons. Photons have spin-1: they are bosons, and their statistics should therefore be described by the Bose-Einstein distribution.

However, we need to make a significant modification to our previous work. Our derivation of the Bose-Einstein distribution included the constraint (10), that the number of particles in the system was fixed:

$$\sum_i n_i = N.$$

This is appropriate for a system of charged, stable (i.e. non-decaying) bosons, such as helium-4. However, the number of photons in an enclosed space is *not* conserved: the total number of photons can change over time, as photons are absorbed by and emitted from the walls of the enclosure.

Our previous analysis included the constraint that the total number of particles was conserved; in that case, the analysis led to the Bose-Einstein distribution (17):

$$n_i = \frac{g_i}{e^{-\alpha - \beta \epsilon_i} - 1}.$$

The constraint that the total number of particles is constant can be lifted by setting $\alpha = 0$. We then find, for a system of photons, that the number of photons $n(\epsilon) d\epsilon$ in a (small) energy range ϵ to $\epsilon + d\epsilon$ is given by:

$$n(\epsilon) d\epsilon = \frac{g(\epsilon) d\epsilon}{e^{\frac{\epsilon}{kT}} - 1}. \quad (55)$$

To complete the expression for the photon energy distribution, we need an expression for the density of states $g(\varepsilon)$. Since photons in an enclosed space are subject to the same boundary conditions that we assumed in the case of the Maxwell-Boltzmann gas, we can simply use the result (from Part 3 of this lecture course):

$$g(k) dk = 2 \times 4\pi \frac{V}{(2\pi)^3} k^2 dk, \quad (56)$$

where V is the volume of the container, and the initial factor 2 comes from the fact that there are two polarisations for the photons.

Now we use the (quantum) relationship between photon energy and wave number:

$$\varepsilon = h\nu = \frac{hc}{\lambda} = hc \frac{k}{2\pi} = \hbar ck. \quad (57)$$

Since the energy is simply proportional to the wave number, we find:

$$g(\varepsilon) d\varepsilon = 8\pi \frac{V}{(2\pi)^3} \frac{\varepsilon^2}{(\hbar c)^3} d\varepsilon. \quad (58)$$

Thus, the number of photons $n(\varepsilon) d\varepsilon$ in the energy range ε to $\varepsilon + d\varepsilon$ becomes:

$$n(\varepsilon) d\varepsilon = 8\pi \frac{V}{(2\pi)^3} \frac{\varepsilon^2}{(\hbar c)^3} \frac{d\varepsilon}{e^{\frac{\varepsilon}{kT}} - 1} = \frac{8\pi V}{(hc)^3} \frac{\varepsilon^2 d\varepsilon}{e^{\frac{\varepsilon}{kT}} - 1}. \quad (59)$$

Using the previous result (59), the energy $u(\varepsilon) d\varepsilon$ in the energy range ε to $\varepsilon + d\varepsilon$ is given by:

$$u(\varepsilon) d\varepsilon = n(\varepsilon) \varepsilon d\varepsilon = \frac{8\pi V}{(hc)^3} \frac{\varepsilon^3 d\varepsilon}{e^{\frac{\varepsilon}{kT}} - 1}. \quad (60)$$

Conventionally, we write the energy density u as a function of the photon frequency ν . Since the energy and frequency are related by the quantum formula:

$$\varepsilon = h\nu, \quad (61)$$

we find that the energy density is:

$$u(\nu) d\nu = \frac{8\pi V}{h^2 c^3} \frac{(h\nu)^3 d\nu}{e^{\frac{h\nu}{kT}} - 1}. \quad (62)$$

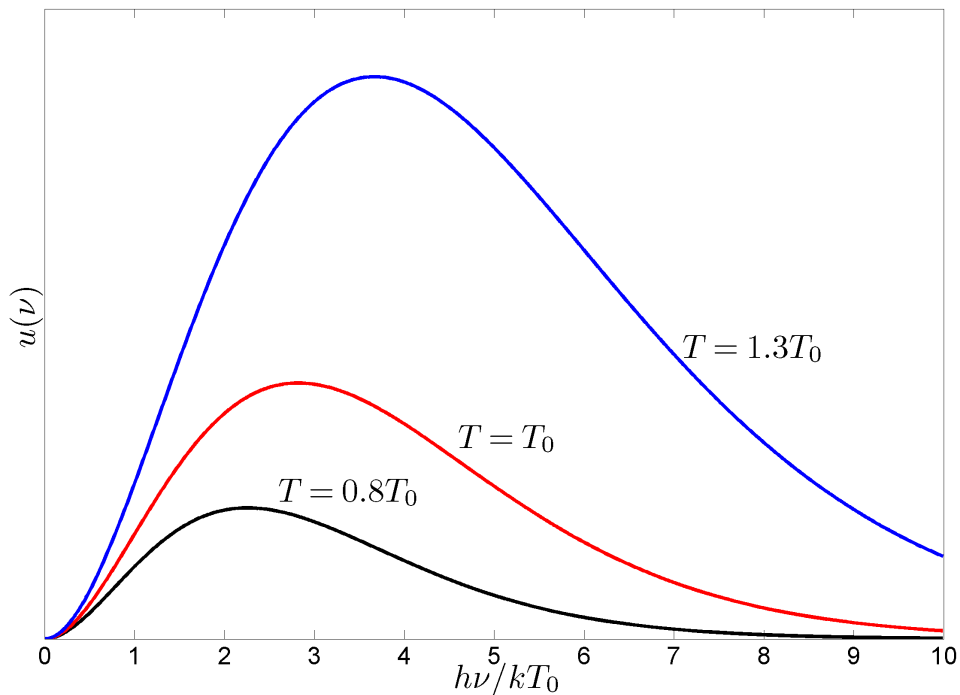
Photon energy spectrum: Planck radiation formula

The energy density in the radiation as a function of frequency and temperature is given by (62):

$$u(\nu) d\nu = \frac{8\pi V}{h^2 c^3} \frac{(h\nu)^3 d\nu}{e^{\frac{h\nu}{kT}} - 1}.$$

This is the Planck radiation formula, giving the energy spectrum of electromagnetic radiation in thermal equilibrium at temperature T .

The predictions from the formula are in excellent agreement with experimental data.



Photon energy spectrum

It is interesting to consider three features of the energy spectrum:

- the position of the peak in the spectrum;
- the total energy;
- the average photon energy.

We shall consider how each of the above quantities varies with temperature.

Let us consider first the peak in the spectrum. This occurs at:

$$\frac{du}{d\nu} = 0. \quad (63)$$

After some algebra, we find that this leads to the result that the peak occurs at:

$$\left(1 - \frac{1}{3}x\right) e^x = 1, \quad (64)$$

where $x = h\nu/kT$. The (numerical) solution gives:

$$\hat{\nu} \approx 2.82 \frac{kT}{h}, \quad (65)$$

i.e. the frequency at which the energy spectrum peaks is proportional to the temperature: this is Wien's law.

Photon energy spectrum: total energy

Now let us consider the total energy, U . This is the area under the graph of the energy spectrum, i.e.:

$$U = \int_0^\infty u(\nu) d\nu = \frac{8\pi V}{h^2 c^3} \int_0^\infty \frac{(h\nu)^3 d\nu}{e^{\frac{h\nu}{kT}} - 1}. \quad (66)$$

We define a new variable of integration:

$$y = \frac{h\nu}{kT}, \quad (67)$$

in terms of which, the expression for the total energy becomes:

$$U = \frac{8\pi V}{(hc)^3} (kT)^4 \int_0^\infty \frac{y^3 dy}{e^y - 1}. \quad (68)$$

The integral has the value $\pi^4/15$, hence:

$$U = \frac{8\pi^5}{15} \frac{V}{(hc)^3} (kT)^4. \quad (69)$$

The average photon energy is found from:

$$\bar{\varepsilon} = \frac{1}{N} \int_0^{\infty} n(\varepsilon) \varepsilon d\varepsilon, \quad (70)$$

where N is the total number of photons:

$$N = \int_0^{\infty} n(\varepsilon) d\varepsilon. \quad (71)$$

Using equation (59) for the number of photons per unit energy range:

$$n(\varepsilon) d\varepsilon = \frac{8\pi V}{(hc)^3} \frac{\varepsilon^2 d\varepsilon}{e^{\frac{\varepsilon}{kT}} - 1},$$

we find:

$$\bar{\varepsilon} = \frac{\int_0^{\infty} \frac{\varepsilon^3}{e^{\frac{\varepsilon}{kT}} - 1} d\varepsilon}{\int_0^{\infty} \frac{\varepsilon^2}{e^{\frac{\varepsilon}{kT}} - 1} d\varepsilon}. \quad (72)$$

Again defining a new variable of integration $y = \varepsilon/kT$, the average photon energy becomes:

$$\bar{\varepsilon} = \frac{\int_0^{\infty} \frac{y^3}{e^y - 1} d\varepsilon}{\int_0^{\infty} \frac{y^2}{e^y - 1} d\varepsilon} kT. \quad (73)$$

Using the results for the integrals:

$$\int_0^{\infty} \frac{y^3}{e^y - 1} d\varepsilon = \frac{\pi^4}{15}, \quad \int_0^{\infty} \frac{y^2}{e^y - 1} d\varepsilon = 2\zeta(3) \approx 2.40, \quad (74)$$

where ζ is the Riemann zeta function, we find:

$$\bar{\varepsilon} = \frac{\pi^4}{30\zeta(3)} kT \approx 2.70 \times kT. \quad (75)$$

We see that the average energy of the photons increases linearly with temperature.

We can use the spectrum of radiation in thermal equilibrium to find the radiation power from an object, as a function of the temperature of that object.

Consider an object that completely absorbs all radiation falling on it, of whatever wavelength. Such an object will appear completely black. If the object is in thermal equilibrium with a “gas” of photons at temperature T , then the object must emit as much radiation as it absorbs, and with the same spectral properties.

If the object emits either more or less radiation than it absorbs, then the energy in the radiation at some wavelength(s) will either increase or decrease; in other words, the object cannot be in equilibrium with the radiation.

Therefore, if we calculate the rate at which the object absorbs radiation, as a function of temperature, then the *same expression* gives the rate at which the object emits radiation. Since we need to assume that the object absorbs all the radiation that fall on it, we will calculate the temperature dependence of “black body” radiation.

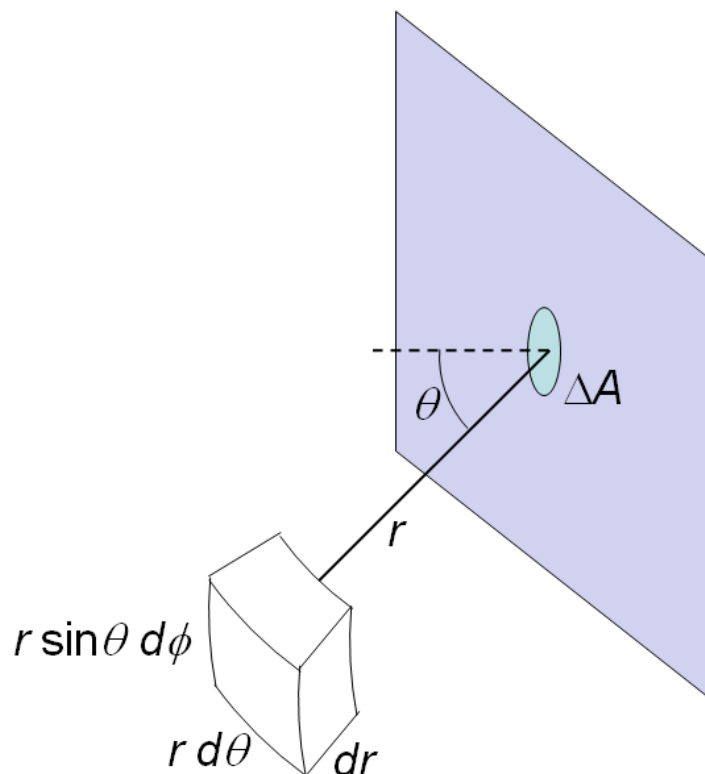
To calculate the rate at which a black body emits radiation, we consider radiation in a box of fixed volume V . The radiation is in thermal equilibrium with the box, which absorbs all the radiation that falls on it. The rate at which the inside walls emit radiation is equal to the rate at which radiation falls on the walls.

Consider a small area element ΔA on an inside wall of the box. Take the centre of this area element to be the origin of a spherical polar coordinate system. A volume element dV of the interior of the box is given by:

$$dV = r^2 \sin \theta \, dr \, d\theta \, d\phi. \quad (76)$$

If the total number of photons in the box is N , and the volume of the box is V , then the number of photons in the volume element dV will be:

$$N \frac{dV}{V} = \frac{N}{V} r^2 \sin \theta \, dr \, d\theta \, d\phi. \quad (77)$$



Assuming that the radiation is isotropic, the photons inside the volume element dV will be travelling with equal probability in all directions.

Therefore, the probability that a given photon in the volume element dV will be incident on the area element ΔA is the *effective area* of the area element (taking into account its orientation with respect to a line joining it to the volume element), divided by the surface area of a sphere centered on the volume element, and passing through the area element:

$$\Delta p = \frac{\cos \theta \Delta A}{4\pi r^2}. \quad (78)$$

The number of photons passing through the area element ΔA in time Δt is found by integrating $\frac{N}{V}\Delta p$ over all volume elements within a distance $r = c \Delta t$ of the area element:

$$n_\gamma \Delta A \Delta t = \int_{r < c \Delta t} \frac{N}{V} \frac{\cos \theta \Delta A}{4\pi r^2} dV, \quad (79)$$

$$= \frac{N \Delta A}{V 4\pi} \int_0^{c \Delta t} dr \int_0^{\frac{\pi}{2}} \cos \theta \sin \theta d\theta \int_0^{2\pi} d\phi, \quad (80)$$

$$= \frac{N \Delta A}{V 4\pi} \times c \Delta t \times \frac{1}{2} \times 2\pi, \quad (81)$$

$$= \frac{N}{4V} c \Delta A \Delta t. \quad (82)$$

Using $N = U/\bar{\varepsilon}$, we find that the radiation energy falling on the inside walls of the box per unit area per unit time is (the “flux” of radiation):

$$P_\gamma = n_\gamma \bar{\varepsilon} = \frac{U}{4V}c. \quad (83)$$

From equation (69) for the total energy:

$$U = \frac{8\pi^5}{15} \frac{V}{(hc)^3} (kT)^4,$$

the flux of radiation is:

$$P_\gamma = \frac{2\pi^5}{15} \frac{(kT)^4}{h^3c^2}. \quad (84)$$

As we argued above, since the box is in thermal equilibrium with the radiation, the rate at which the walls emit radiation must equal the rate at which radiation falls on the walls (and is absorbed).

We now claim that a perfectly absorbing surface at some temperature T will emit radiation at the same rate, whether or not the surface forms the inside of a box.

Hence, the rate of radiation of energy per unit area from a perfectly absorbing surface at temperature T is given by (84):

$$P_\gamma = \sigma T^4, \quad (85)$$

where:

$$\sigma = \frac{2\pi^5}{15} \frac{k^4}{h^3c^2}. \quad (86)$$

This is Stefan’s law; σ is Stefan’s constant.

Finally for the photon gas, we note that since the total energy U depends on the volume V , we expect the radiation to exert a non-zero pressure on the walls of its container. From the first law of thermodynamics, we find that:

$$p = - \left(\frac{\partial U}{\partial V} \right)_S. \quad (87)$$

The total energy can be expressed in terms of the number of particles in the various energy states:

$$U = \sum_j n_j \varepsilon_j. \quad (88)$$

The entropy S is related (by Boltzmann's equation) to the total number of accessible microstates, which in turn is related to the number of particles in each state. Hence, the constraint that S is constant is equivalent to the constraint that the energy state populations n_j are constant:

$$p = - \sum_j n_j \frac{d\varepsilon_j}{dV}. \quad (89)$$

Now, for photons, the energy of a state is proportional to the wave number, k :

$$\varepsilon = \hbar ck, \quad \text{so:} \quad \frac{d\varepsilon}{dV} = \hbar c \frac{dk}{dV}. \quad (90)$$

The boundary conditions impose constraints on the possible wave numbers. In a cube of side length L , we have:

$$k = \frac{2\pi}{L} \sqrt{n_x^2 + n_y^2 + n_z^2}, \quad (91)$$

for positive integers n_x , n_y and n_z . This can be written:

$$k = \frac{2\pi}{V^{\frac{1}{3}}} \sqrt{n_x^2 + n_y^2 + n_z^2}, \quad (92)$$

from which it follows that:

$$\frac{dk}{dV} = -\frac{1}{3} \frac{k}{V}, \quad \text{so:} \quad \frac{d\varepsilon}{dV} = -\frac{1}{3} \frac{\varepsilon}{V}. \quad (93)$$

Substituting (93) into (89) gives:

$$p = \frac{1}{3} \sum_j n_j \frac{\varepsilon_j}{V} = \frac{1}{3} \frac{U}{V}. \quad (94)$$

The radiation pressure depends on the energy density in the radiation.

Using equation (69) for the total energy gives:

$$p = \frac{8\pi^5}{45} \frac{(kT)^4}{(hc)^3}. \quad (95)$$

The radiation pressure depends only on the temperature (and some fundamental physical constants); and increases as the fourth power of the temperature.

Pressure of a gas of massive bosons

Note that equation (94) for the pressure in a “gas” of photons:

$$p = \frac{1}{3} \frac{U}{V} \quad (\text{photons})$$

differs from the expression we would find for a gas of massive bosons. In the latter case, the energy of a state is quadratic in the wave number k , rather than linear:

$$\varepsilon = \frac{\hbar^2 k^2}{2m}. \quad (96)$$

We have the same boundary conditions for massive bosons as for massless photons. The result is that the pressure in a gas of massive bosons depends on the energy density as:

$$p = \frac{2}{3} \frac{U}{V} \quad (\text{massive bosons}). \quad (97)$$

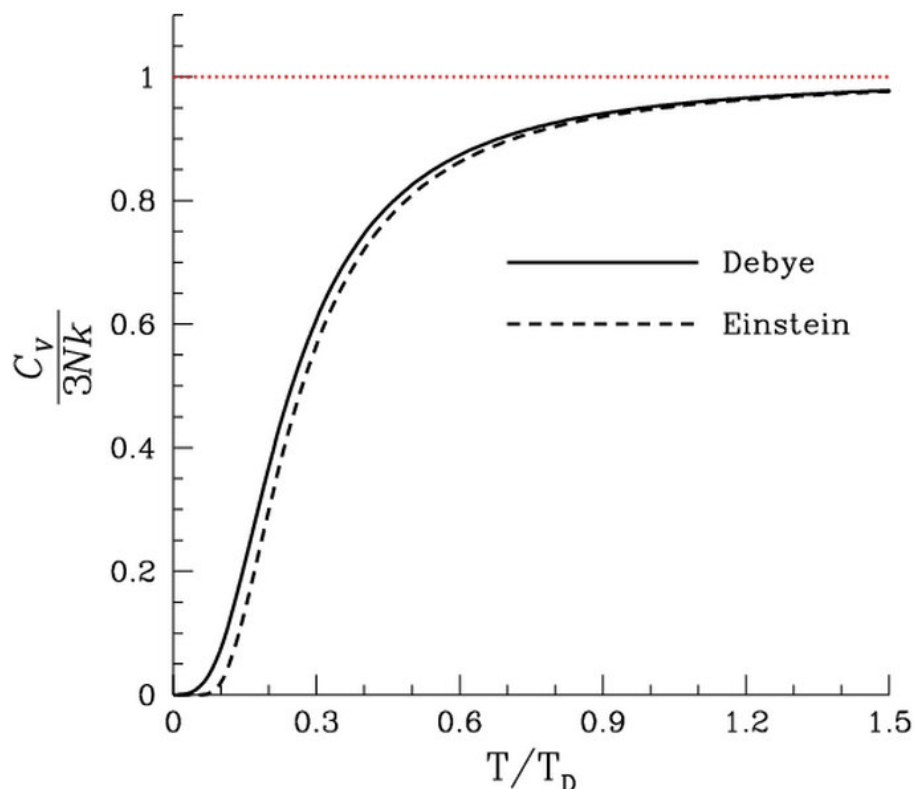
In Part 2 of this course, we considered a simple model of a solid, in which the atoms were represented as weakly-coupled quantum harmonic oscillators. The energies of the single-particle energy eigenstates were then:

$$\varepsilon_j = \left(\frac{1}{2} + j\right)\hbar\omega, \quad (98)$$

where j is zero or a positive integer, and ω is a constant, characteristic of the force between atoms, and the mass of each atom. This is the “Einstein model” of a solid.

With the above energy levels, we were able to perform an analysis of the system using statistical mechanics, to derive quantities such as the total energy, entropy and heat capacity as functions of temperature. For the heat capacity, we found qualitative agreement with experiment, in that the heat capacity goes towards zero at zero temperature. However, quantitatively, the predictions are not very accurate.

Heat capacity of a solid



A more sophisticated model of a solid has been suggested by Debye. In Debye's model, we consider not the vibrations of individual particles, but "collective" vibrations, comprising standing waves in the solid. The key difference when compared to the Einstein model, is that the frequency of a wave depends on its wavelength:

- In the Einstein model, the vibrations have fixed frequency, and the energy levels are uniformly distributed in energy.
- In the Debye model, the vibrations cover a range of frequencies, and the density of states varies with frequency.

Debye model: cut-off frequency

Another key feature of the Debye model is the cut-off frequency. A solid can only support waves with frequencies below a set limit. This is equivalent to saying that waves in the solid have a *minimum* wavelength. The minimum wavelength is determined by the spacing of atoms in the solid: clearly, there cannot be waves with wavelength less than twice the spacing between atoms.

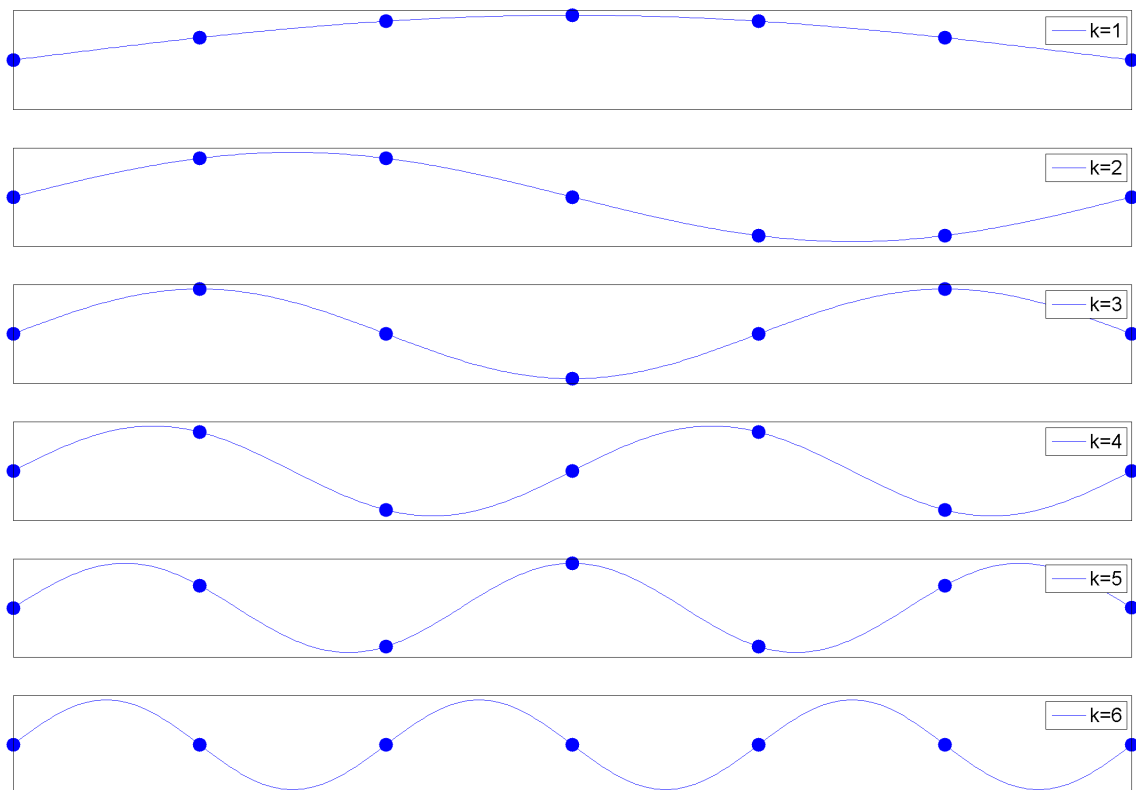
To find the cut-off frequency, let us consider standing waves in the solid. We shall assume the boundary condition that atoms at the surface of the solid are in fixed positions (i.e. atoms at the surface cannot vibrate). To make things simple, let consider initially a one-dimensional solid consisting of just a small number of atoms...

Let the atoms in the one-dimensional solid be numbered $m = 0, 1, 2, \dots, N$. The total number of atoms is $N + 1$. If there exists a standing wave with wave number k in the solid, then the displacement of atom m is given by:

$$y_k(m) = A \sin\left(k\pi \frac{m}{N}\right). \quad (99)$$

The boundary conditions, that $y_k(0) = 0$ and $y_k(N) = 0$, impose the constraint that k must be an integer, $k = 1, 2, 3, \dots$. Standing waves with different values of k are known as different vibrational *modes*.

Debye model: vibrational modes



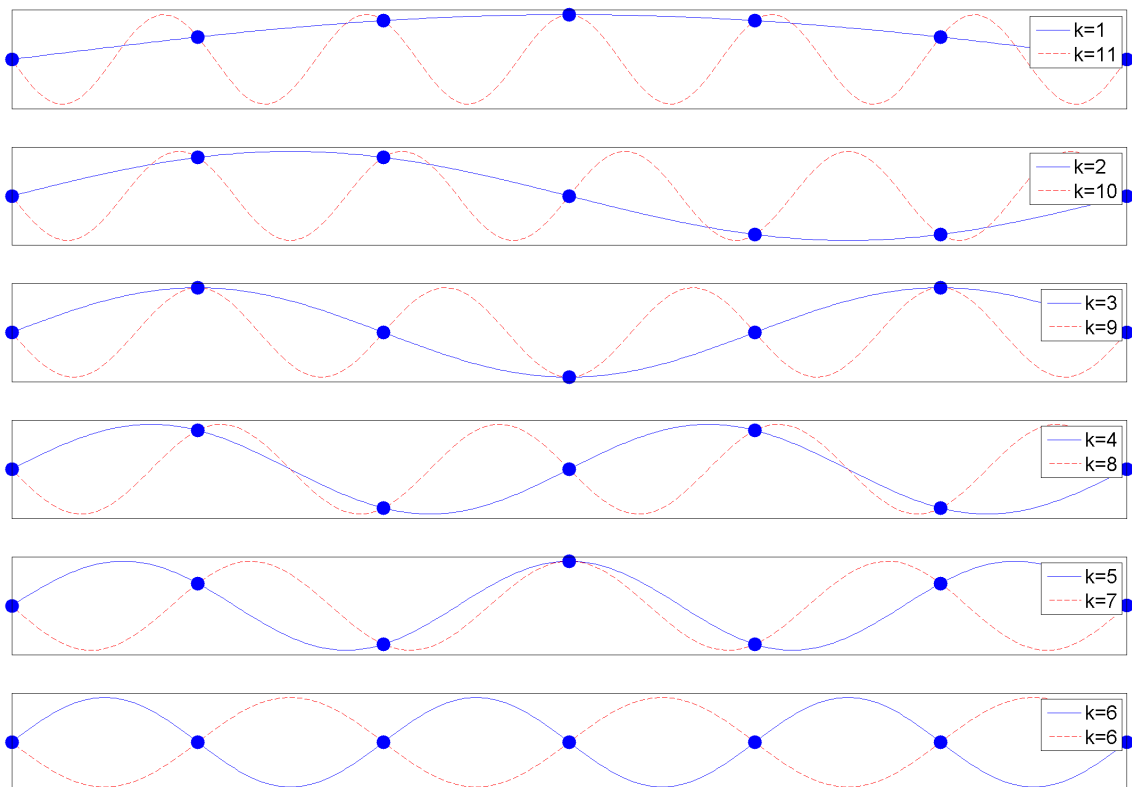
From the plot on the previous slide, we see that in mode $k = 6$, the atoms do not vibrate at all: a wave with $k = 6$ does not “exist” as a distinct vibrational mode.

In fact, further analysis shows that waves with $k = 7, 8, 9...$ simply reproduce vibrational modes with smaller values of k . This is because, for example:

$$y_{2N-k}(m) = A \sin \left((2N - k)\pi \frac{m}{N} \right) = -A \sin \left(k\pi \frac{m}{N} \right) = -y_k(m). \quad (100)$$

The overall phase (minus sign) has no significance for our purposes.

Debye model: vibrational modes



In general, only waves with $k = 1, 2, 3, \dots, N - 2$ exist as distinct modes. In other words, there is a maximum wave number, and hence a maximum frequency, determined by the number of atoms in the solid.

To determine the maximum frequency, we need to know the relationship between the wave number and the frequency. Such a relationship is known, in general, as a *dispersion relation*. For a wave propagating through a solid, the dispersion relation depends on the forces between the atoms constituting the solid.

The dispersion relation is the final “ingredient” in the Debye model. In the Einstein model, there was only one frequency at which the atoms could vibrate. A more realistic assumption, often adopted in the Debye model, is that the frequency ω of the vibration is related to the wave number k by the speed of sound c_s in the material:

$$\omega = kc_s. \tag{101}$$

Finally, we assume that the energy ε in a wave is quantised, and that the usual Planck formula applies:

$$\varepsilon = \hbar\omega = \hbar c_s k. \tag{102}$$

It is important to understand that ε is not the vibrational energy of a single atom. It represents the energy of a vibrational mode in the material, to which many atoms contribute. In essence, we are departing from our usual assumption that the energy levels in a system of many particles are essentially the same as the energy levels of individual particles. To do things properly in this case, we should solve the Schrödinger equation for the complete system consisting of many particles. However, if there are of order 10^{23} particles, this is not practical. Instead, we arrive at the energy levels using the argument outlined above.

A vibrational mode with energy ε is called a *phonon*. Phonons are quanta of vibrational (sound) energy in a material.

In three dimensions, the vibrational modes are the same as those for photons (electromagnetic radiation) in a closed box. The difference is that for phonons, there is a maximum frequency (related to the number of particles in the object), whereas for photons there is no upper limit on the frequency.

If $g(\nu) d\nu$ is the number of states (vibrational modes) in the frequency range ν to $\nu + d\nu$, then:

$$\int_0^{\nu_D} g(\nu) d\nu = 3N, \quad (103)$$

where ν_D is the maximum frequency of a vibrational mode, known as the cut-off or Debye frequency. Strictly speaking, the right hand side should be less than $3N$, since particles at the surface of the object cannot vibrate. However, for a macroscopic object, the number of particles at the surface is small compared to the number of particles in the interior.

Recall, from Part 3 of this lecture course, that the number of states with wave number in the range k to $k + dk$ is:

$$g(k) dk = 3 \times 4\pi \frac{V}{(2\pi)^3} k^2 dk, \quad (104)$$

where the initial factor 3 accounts for the three “polarisations” (two transverse, and one longitudinal) that a phonon can have.

Using the dispersion relation (101):

$$\omega = 2\pi\nu = kc_s,$$

we find that the number of states in frequency range ν to $\nu + d\nu$ is:

$$g(\nu) d\nu = 12\pi \frac{V}{c_s^3} \nu^2 d\nu. \quad (105)$$

Combining equations (103) and (105), we find that the cut-off frequency ν_D is then given by:

$$\int_0^{\nu_D} g(\nu) d\nu = \int_0^{\nu_D} 12\pi \frac{V}{c_s^3} \nu^2 d\nu = 3N. \quad (106)$$

This gives:

$$\nu_D^3 = \frac{3}{4\pi} \frac{N}{V} c_s^3. \quad (107)$$

The cut-off frequency ν_D should be the upper limit in any integral over the density of states.

Debye model: total energy

Let us proceed to calculate the total vibrational energy U in a solid as a function of temperature. Since phonons are bosons (they have three possible “spin” or polarisation states), and the total number of phonons in a system is not conserved, they should follow the same statistical distribution as photons.

Thus, the total phonon energy is given by:

$$U = \int_0^{\varepsilon_D} \frac{\varepsilon g(\varepsilon)}{e^{\frac{\varepsilon}{kT}} - 1} d\varepsilon, \quad (108)$$

where $\varepsilon_D = h\nu_D$ is the energy of a phonon at the cut-off frequency.

Using equation (104):

$$g(k) dk = 12\pi \frac{V}{(2\pi)^3} k^2 dk,$$

and equation (102):

$$\varepsilon = \hbar c_s k,$$

we find that the density of states as a function of energy is given by:

$$g(\varepsilon) d\varepsilon = 12\pi V \frac{\varepsilon^2}{(hc_s)^3} d\varepsilon. \quad (109)$$

Substituting (109) into (108) gives:

$$U = \frac{12\pi V}{(hc_s)^3} \int_0^{\varepsilon_D} \frac{\varepsilon^3}{e^{\frac{\varepsilon}{kT}} - 1} d\varepsilon. \quad (110)$$

Then, defining:

$$y = \frac{\varepsilon}{kT}, \quad (111)$$

the expression for the total energy (110) becomes:

$$U = \frac{12\pi V}{(hc_s)^3} (kT)^4 \int_0^{\varepsilon_D/kT} \frac{y^3}{e^y - 1} dy. \quad (112)$$

We define the *Debye temperature* θ_D :

$$\theta_D = \frac{\varepsilon_D}{k} = \frac{\hbar \nu_D}{k}, \quad \theta_D^3 = \frac{3 h^3 N}{4\pi k^3 V} c_s^3. \quad (113)$$

In terms of the Debye temperature, the total energy can be written:

$$U = 9NkT \left(\frac{T}{\theta_D} \right)^3 \int_0^{\theta_D/T} \frac{y^3}{e^y - 1} dy. \quad (114)$$

The definite integral in equation (114) is difficult to evaluate, so we consider two limiting cases, of low and high temperature.

First, consider the low temperature case, $T \ll \theta_D$. In this case, $\theta_D/T \gg 1$. Since the integrand becomes extremely small for large y , the integral may be approximated by taking the upper limit to infinity:

$$\int_0^{\theta_D/T} \frac{y^3}{e^y - 1} dy \approx \int_0^\infty \frac{y^3}{e^y - 1} dy = \frac{\pi^4}{15}. \quad (115)$$

Then, using (114) we find:

$$U \approx \frac{3\pi^4}{5} NkT \left(\frac{T}{\theta_D} \right)^3, \quad \text{if } T \ll \theta_D. \quad (116)$$

The heat capacity is given by:

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V, \quad (117)$$

which gives:

$$C_V \approx \frac{12\pi^4}{5} Nk \left(\frac{T}{\theta_D} \right)^3, \quad \text{if } T \ll \theta_D. \quad (118)$$

At low temperature, the heat capacity varies with the cube of the temperature:

$$\frac{C_V}{T^3} \rightarrow \frac{12\pi^4 Nk}{5 \theta_D^3} \quad \text{as } T \rightarrow 0 \quad (\text{Debye model}). \quad (119)$$

This is a different behaviour from that predicted by the Einstein model:

$$\frac{C_V}{T^3} \rightarrow 0 \quad \text{as } T \rightarrow 0 \quad (\text{Einstein model}). \quad (120)$$

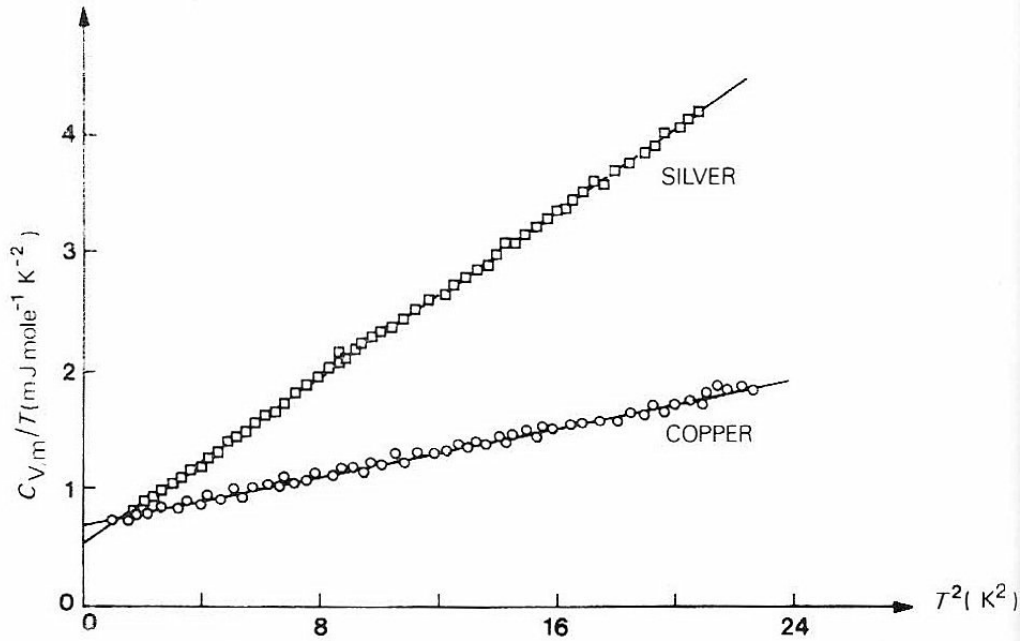


Figure 12.7—Low temperature molar heat capacity of metals; $C_{V,m}/T$ is plotted against T^2 . The results are consistent with equation (12.29), according to which $C_{V,m}$ is equal to $\gamma T + AT^3$. The intercepts give the values of γ . The values of A can be determined from the slopes. (Reproduced with permission from *Statistical Mechanics and Properties of Matter* by E. S. R. Gopal, Ellis Horwood Ltd., Chichester.)

Debye model: total energy when $T \gg \theta_D$

Now, consider the high temperature case, $T \gg \theta_D$. In this case, $\theta_D/T \ll 1$, and the variable in the integrand remains small compared to 1. Then we can approximate $e^y - 1 \approx y$, and the integral becomes:

$$\int_0^{\theta_D/T} \frac{y^3}{e^y - 1} dy \approx \int_0^{\theta_D/T} y^2 dy = \frac{1}{3} \left(\frac{\theta_D}{T} \right)^3. \quad (121)$$

Then, from (114), we find:

$$U \approx 3NkT, \quad \text{if } T \gg \theta_D. \quad (122)$$

Again, we can find the heat capacity:

$$C_V = \left(\frac{\partial U}{\partial T} \right)_V. \quad (123)$$

At high temperatures, with $U = 3NkT$ (122), we find:

$$C_V \approx 3Nk, \quad \text{if } T \gg \theta_D. \quad (124)$$

At high temperatures, the Debye model and the Einstein model give the same value for the heat capacity.

Summary: Bose-Einstein Statistics

You should be able to:

- Explain that the wave function for a system of identical bosons must be symmetric under the interchange of any two bosons; and show that this property allows an unlimited number of bosons to occupy any given state.
- Derive the Bose-Einstein distribution for a system of indistinguishable bosons.
- Apply the Bose-Einstein distribution to a Bose-Einstein gas, to show the existence of the Bose-Einstein condensation below the Bose temperature.
- Derive the heat capacity of a Bose-Einstein gas, below and above the Bose temperature.
- Explain the difference between a Bose-Einstein gas, and a gas of photons.
- Apply the Bose-Einstein distribution to a gas of photons, to derive Planck's radiation law; Wien's law; and Stefan's law (for black body radiation).
- Explain Debye's model of a solid, and discuss the significance of vibrational modes and their quantisation (phonons).
- Use Debye's model to derive expressions for the heat capacity of a solid in the limits of low and high temperature.