

Section 4

Statistical Thermodynamics of delocalised particles

4.1 Classical Ideal Gas

4.1.1 Indistinguishability

Since the partition function is proportional to probabilities it follows that for composite systems the partition function is 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. In Section 2.6 we saw how this could be done for localised systems where the particles, although indistinguishable, could be individually identified by the sites they occupied. In that case for an assembly of N identical but *distinguishable* particles the resultant partition function would be the product of the (same) partition functions of a single particle, z

$$Z = z^N.$$

For delocalised particles, as in a gas, this is not possible. The key question 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

$$\frac{N!}{n_1! n_2! n_3! \dots}$$

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

$$Z = \frac{n_1! n_2! n_3! \dots}{N!} z^N$$

4.1.2 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. 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

$$Z = \frac{1}{N!} z^N.$$

The Helmholtz free energy

$$F = -kT \ln Z$$

is thus

$$F = -NkT \ln z + kT \ln N!.$$

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 . Thus when differentiating with respect to volume to find the pressure, the result is N times that for a single particle.

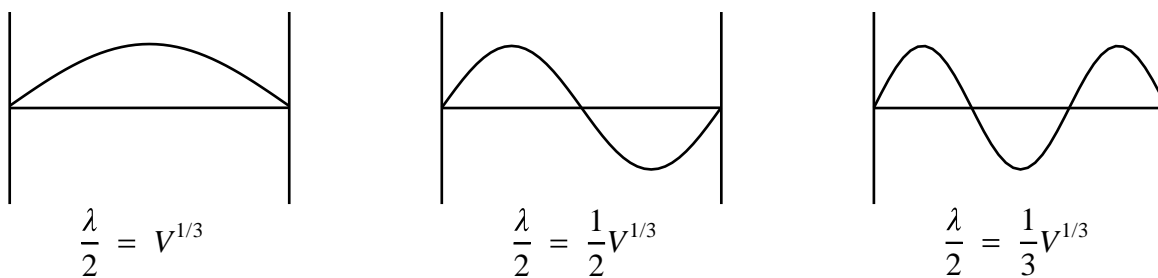
The problem then boils down to finding the partition function z for a single particle

$$z = \sum_i e^{-\varepsilon_i/kT}$$

so the first thing we must do is to find what these energies ε_i are.

4.1.3 Specifying the single-particle energy 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 must go to zero at the walls of the box – only standing waves are allowed.



Standing waves in a box

In the general case the allowed wave lengths λ satisfy $\lambda/2 = V^{1/3}/n$ or

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

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

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

We can now use the deBroglie relation $p = h/\lambda = 2\pi\hbar/\lambda$ to obtain the momentum and hence the energy.

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

and so for a free particle the energy is then

$$\varepsilon = \frac{p^2}{2m} = \frac{p_x^2 + p_y^2 + p_z^2}{2m}$$

which is

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

In this expression it is the triple of quantum numbers (n_x, n_y, n_z) which specify the quantum state, so we may write

$$\varepsilon = \varepsilon(n_x, n_y, n_z).$$

4.1.4 Density of states

In principle, since the quantum states are now specified, it is possible to evaluate the partition function sum. In practice – for a box of macroscopic dimensions – the energy levels are extremely closely spaced and it proves convenient to approximate the sum by an integral:

$$\sum_i e^{-\varepsilon_i/kT} \rightarrow \int_0^\infty g(\varepsilon) e^{-\varepsilon/kT} d\varepsilon$$

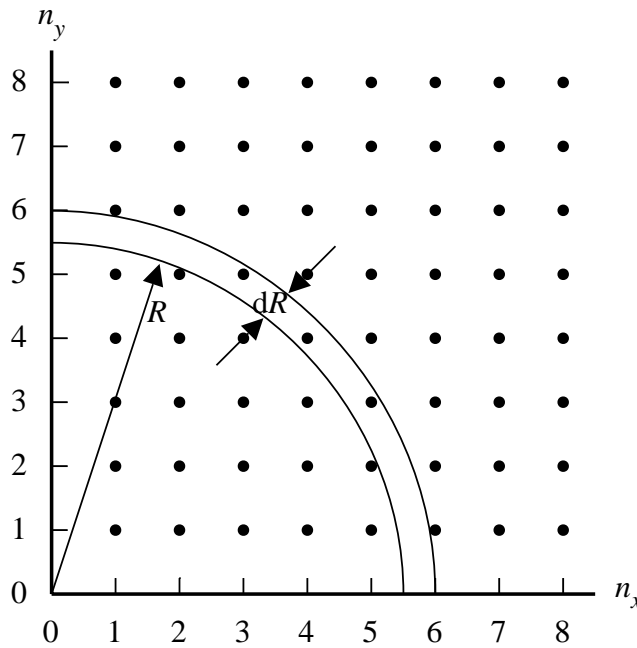
where $g(\varepsilon) d\varepsilon$ is the number of single particle quantum states with energy between ε and $\varepsilon + d\varepsilon$. The quantity $g(\varepsilon)$ is called the *density of states*.

To find an expression for the density of states we note that each triple of quantum numbers (n_x, n_y, n_z) specifies point on a cubic grid. If we put

$$R^2 = n_x^2 + n_y^2 + n_z^2$$

then the energy is given by

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



Counting of quantum states

Now 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* since n_x, n_y and n_z are positive). And the number of points in the octant is approximately equal to the volume of the octant:

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

But since

$$R = \left[\frac{2mV^{2/3}}{\pi^2 \hbar^2} \right]^{1/2} \varepsilon^{1/2},$$

we then obtain

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

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

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

or, simply

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

So differentiating $N(\varepsilon)$ we obtain

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

which is the required expression for the density of states.

4.1.5 Calculating the partition function

The partition function, in integral form, is given by

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

This integral is evaluated by making the substitution

$$x = \varepsilon/kT$$

so that

$$z = \frac{V}{4\pi^2 \hbar^3} (2mkT)^{3/2} \int_0^\infty x^{1/2} e^{-x} dx.$$

Here the physics is all outside the integral. The integral is a pure number (an example of the gamma function), given by $\sqrt{\pi}/2$, so that

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

For a gas of N particles we then have

$$Z = \frac{1}{N!} z^N.$$

We use Stirling's approximation when evaluating the logarithm:

$$\ln Z = -N \ln N + N + N \ln z = N \ln \left[\left(\frac{mkT}{2\pi\hbar^2} \right)^{3/2} \frac{Ve}{N} \right]$$

from which all thermodynamic properties can be found.

[We note parenthetically that the (single particle) partition function *could* have been evaluated classically without enumeration of the quantum states and without the consequent need for the energy density of states.

The classical partition function is given by the integral

$$z = \frac{1}{h^3} \int \exp(-\varepsilon/kT) d^3p d^3q$$

where the classical "state" is specified as a cell in $p-q$ space, or phase space. The extent in phase space of such a state is given by the unspecified quantity h . For the ideal gas

$$\varepsilon = p^2/2m.$$

Thus the q integrals are trivial, giving a factor V , and we have

$$z = \frac{V}{h^3} \left[\int_{-\infty}^{\infty} \exp(-p^2/2mkT) dp \right]^3.$$

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

$$z = \frac{V}{h^3} \{2mkT\}^{3/2} \left[\int_{-\infty}^{\infty} \exp -x^2 dx \right]^3.$$

The integral is $\sqrt{\pi}$ so that

$$z = \left(\frac{2\pi mkT}{h^2} \right)^{3/2} V$$

just as in the “quantum” calculation. Thus we obtain the partition function from purely classical arguments and as a bonus we see that by comparison with the quantum result, this justifies the use of Planck’s constant in the normalization factor for the classical state element of phase space.]

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4.1.6 Thermodynamic properties

We start from the Helmholtz free energy:

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

giving

$$p = kT \left. \frac{\partial \ln Z}{\partial V} \right|_T = NkT \left. \frac{\partial \ln z}{\partial V} \right|_T = \frac{NkT}{V}.$$

This is the ideal gas equation, and from this we identify directly our statistical temperature T with the temperature as measured by an ideal gas thermometer.

The internal energy is

$$E = kT^2 \left. \frac{\partial \ln Z}{\partial T} \right|_V = NkT^2 \frac{d \ln T^{3/2}}{dT} = \frac{3}{2} NkT.$$

This is another important property of an ideal gas. On purely macroscopic grounds we saw that the ideal gas equation of state leads to an internal energy which depends *only* on temperature (not pressure or density). Here we have calculated this dependence for a monatomic gas. From the energy expression we obtain the thermal capacity

$$C_V = \left. \frac{\partial E}{\partial T} \right|_V = \frac{3}{2} Nk.$$

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.

The entropy is found from

$$S = - \left. \frac{\partial F}{\partial T} \right|_V$$

which leads to

$$S = Nk \ln \left[\left(\frac{mkT}{2\pi\hbar^2} \right)^{3/2} \frac{Ve^{5/2}}{N} \right].$$

This is the Sackur-Tetrode equation, quoted before in Section 3.5.1. Note that the $T \rightarrow 0$ value of the entropy is $-\infty$. This is totally un-physical and it is in violation of the third law of thermodynamics. Of course this problem is all tied up with quantum mechanics and multiple occupancy; this semiclassical model lets us down here.

4.1.7 Thermal deBroglie wavelength

It is instructive to examine further the expression we have derived for the single-particle partition function. We found

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

and since z must be dimensionless it follows that the quantity $\sqrt{2\pi\hbar^2/mkT}$ must have the dimensions of length. This can be verified directly. Let us therefore define a quantity Λ by

$$\Lambda = \left(\frac{2\pi\hbar^2}{mkT} \right)^{1/2},$$

which we shall call the *thermal deBroglie wavelength*. Then in terms of this the partition function is given, simply, by

$$z = \frac{V}{\Lambda^3}.$$

The explanation for the name is as follows. A temperature T is associated with a thermal energy kT which manifests itself in the form of kinetic energy. We may therefore equate this to $p^2/2m$ which gives us a corresponding thermal momentum. And from the momentum we can find a wavelength using the deBroglie relation $p = h/\lambda$. Thus we have

$$E = kT = \frac{p^2}{2m} = \frac{(2\pi\hbar/\lambda)^2}{2m}$$

from which we find

$$\lambda = \left(\frac{2\pi^2\hbar^2}{mkT} \right)^{1/2}$$

which, apart from a numerical factor, corresponds to the thermal deBroglie wavelength Λ defined above.

So Λ represents the quantum-mechanical ‘size’ of the particle due to its thermal energy. By ‘size’ here we mean the distance over which the particle may be found – the uncertainty in its position. We then have a simple interpretation of the partition function:

$$z = \frac{\text{volume of the box}}{\text{‘thermal volume’ of the particle}}.$$

4.1.8 Breakdown of the classical approximation

Let us now briefly examine the region of validity of our treatment of the ideal gas. In particular we are concerned with the adding together of the independent effects of a number of particles. And clearly this must be related to the question of multiple occupancy of quantum states.

The classical approximation can only hold if the particles can be regarded as being truly independent. In other words, we require that quantum mechanical effects don’t cause the particles to ‘see’ one another. We may express this condition as

$$\text{thermal volume of particle} \ll \frac{\text{volume of box}}{\text{number of particles}}$$

or

$$\frac{\Lambda^3 N}{V} \ll 1.$$

We tabulate below this parameter $\Lambda^3 N/V$ for a number of gases at their normal boiling point

	T in K	$\Lambda^3 N/V$
He	4.2	1.5
H ₂	20.4	0.44
Ne	27.2	0.015
A	87.4	0.00054

Since $\Lambda \propto m^{-1/2}$ it follows that deviations from classical behaviour are more likely to be observed with lighter atoms. The table indicates that the classical condition is satisfied for most gases right down to the liquefaction point, except for helium. In considering liquid and gaseous helium the effects of quantum mechanics must be taken into account. Thus the remarkable properties of cooled helium.

4.2 Quantum statistics

4.2.2 Bosons and Fermions

All particles in nature can be classified into two groups according to the behaviour of the wave function under the exchange of identical particles. For simplicity let us consider only two identical particles. The wave function can then be written

$$\Psi = \Psi(r_1, r_2)$$

where

r_1 is the position of the 1st particle

and

r_2 is the position of the 2nd particle.

Let us interchange the particles. The operator to effect this is denoted by P (the permutation operator). Then

$$P\Psi(r_1, r_2) = \Psi(r_2, r_1).$$

We are interested in the behaviour of the wave function under interchange of the particles. Since the particles are indistinguishable, all observed properties will be the same before and after the interchange. This means that the wave function can only be multiplied by a phase factor $p = e^{i\varphi}$:

$$P\Psi = e^{i\varphi}\Psi.$$

Thus far it is not much of a conclusion. But let us now perform the swapping operation again. Then we have

$$P^2\Psi(r_1, r_2) = P\Psi(r_2, r_1) = \Psi(r_1, r_2);$$

the effect is to return the particles to their original states. Thus the operator P must obey

$$P^2 = 1.$$

And taking the square root of this we find for p , the eigenvalues of P :

$$p = \pm 1.$$

In other words the effect of swapping two identical particles is either to leave the wave function unchanged or to change the sign of the wave function.

All particles in nature belong to one class or the other. Particles for which

$$p = +1 \text{ are called } \textit{Bosons}$$

while those for which

$$p = -1 \text{ are called } \textit{Fermions}.$$

This property continues for all time since the permutation operator commutes with the Hamiltonian. Fermions have the important property of not permitting multiple occupancy of quantum states. Consider two particles in the same state, at the same position r . The wave function is then

$$\Psi = \Psi(r, r).$$

Swapping over the particles we have

$$P\Psi = -\Psi.$$

But $\Psi = \Psi(r, r)$ so that $P\Psi = +\Psi$ since both particles are in the same state. The conclusion is that

$$\Psi(r, r) = -\Psi(r, r)$$

and this can only be so if

$$\Psi(r, r) = 0.$$

Now since Ψ is related to the *probability* of finding particles in the given state, the result $\Psi = 0$ implies a state of zero probability – an impossible state. We conclude that it is impossible to have more than one Fermion in a given quantum state.

This discussion was carried out using r_1 and r_2 to denote *position* states. However that is not an important restriction. In fact they could have designated any sort of quantum state and the same argument would follow.

This is the explanation of the Pauli exclusion principle obeyed by electrons.

We conclude:

For Bosons we can have any number of particles in a quantum state.

For Fermions we can have either 0 or 1 particle in a quantum state.

But what determines whether a given particle is a Boson or a Fermion? The answer is provided by relativistic quantum mechanics and it depends on the *spin* of the particle. Particles whose spin angular momentum is an integral multiple of \hbar are Bosons while particles whose spin angular momentum is integer plus a half \hbar are Fermions. (In quantum theory $\hbar/2$ is the smallest unit of spin angular momentum.)

For some elementary particles we have:

$$\left. \begin{array}{l} \text{electrons} \\ \text{protons} \\ \text{neutrons} \end{array} \right\} S = \frac{1}{2} \rightarrow \text{Fermions}$$

$$\left. \begin{array}{l} \text{photons} \\ \pi \text{ mesons} \\ \kappa \text{ mesons} \end{array} \right\} \begin{array}{l} S = 1 \\ S = 0 \end{array} \rightarrow \text{Bosons}$$

For composite particles (such as atoms) we simply add the spins of the constituent parts. And since protons, neutrons and electrons are all Fermions we can say:

Odd number of Fermions \rightarrow Fermion
 Even number of Fermions \rightarrow Boson.

The classic example of this is the two isotopes of helium. Thus

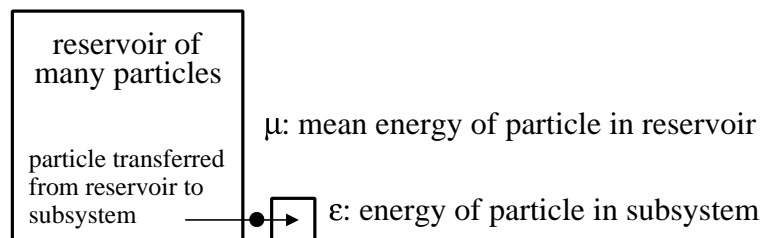
^3He is a Fermion
 ^4He is a Boson.

At low temperatures these isotopes have very different behaviour.

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4.2.3 The quantum distribution functions

We shall obtain the distribution functions for particles obeying Fermi-Dirac statistics and those obeying Bose-Einstein statistics. Thus we want to know the mean number of particles which may be found in a given quantum state. The method is based on an idea in Feynman's book *Statistical Mechanics*, Benjamin (1972). We start by considering an idealised model, of a subsystem comprising a single quantum state of energy ε , in thermal equilibrium with a reservoir of many particles. The mean energy of a particle in the reservoir is denoted by μ (we will tighten up on the precise definition of *mean energy* later).



Transfer of a particle from reservoir to the subsystem

A particle may be in the reservoir or may be in the subsystem. The probability that it is in the subsystem is proportional to the Boltzmann factor $\exp(-\varepsilon/kT)$, while the probability that it is in the reservoir is proportional to $\exp(-\mu/kT)$. If $P(1)$ is the probability that there is one particle in the subsystem and $P(0)$ is the probability of no particles in the subsystem, then we may write

$$\frac{P(1)}{P(0)} = \exp\left(-\frac{\varepsilon - \mu}{kT}\right) \quad \text{or} \quad P(1) = P(0) \exp\left(-\frac{\varepsilon - \mu}{kT}\right).$$

If the statistics allow (for Bosons, but not for Fermions) then we may transfer more particles from the reservoir to the subsystem. Each particle transferred will lose an energy μ and gain an energy ε . Associated with the transfer of n particles there will therefore be a Boltzmann factor of $\exp(-n(\varepsilon - \mu)/kT)$. And so the probability of having n particles in the subsystem is

$$P(n) = P(0) \exp -\frac{n(\varepsilon - \mu)}{kT}.$$

Let us put

$$x = \exp -\frac{(\varepsilon - \mu)}{kT}. \quad (1)$$

Then

$$P(n) = P(0)x^n. \quad (2)$$

Normalisation requires that all possible probabilities sum to unity. For Fermions we know that n can take on only the values 0 and 1, while for Bosons n can be any integer. Thus we have

$$P(0) + P(1) = 1 \quad \text{for Fermions}$$

$$\sum_{n=0}^{\infty} P(n) = 1 \quad \text{for Bosons}$$

which can be written, quite generally as

$$\sum_{n=0}^a P(n) = 1$$

where $a = 1$ for Fermions and $a = \infty$ for Bosons.

Since $P(n)$ is given by Equation (2), the normalisation requirement may be expressed as

$$P(0) \sum_{n=0}^a x^n = 1$$

which gives us $P(0)$:

$$P(0) = \left\{ \sum_{n=0}^a x^n \right\}^{-1}.$$

We will be encountering the above sum of powers of x quite frequently, so let's denote it by the symbol Σ :

$$\Sigma = \sum_{n=0}^a x^n. \quad (3)$$

In terms of this

$$P(0) = \Sigma^{-1},$$

and then from Equation (2)

$$P(n) = x^n / \Sigma.$$

What we want to know is the *mean* number of particles in the subsystem. That is, we want to calculate

$$\bar{n} = \sum_{n=0}^a nP(n),$$

which is given by

$$\bar{n} = \frac{1}{\Sigma} \sum_{n=0}^a nx^n.$$

The sum of nx^n may be found by using a trick (which is really at the heart of many Statistical Mechanics calculations). The sum differs from the previous sum Σ which we used, because of the extra factor of n . Now we can bring down an n from x^n by differentiation. Thus we write

$$nx^n = x \frac{d}{dx} x^n,$$

so that

$$\sum_{n=0}^a nx^n = x \frac{d}{dx} \sum_{n=0}^a x^n.$$

Observe that the sum on the right hand side here is our original sum Σ . This means that \bar{n} can be expressed as

$$\bar{n} = x \frac{1}{\Sigma} \frac{d\Sigma}{dx}$$

or

$$\bar{n} = x \frac{d \ln \Sigma}{dx}.$$

It remains, then, to evaluate Σ for the two cases. For Fermions we know that $a = 1$, so that the sum in Equation (3) is $1 + x$. For Bosons a is infinity; the sum is an infinite (convergent) geometric series. The sum of such a geometric progression is $1/(1 - x)$. Thus we have

Fermions

$$\Sigma = 1 + x$$

$$\ln \Sigma = \ln(1 + x)$$

$$\frac{d \ln \Sigma}{dx} = \frac{1}{1 + x}$$

$$x \frac{d \ln \Sigma}{dx} = \frac{x}{1 + x}$$

$$\bar{n} = \frac{1}{x^{-1} + 1}$$

$$\bar{n} = \frac{1}{\exp(\epsilon - \mu)/kT + 1}$$

Bosons

$$\Sigma = (1 - x)^{-1}$$

$$\ln \Sigma = -\ln(1 - x)$$

$$\frac{d \ln \Sigma}{dx} = \frac{1}{1 - x}$$

$$x \frac{d \ln \Sigma}{dx} = \frac{x}{1 - x}$$

$$\bar{n} = \frac{1}{x^{-1} - 1}$$

$$\bar{n} = \frac{1}{\exp(\epsilon - \mu)/kT - 1}$$

upon differentiating

so that

and \bar{n} is then given by

Finally, substituting
for x from Eq (1):

These expressions will be recognised as the Fermi-Dirac and the Bose-Einstein distribution functions. However, it is necessary to understand the way in which this idealised model relates to realistic assemblies of Bosons or Fermions. We have focussed attention on a given quantum state, and treated it as if it were apart from the reservoir. In reality the reservoir is the entire system and the quantum state of interest is *in* that system. The entire analysis then follows through so long as the mean energy of a particle, μ , in the system is changed by a negligible amount if a single quantum state is excluded. And this must be so for any macroscopic system.

4.2.4 The chemical potential

We now turn to an examination of the meaning of μ within the spirit of this picture. We said that it was the mean energy lost when a particle is removed from the reservoir, which we now understand to mean the entire system. When a particle is removed the system remains otherwise unchanged. There are two ways in which the system is unchanged.

- The distribution of particles in the other (single particle) energy states is unchanged - the entropy remains constant.
- The energy of the various states (single particle energy levels) is unchanged as the volume remains constant.

Thus our μ is equal to $\partial E / \partial N$ at constant S and V . This tells us that we have an extension of the first law of thermodynamics; there is another way in which the internal energy of a system can be changed. As well as adding heat and doing work, we can add particles. So the extended differential expression for E is:

$$dE = TdS - pdV + \mu dN.$$

The quantity μ is called the *chemical potential*, and it is defined as

$$\mu = \left. \frac{\partial E}{\partial N} \right|_{S,V}.$$

An expression in terms of the Helmholtz free energy is more amenable to calculation (from the partition function). Recall that F is defined as

$$F = E - TS$$

form which we obtain

$$dF = dE - TdS - SdT.$$

Using the extended version of the First Law expression for dE , this then gives

$$dF = -SdT - pdV + \mu dN$$

form which we may express the chemical potential μ as

$$\mu = \left. \frac{\partial F}{\partial N} \right|_{T,V}.$$

[For the classical ideal gas, whose free energy was found to be

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

the chemical potential is obtained by differentiation:

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

At high temperatures μ is large and negative. It goes to zero as $T \rightarrow 0$, but of course then the classical approximation breaks down and the correct quantum-mechanical expression for μ must be used, which will be different for Fermions and Bosons.]

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4.2.5 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 . These are the *intensive* variables which determine the equilibrium distribution $\bar{n}(\epsilon)$. Now 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 the system when it is in a state of equilibrium. In reality, however, it is more intuitive to speak of a system containing a given (mean) number of particles. In that case it is the number of particles in the system which determines the chemical potential.

Now the number of particles in the system is given by

$$N = \sum_i \bar{n}(\epsilon_i)$$

which converts to the integral

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

where 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 $1/2$; in general it will be $(2S + 1)$.

The expression for N is 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

$$E = \sum_i \epsilon_i \bar{n}(\epsilon_i)$$

or, in integral form

$$E = \int_0^{\infty} \alpha \epsilon \bar{n}(\epsilon) g(\epsilon) d\epsilon$$

4.3 The Fermi Gas

4.3.1 The Fermi-Dirac distribution

One has to use the Fermi distribution for fermions whenever the classical low density / high temperature approximation breaks down. That is, when

$$\frac{N}{V} \left(\frac{2\pi\hbar^2}{mkT} \right)^{1/2} \gtrsim 1.$$

Some examples of this are:

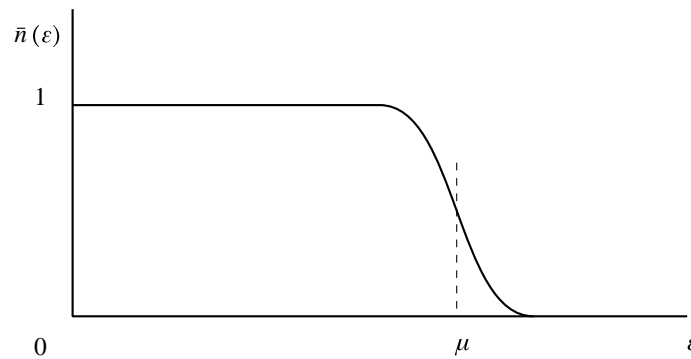
- Conduction electrons in a metal – Here, because the electrons are so light, even at room temperatures one is “well-into” the quantum régime.
- Liquid ^3He – When the helium is a liquid, at temperatures in the region of 1K, one is in the quantum régime because the helium atoms are sufficiently light.
- Neutron stars – In such stars the density of matter is very high indeed.
- Nuclear matter – Although the numbers of particles involved makes the concept of thermal equilibrium rather suspect, the high density of nuclear matter requires a quantum treatment.

On the other hand, usually the density of electrons in a semiconductor is sufficiently small to permit the use of classical statistics.

The Fermi-Dirac distribution for the mean number of fermions in the state of energy ϵ is given by

$$\bar{n}(\epsilon) = \frac{1}{\exp(\epsilon - \mu)/kT + 1}$$

We see that $\bar{n}(\epsilon)$ goes from zero at high energies to one at low energies. The changeover occurs at $\epsilon = \mu$, where $\bar{n}(\epsilon) = 1/2$.



Fermi-Dirac distribution

The transition from zero to one becomes sharper as the temperature is reduced.

4.3.2 Fermi gas at zero temperature

At zero temperature the Fermi-dirac distribution function

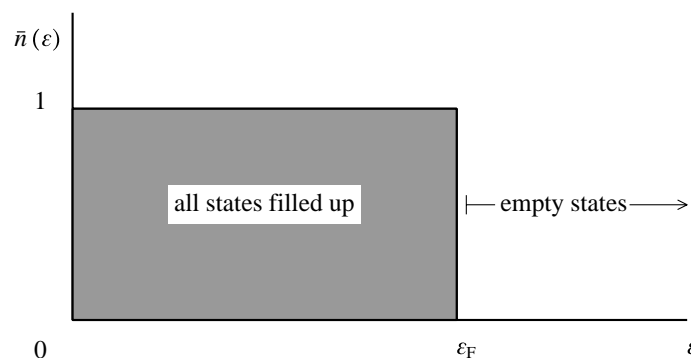
$$\bar{n}(\epsilon) = \frac{1}{\exp(\epsilon - \mu)/kT + 1}$$

becomes a box function

$$\begin{aligned} \bar{n}(\epsilon) &= 1 & \epsilon < \mu \\ &= 0 & \epsilon > \mu. \end{aligned}$$

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

$$\epsilon_F = \mu(T = 0).$$



Fermi-Dirac distribution at $T = 0$

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

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

and we shall consider spin $\frac{1}{2}$ particles, so we have set $\alpha = 2$. The total number of particles in the system is then

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

This may be inverted to obtain the Fermi energy

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

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

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 internal energy of the system. This is given by

$$E = \frac{V}{2\pi^2\hbar^3} (2m)^{3/2} \int_0^{\varepsilon_F} \varepsilon^{3/2} d\varepsilon$$

which may be expressed as

$$E = \frac{3}{5} N \varepsilon_F.$$

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

4.3.3 Fermi temperature and Fermi wavevector

Corresponding to the Fermi energy it proves convenient to introduce a *Fermi temperature* T_F defined by

$$kT_F = \varepsilon_F.$$

The Fermi temperature is then given by

$$T_F = \frac{\hbar^2}{2mk} \left(\frac{3\pi^2 N}{V} \right)^{2/3}$$

and in terms of this the condition for the classical approximation to be valid:

$$\frac{N}{V} \left(\frac{2\pi\hbar^2}{mkT} \right)^{1/2} \ll 1$$

becomes, to within a numerical factor

$$T \gg T_F.$$

We can estimate T_F for electrons in a metal. The interatomic spacing is roughly

$$\left(\frac{V}{N} \right)^{1/3} \sim 2.7 \text{ \AA},$$

giving a number density of

$$\frac{N}{V} \sim 5 \times 10^{22} \text{ electrons per cm}^3$$

if we assume that each atom contributes one electron. This gives

$$\varepsilon_F \sim 4.56 \text{ eV}$$

or

$$T_F \sim 5 \times 10^4 \text{ K.}$$

The conclusion, from this, is that the behaviour of electrons in a metal at room temperature are determined very much by quantum mechanics and the exclusion principle. For temperatures $T \ll T_F$ most of the energy states below ε_F are filled, while most above are empty. In this case the system is said to be *degenerate*. Thus electrons in a metal are degenerate at room temperatures.

Some values of Fermi temperatures calculated from known electron densities for monovalent metals are

	electron concentration in cm^{-3}	T_F in K
Li	4.7×10^{22}	5.5×10^4
Na	2.7×10^{22}	3.8×10^4
K	1.4×10^{22}	2.5×10^4
Rb	1.2×10^{22}	2.2×10^4
Cs	0.9×10^{22}	1.8×10^4

The case of ^3He is a little more complicated. The calculated value of T_F is $\sim 5\text{K}$, but the observed value is more in the region of 0.05K . This discrepancy is understood in terms of the interatomic interactions. A remarkably successful theory for this has been developed – Landau's Fermi liquid theory.

Other parameters can be used to specify the properties of the highest-energy fermions at $T = 0$. The energy of such a particle is ε_F . Alternatively we could talk of the velocity of the particle – the Fermi velocity. Similarly we can specify the Fermi momentum or the Fermi wavevector. The wavevector of the particles of energy ε_F is found from the expression

$$\varepsilon_F = \frac{\hbar^2}{2m} k_F^2,$$

or

$$k_F = \frac{1}{\hbar} \sqrt{2m\varepsilon_F}.$$

Using the expression for ε_F we then find:

$$k_F = \left(\frac{3\pi^2 N}{V} \right)^{1/3}$$

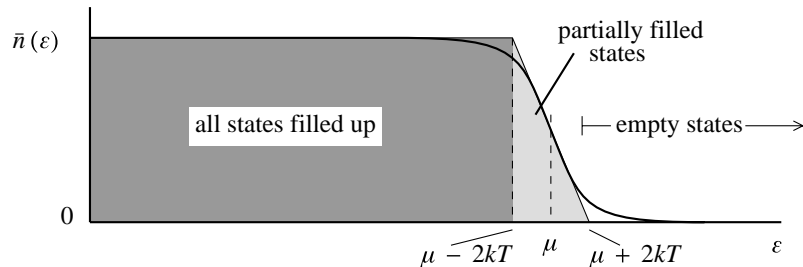
which depends only on concentration. In fact we see that the Fermi wavevector is approximately equal to the inter-particle spacing.

End of lecture 21

4.3.4 Qualitative behaviour of degenerate Fermi gas

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

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



Simple modelling of Fermi-Dirac distribution

In this model we see that there is a region of partially-occupied states extending from $\varepsilon = \mu - 2kT$ to $\varepsilon = \mu + 2kT$. States below this are totally filled and states above are empty. Most of the particles are “frozen in” to states below the Fermi energy. Only a small fraction $\sim T/T_F$ of the particles are practically excitable – having vacant states above and below them. It is only this fraction of the particles which is available for responding to stimuli.

Very crudely this is saying that at a temperature T extensive properties of a degenerate Fermi gas will be a fraction T/T_F of that of the corresponding classical system. The thermal capacity of a classical gas is $\frac{3}{2}Nk$, so we would expect the thermal capacity of a Fermi gas to be

$$C \sim \frac{T}{T_F} Nk$$

— the prediction is that C depends linearly on temperature. And indeed it does, as we shall see.

Similarly, since we saw that the magnetisation of a classical system of magnetic moments was inversely proportional to temperature: $M = CB/T$, Curie’s law where C here is the curie constant. So we expect the thermal capacity of a Fermi gas to be

$$M \sim \frac{CB}{T_F}$$

— the prediction is that the magnetisation will tend to a temperature-independent value. This is observed to be so.

4.3.5 Fermi gas at low temperatures – simple model

We shall now use the above piecewise approximation to calculate properties of the Fermi gas. At each stage we will compare the approximate result with the correct expression. The distribution function, in this approximation, is

$$\begin{aligned} \bar{n}(\varepsilon) &= 1 & 0 < \varepsilon < \mu - 2kT \\ &= 1 - \frac{\varepsilon - \mu + 2kT}{4kT} & \mu - 2kT < \varepsilon < \mu + 2kT \\ &= 0 & \mu + 2kT < \varepsilon \end{aligned}$$

from which the thermodynamic properties may be calculated.

The chemical potential may now be found by considering the total number of particles in the system:

$$N = \frac{4\pi V}{h^3} (2m)^{3/2} \int_0^\infty \bar{n}(\epsilon) \epsilon^{1/2} d\epsilon.$$

Using the approximate form for $\bar{n}(\epsilon)$ this gives

$$N = \frac{8\pi V}{3h^3} (2m\mu)^{3/2} + \frac{4}{3} (kT)^2 \frac{\pi V}{h^3} (2m)^{3/2} \mu^{-1/2} + \dots$$

If we express N in terms of the previously-calculated Fermi energy, in other words, in terms of the zero temperature chemical potential, then we have

$$\epsilon_F^{3/2} = \mu^{3/2} \left\{ 1 + \frac{1}{2} \left(\frac{kT}{\mu} \right)^2 + \dots \right\},$$

which, by the binomial theorem, gives ϵ_F as

$$\begin{aligned} \epsilon_F &= \mu \left\{ 1 + \frac{1}{2} \left(\frac{kT}{\mu} \right)^2 + \dots \right\}^{2/3} \\ &= \mu + \frac{1}{3} \frac{(kT)^2}{\mu} + \dots \end{aligned}$$

This may be solved for μ and re-expanded in powers of T to give (in terms of T_F rather than ϵ_F)

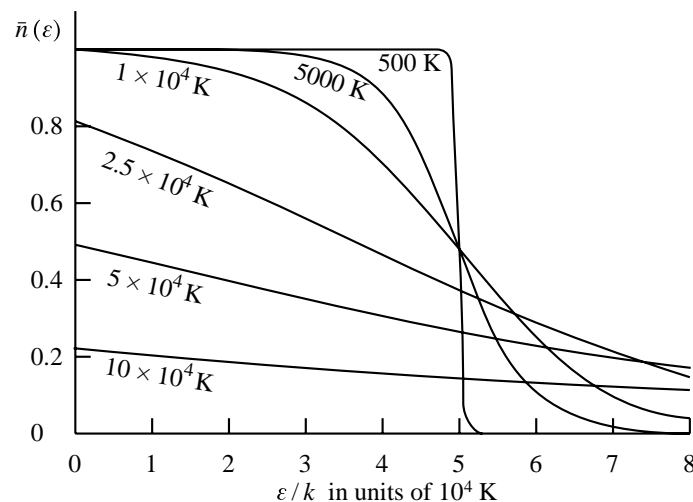
$$\mu = \epsilon_F \left\{ 1 - \frac{1}{3} \left(\frac{T}{T_F} \right)^2 + \dots \right\}.$$

The correct expression (i.e. not approximating the Fermi distribution) is very similar:

$$\mu = \epsilon_F \left\{ 1 - \frac{\pi^2}{12} \left(\frac{T}{T_F} \right)^2 + \dots \right\},$$

the leading temperature term being some 2.5 times greater. This result 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 .

From a knowledge of the temperature dependence of the chemical potential the Fermi-Dirac distribution is then given as a function of temperature and energy. The function is plotted below for electrons in a metal for which $T_F = 5 \times 10^4$ K.



Fermi-Dirac distribution function at different temperatures for a system for which $T_F = 5 \times 10^4$ K (electrons in a metal)

4.3.6 Internal energy and thermal capacity

In the spirit of the piecewise approximation of the Fermi-Dirac distribution, we can take the approximate chemical potential and use it in the piecewise approximation to find the internal energy of the fermions. In this way one finds

$$E = E_0 \left\{ 1 + \frac{5\pi^2}{2} \left(\frac{T}{T_F} \right)^2 + \dots \right\},$$

while the exact series expression is

$$E = E_0 \left\{ 1 + \frac{5\pi^2}{12} \left(\frac{T}{T_F} \right)^2 + \dots \right\},$$

up to terms in T^2 .

The thermal capacity at low temperatures is found by differentiating this expression for the internal energy. Thus we obtain

$$C_V = \left. \frac{\partial E}{\partial T} \right|_V = \frac{5}{6} \pi^2 E_0 \frac{T}{T_F^2},$$

or, eliminating E_0 in favour of T_F ,

$$C_V = \frac{1}{2} \pi^2 Nk \frac{T}{T_F}.$$

So at low temperatures the thermal capacity of a fermi gas is *linear* in temperature. Thus C_V goes to zero as T goes to zero, as required by the third law of thermodynamics.

The figure below shows the measured thermal capacity of potassium at low temperatures. It is conventional to plot C_V/T against T^2 in order to distinguish the linear electronic thermal capacity and the cubic phonon thermal capacity. In other words we are saying that the expected behaviour, when the effect of lattice vibrations is included, is

$$C_V = \frac{1}{2} \pi^2 Nk \frac{T}{T_F} + \text{const} \times T^3,$$

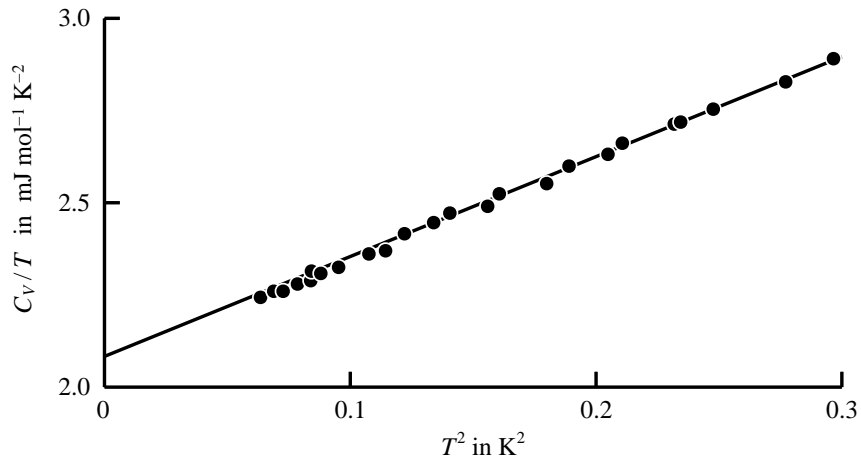
so that

$$\frac{C_V}{T} = \frac{1}{2} \pi^2 Nk \frac{1}{T_F} + \text{const} \times T^2.$$

Thus when C_V/T is plotted against T^2 the intercept gives the electronic contribution to C_V . The straight line fit to the data is given by

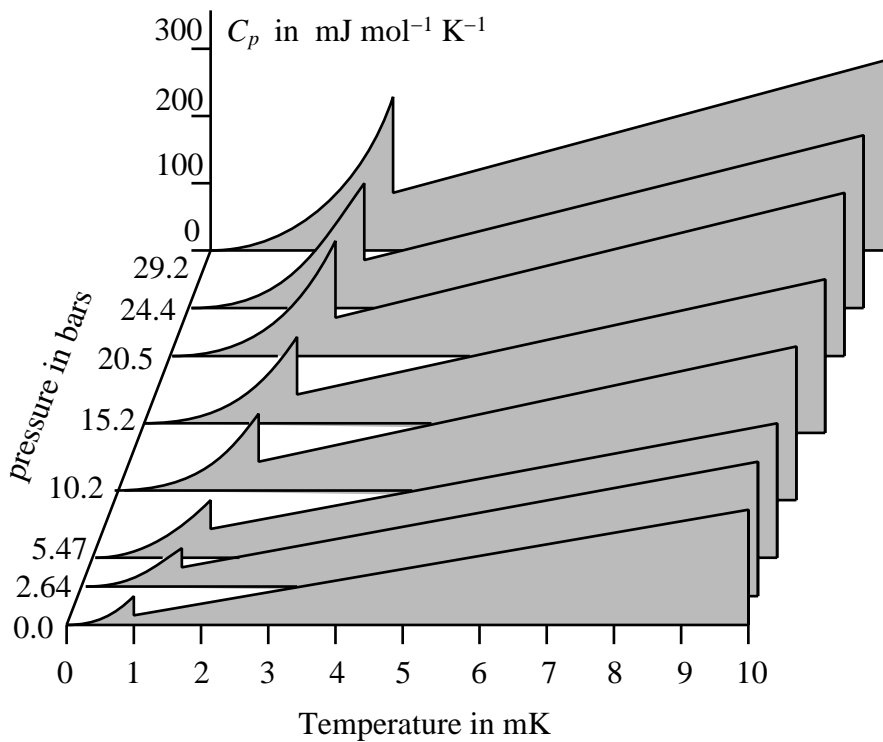
$$C_V/T = 2.08 + 2.57 T^2.$$

This corresponds to a Fermi temperature of 1.97×10^4 K (check this). This is in qualitative agreement with the T_F calculated from the known electron density, which was 2.5×10^4 K.



Thermal capacity of potassium

The thermal capacity of liquid ^3He at very low temperatures exhibits the expected linear temperature dependence. Measurements of C_p taken over a range of pressures are shown in the figure below. The linear behaviour is quite apparent. The strange behaviour occurring at very low temperatures corresponds to the superfluid phase transition. But that is another story ...



thermal capacity of liquid ^3He at different pressures

4.3.6 Equation of state.

— Not covered.

End of lecture 22

4.4 The Bose Gas

4.4.1 Generalisation of the density of states function

This section on the density of states is *not* specific to bosons. It is just that it is convenient to take a fresh look at the density of states at this stage with a view to some future applications, which *happen* to be boson systems.

Recall that the fundamental problem which the density of states addresses is the conversion of sums over states to integrals – in the case considered, integrals over energy. The energy density of states $g(\varepsilon)$ was defined by saying that the number of states with energy between ε and $\varepsilon + d\varepsilon$ is $g(\varepsilon)d\varepsilon$. This is compactly expressed in the equation

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

where $N(\varepsilon)$ is the number of states having energy less than ε . In Section 4.1.4 we obtained the expression for $g(\varepsilon)$ as

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

— in particular, the energy dependence goes as $\varepsilon^{1/2}$.

The derivation of this expression relied on a number of assumptions. It was for *free and nonrelativistic particles*: $\varepsilon = p^2/2m$. And the result applied to *three-dimensional systems*: we had three quantum numbers for the three spatial dimensions and we evaluated the *volume* of an octant. (So for instance we could not use the result for the treatment of surface waves or adsorbed films.)

In this section we shall relax the first restriction, allowing for other energy – momentum relations. The extension to other dimensions will simply be quoted. That derivation (actually quite simple) is left to the student. The general treatment here is best treated from a consideration of the density of states in k – space.

The starting point for the specification of the state of a system confined to a box is the fact that the wavefunction must go to zero at the walls of the box. This leads us to admit only states which comprise an integral number of half wavelengths within the box. The allowed values were denoted by

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

where

$$n_x, n_y, n_z = 1, 2, 3, 4, \dots$$

This gives us the components of the wave vector as

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

so that the wavevector is simply

$$\mathbf{k} = \frac{\pi}{V^{1/3}} \{n_x \mathbf{i} + n_y \mathbf{j} + n_z \mathbf{k}\}.$$

This is telling us that the allowed states of the system can be represented by the points on a rectangular grid in k – space. And in particular this indicates that the density of points in k – space is *uniform*.

To discuss the magnitude k of the wavevector \mathbf{k} it is convenient to define the quantity R as

$$R = \sqrt{n_x^2 + n_y^2 + n_z^2}$$

so that

$$k = \frac{\pi}{V^{1/3}} R.$$

Then we may say that the number of states for which the magnitude of the wavevector is less than k is given by the volume of the octant of radius R . That is,

$$N(k) = \frac{1}{8} \frac{4}{3} \pi R^3,$$

giving us

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

The density of states in k – space is the derivative of this:

$$g(k) = \frac{dN}{dk} = \frac{V}{2\pi^2} k^2.$$

Previously we were interested in the *energy* density of states $g(\varepsilon) = dN/d\varepsilon$, and this can now be found by the chain rule

$$\begin{aligned} g(\varepsilon) &= \frac{dN}{d\varepsilon} = \frac{dN}{dk} \frac{dk}{d\varepsilon} \\ &= \frac{V}{2\pi^2} k^2 \left| \frac{d\varepsilon}{dk} \right|, \end{aligned}$$

which is the most convenient way to represent the energy – wavevector derivative.

We also note here that the procedure generalises to the density of states expressed in terms of any other variable. For instance, we will be using (angular) frequency ω in a future application, and the chain rule may be used in exactly the same way to give

$$\begin{aligned} g(\omega) &= \frac{dN}{d\omega} = \frac{dN}{dk} \frac{dk}{d\omega} \\ &= \frac{V}{2\pi^2} k^2 \left| \frac{d\omega}{dk} \right|. \end{aligned}$$

Finally we quote the density of states in k – space for other dimensions:

$$\begin{aligned} g(k) &= \frac{L}{\pi} && \text{one dimension} \\ g(k) &= \frac{A}{2\pi} k && \text{two dimensions} \\ g(k) &= \frac{V}{2\pi^2} k^2. && \text{three dimensions} \end{aligned}$$

From these the density of states in any other variable may be found.

4.4.2 Examples of Bose systems

There are two important cases of bosons to consider.

- “Real” particles such as Helium-4, rubidium vapour etc.
- “Zero-mass” particles such as Photons and Phonons

Only the first is a real particle in the classical meaning of the word. The number of particles is conserved in the first case. This is in marked contrast to the second case; the number of photons or phonons is not conserved. This has important thermodynamic consequences. We will explore this later. We start the discussion of bosons with a survey of the properties of ^4He .

4.4.3 Helium - 4

Liquid ^4He displays the remarkable property of superfluidity below a temperature of 2.17 K. Two of the most startling properties of the system are

- Viscosity $\rightarrow 0$
- Thermal conductivity $\rightarrow \infty$!!

On the other hand liquid ^3He shows no such behaviour (at these temperatures). This implies that superfluidity is closely related to the statistics of the particles.

If we consider an assembly of non-interacting bosons it is quite clear that at $T = 0$ all particles will be in the same quantum state – the single-particle ground state. This is in contrast to the Fermi case where the Pauli exclusion principle forbids such behaviour. For bosons it then seems obvious that at very low temperatures there will be a macroscopic number of particles still in the ground state. This number may be calculated:

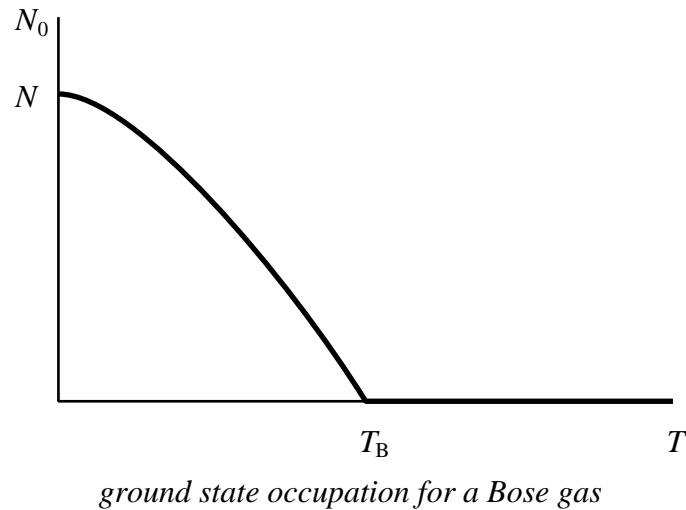
$$N_0 = N \left[1 - \left(\frac{T}{T_B} \right)^{3/2} \right]$$

where N is the total number of particles in the system and the temperature T_B in the expression is given by

$$T_B = \frac{h^2}{2\pi mk} \left[\frac{N}{2.612 V} \right]^{2/3}.$$

[The calculation of N_0 is slightly messy. It follows the calculation of N as in the Fermi case, converting the sum over single-particle states for N by an integral using the energy density of states $g(\epsilon)$. But in this case one must recognise that the density of states, being proportional to $\epsilon^{1/2}$, excludes the ground state which must be put in “by hand”.]

The temperature T_B is close to the Fermi temperature, so it indicates the temperature at which specifically *quantum* behaviour will occur. Below we plot a graph of the ground state occupation.



For temperatures $T > T_B$ there will be some particles in the ground state. However it will not be a *macroscopic* number. The plot indicates that for temperatures $T < T_B$ there *will* be a macroscopic number of particles in the ground state.

The particles in the ground state will have no entropy. It is therefore to be expected that the behaviour of this system will be different below and above this temperature T_B . If we estimate this temperature for liquid ${}^4\text{He}$, using the measured molar volume of 27 cm^3 then we obtain

$$T_B \sim 3.13 \text{ K.}$$

The agreement with the superfluid transition temperature of liquid ${}^4\text{He}$, 2.17 K, is fair when we consider that the atoms of ${}^4\text{He}$ do actually interact and so they cannot really be considered as an ideal (noninteracting) gas,

This collapse of particles into the ground state below T_B is known as *Bose-Einstein condensation*. It is the only example of a phase transition occurring in a system of noninteracting particles.

We see then that the superfluidity of ${}^4\text{He}$ is understood in terms of a Bose-Einstein condensation.

⌈ Superfluidity of ${}^3\text{He}$ is observed at temperatures below 3 mK; we saw the indication of this in the heat capacity curves for liquid ${}^3\text{He}$ above. And superfluidity of electrons – superconductivity – is observed in some metals and metal oxide compounds. These examples of the superfluidity of fermions cannot be understood in terms of a simple Bose-Einstein condensation. In these cases it is believed that the fermions form pairs, that will be bosons. Superfluidity in Fermi systems is understood in terms of a Bose-Einstein condensation of these pair bosons. ⌋

End of lecture 23

4.4.4 Phonons and photons — quantised waves

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

$$\varepsilon_n = n\hbar\omega + \text{zero point energy.}$$

We have already calculated the internal energy of a harmonic oscillator. We shall write this result here as

$$E = \frac{\hbar\omega}{\exp\frac{\hbar\omega}{kT} - 1} + \text{zero point contribution.}$$

We shall, in the following sections, ignore the (constant) zero point energy contribution. This is allowed since in reality we would always differentiate such expressions to obtain measurable quantities.

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

$$E = \bar{n} \hbar\omega$$

where \bar{n} is the Bose distribution, the mean number of bosons of energy $\hbar\omega$. But here 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:

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

(E and V are constant since the system is isolated.)

Now from the differential expression for the First Law

$$dE = TdS - pdV + \mu dN$$

we see that

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

So the entropy derivative is

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

and we conclude that the equilibrium condition for this system (at finite temperature) is simply

$$\mu = 0.$$

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

We seem to have arrived at a particle description through the quantisation of harmonic vibrations. These ideas can be applied to simple harmonic oscillations in:

- waves in solids (and liquids) — phonons
- electromagnetic waves — photons.

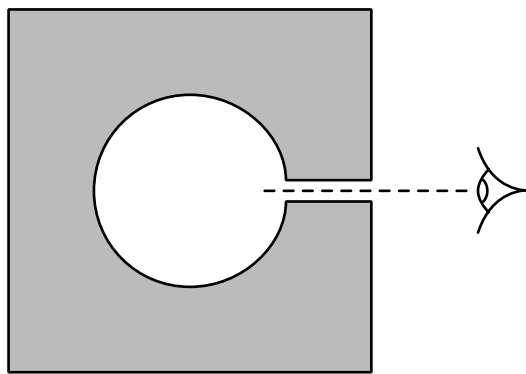
In both these cases we may have a range of frequencies or energies ($\varepsilon = \hbar\omega$) so that in calculations of thermodynamic properties we will need to calculate the density of these states.

4.4.5 Photons in thermal equilibrium – black body radiation

Black body radiation was a big problem before the advent of quantum theory. There was a simply-stated problem without a satisfactory solution. It is known that bodies glow and emit light when heated sufficiently. The spectrum of colours seems to depend little on the nature of the body, particularly if the surface is black. The problem is to explain this *universal* behaviour – the shape of the spectrum as a function of temperature.

In considering the spectrum of the radiation the universality gives the first hint of the solution; it must be a property of the body 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.



radiation from a cavity

We consider the light waves in the cavity 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. To calculate the properties of this system we then use the Bose-Einstein distribution function together with the photon density of states. The internal energy can immediately be written down:

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

where α is the degeneracy factor, here 2 for the 2 transverse polarisations of the photon. The energy of a photon of frequency ω is

$$\varepsilon(\omega) = \hbar\omega.$$

The formula for the density of frequency states is

$$g(\omega) = \frac{V}{2\pi^2} k^2 \left| \frac{d\omega}{dk} \right|$$

and since for photons

$$\omega = ck$$

where c is the speed of light. This gives us the frequency density of states as

$$g(\omega) = \frac{V}{2\pi^2} \frac{\omega^2}{c^3}.$$

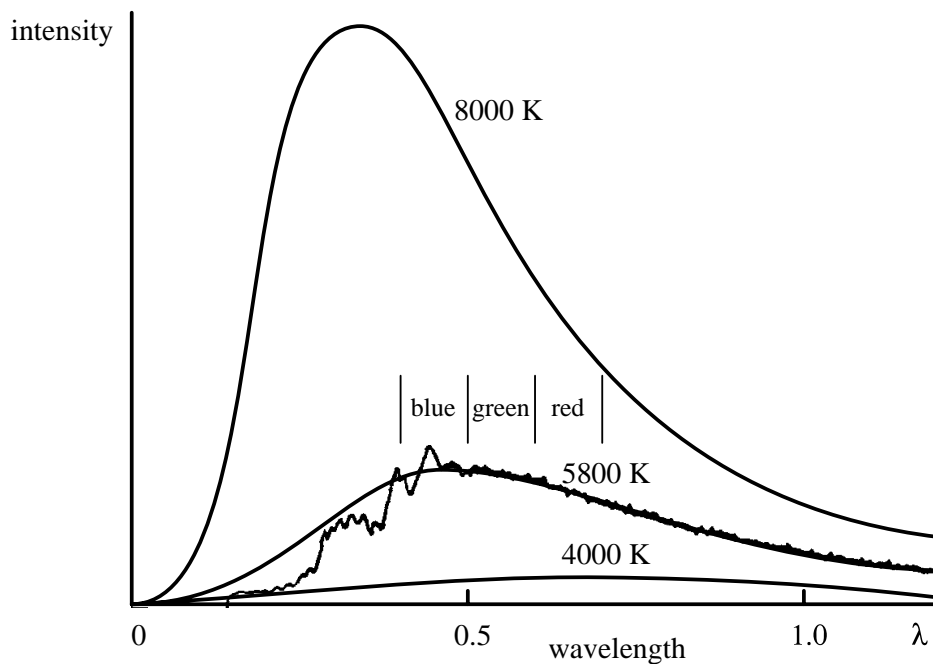
The internal energy is then

$$E = \frac{Vh}{\pi^2 c^3} \int_0^\infty \frac{\omega^3 d\omega}{\exp \frac{h\omega}{kT} - 1}.$$

Before performing this integral we note that its argument gives the energy density per unit frequency range:

$$\frac{dE}{d\omega} = \frac{Vh}{\pi^2 c^3} \frac{\omega^3}{\exp \frac{h\omega}{kT} - 1}.$$

This is *Planck's formula* for the spectrum of black body radiation. An example is shown in the figure, but plotted as a function of wavelength, which is more popular with spectroscopists.

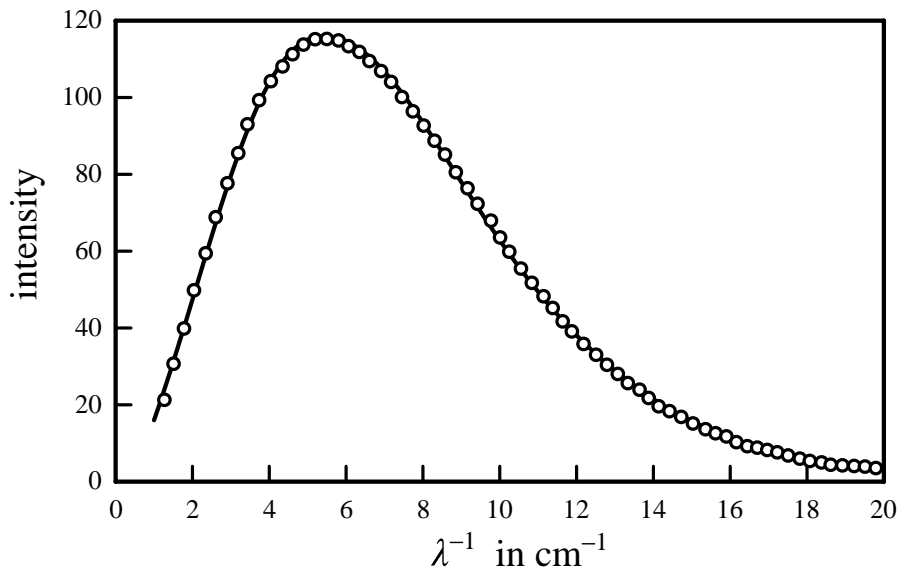


*black body radiation at three different temperatures
the wiggly line is the spectrum from the sun*

The spectrum from the sun indicates that the sun's surface temperature is about 5800 K. It is also interesting 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 observed arriving from outer space. It is found that when looking into space with radio telescopes, a uniform background of electromagnetic "noise" is seen. The spectrum of this is found to fit the black body curve – for a temperature of about 2.7 K. The conclusion is that the equilibrium temperature of the

universe is 2.7 K, which is understood as the remaining “glow” from the Big Bang. The data shown below comes from the COBE satellite, and it fits to the Planck black body curve for a temperature of 2.735 K. The quality of the fit of the data to the theoretical curve is quite remarkable.



cosmic background radiation plotted on 2.735 K black body curve

End of lecture 24

4.4.6 The spectrum maximum

When a body is heated it goes from a dull red at lower temperatures, to a bluish white at higher temperatures. The perceived colour of the radiation can be found by examining the peak in the emission spectrum. Let us first find the maximum of the energy density

$$\frac{dE}{d\omega} = \frac{V\hbar}{\pi^2 c^3} \frac{\omega^3}{\exp \frac{\hbar\omega}{kT} - 1}.$$

Upon differentiation and setting equal to zero we obtain

$$\left(3 - \frac{\hbar\omega}{kT}\right) \exp \frac{\hbar\omega}{kT} = 3.$$

This can not be solved analytically, but the solution may be found very easily by iteration using a pocket calculator. The result is

$$\frac{\hbar\omega}{kT} = 2.8214\dots$$

This specifies the maximum in the spectrum:

$$\omega_{\max} = 2.8214 \frac{kT}{\hbar},$$

which in S.I. units is

$$\omega_{\max} = 3.67 \times 10^{11} T.$$

The peak in the spectrum, ω_{\max} is proportional to the temperature. This is known as *Wein's displacement law*. The magnitude of the energy density at the maximum may be found by substituting ω_{\max} back into the expression for the energy density spectrum:

$$\left. \frac{dE}{d\omega} \right|_{\text{peak}} = 1.421 \frac{V k^3 T^3}{\pi^2 c^3 \hbar^2}$$

so the magnitude of the peak scales with the cube of the temperature.

4.4.7 Internal energy and thermal capacity of a photon gas

The internal energy is found by integrating the expression for the energy density. We have already encountered the expression:

$$E = \frac{V\hbar}{\pi^2 c^3} \int_0^\infty \frac{\omega^3 d\omega}{\exp \frac{\hbar\omega}{kT} - 1}.$$

By changing the variable of integration to

$$x = \frac{\hbar\omega}{kT}$$

the integral becomes a dimensionless number

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

The integral may be evaluated numerically, or it may be solved in terms of the gamma function to give

$$\int_0^\infty \frac{x^3 dx}{e^x - 1} = \frac{\pi^4}{15}$$

so that the internal energy is

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

From the expression for the internal energy we may find the pressure of the photon gas using

$$pV = \frac{1}{3}E,$$

which gives, in S.I. units

$$p = 2.47 \times 10^{-16} T.$$

This is obviously related to the radiation pressure treated in electromagnetism. Note that the pressure is very small indeed.]

Turning now to the thermal capacity, we obtain this by differentiating the internal energy:

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

giving

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

We see that C_V is proportional to T^3 . Also note that the thermal capacity goes to zero as $T \rightarrow 0$ as required by the Third Law.

4.4.8 Energy flux

Finally we consider the energy carried by a photon gas. This is particularly important when treating the energy flow through radiation from a hot body to a cold body.

Kinetic theory tells us that the energy flux, the power per unit area e carried by particles of velocity c is given by

$$e = \frac{1}{4} c \frac{E}{V}.$$

We thus find immediately

$$e = \frac{\pi^2 k^4}{60 \hbar^3 c^2} T^4.$$

The energy flux is proportional to the *fourth* power of the temperature. This is known as the *Stefan-Boltzmann radiation law*. This result is conveniently written as

$$e = \sigma T^4$$

where σ is Stefan's constant:

$$\sigma = 5.68 \text{ W m}^{-2} \text{ K}^{-4}.$$

The net energy flux between two bodies at different temperatures is given by the difference between the fluxes in either directions. Thus

$$e_{\text{net}} = \sigma (T_{\text{h}}^4 - T_{\text{c}}^4)$$

where T_{h} is the temperature of the hot body and T_{c} is the temperature of the cold body.

Remember that these results hold for black bodies – perfect absorbers of the radiation. The flux between shiny surfaces will be considerably reduced.

4.4.9 Phonons – Debye model of a solid

The Einstein model of a solid was successful in that it showed that the thermal capacity went to zero as the temperature was reduced. But the exponential reduction in C_V was not in accord with the experimentally-observed T^3 behaviour. The problem with the Einstein model was that it treated each atom as if its motion were independent of that of its neighbours. In practice the vibrations are coupled and this leads to the propagation of waves throughout the solid with a range of oscillation frequencies.

Phonons (sound waves) are different from photons (light waves) in that they propagate in a discrete medium. This leads to a maximum frequency of oscillation since the wavelength can not be less than the interparticle spacing. Since there are N particles, each with three directions of oscillation, the system will have $3N$ degrees of freedom. There will then be $3N$ modes of oscillation – recall ideas on normal modes from your mechanics courses. This will enable us to find the maximum frequency of oscillation of the propagating waves. Counting all the modes up to the maximum frequency we have

$$\int_0^{\omega_{\text{max}}} \alpha g(\omega) d\omega = 3N$$

where α is the degeneracy factor, here 3 for the three polarisations of the wave or three directions of oscillation and $g(\omega)$ is the frequency density of states given by

$$g(\omega) = \frac{V}{2\pi^2} k^2 \left| \frac{d\omega}{dk} \right|.$$

To proceed we must thus find the $\omega - k$ relation, the *dispersion relation* for the propagating waves. You might recall having calculated $\omega \propto |\sin ka/2|$ for a one-dimensional chain. For small wavenumber k this reduces to a linear relation, $\omega = ck$. Here the speed of propagation is independent of k . In the Debye model this linear relation is assumed to hold over the entire allowed frequency range. We have an indication that we should be on the right track to obtain the correct low-temperature behaviour since at low temperatures only the lowest k states will be excited. And we have

already seen that a linear dispersion relation leads, in three dimensions, to a cubic thermal capacity (photons). So we are assuming the relation

$$\omega = ck,$$

where c is the speed of sound, up to the cutoff frequency. This gives us the frequency density of states as in the photon case

$$g(\omega) = \frac{V}{2\pi^2} \frac{\omega^2}{c^3}.$$

In practice the velocity of propagation may be different for the different polarisations. This may be accounted for by writing

$$\frac{1}{c^3} = \frac{1}{3} \left\{ \frac{1}{c_1^3} + \frac{1}{c_2^3} + \frac{1}{c_3^3} \right\}.$$

The cutoff frequency ω_{\max} is found from

$$\int_0^{\omega_{\max}} 3 \frac{V}{2\pi^2} \frac{\omega^2}{c^3} d\omega = 3N,$$

which may be integrated up to give

$$\omega_{\max} = \frac{6N\pi^2 c^3}{V}.$$

And the density of states may be expressed in terms of this frequency:

$$g(\omega) = 3N \frac{\omega^2}{\omega_{\max}^3}.$$

4.4.10 Phonon internal energy and thermal capacity

The internal energy is similar to that for the photon case, except that here the integral over frequency has a cutoff rather than going of to infinity:

$$E = \int_0^{\omega_{\max}} \alpha \varepsilon(\omega) g(\omega) \bar{n}(\omega) d\omega.$$

Here α is the degeneracy factor 3 and the energy of a phonon of frequency ω is

$$\varepsilon(\omega) = \hbar\omega.$$

Using our above formula for the phonon density of frequency states, this gives

$$E = \frac{9N\hbar}{\omega_{\max}^3} \int_0^{\omega_{\max}} \frac{\omega^3 d\omega}{\exp \frac{\hbar\omega}{kT} - 1}.$$

Because of the finite upper limit of the integral, it is impossible to obtain an analytic expression for E . Only a numerical solution is possible.

To find the thermal capacity we must differentiate the internal energy. Only the Bose-Einstein factor depends on temperature, and differentiating this gives

$$\frac{d}{dT} \frac{1}{\exp \frac{\hbar\omega}{kT} - 1} = \frac{\hbar\omega}{kT^2} \frac{\exp \frac{\hbar\omega}{kT}}{(\exp \frac{\hbar\omega}{kT} - 1)^2}.$$

The expression for C_V is then

$$C_V = \left. \frac{\partial E}{\partial T} \right|_V = \frac{9N\hbar^2}{\omega_{\max}^3 kT^2} \int_0^{\omega_{\max}} \frac{\omega^4 \exp \frac{\hbar\omega}{kT} d\omega}{(\exp \frac{\hbar\omega}{kT} - 1)^2}.$$

Again, this is impossible to integrate. However simplification is possible by changing the variable of integration to

$$x = \frac{\hbar\omega}{kT}.$$

Also we introduce a temperature corresponding to the cutoff frequency:

$$\theta_D = \frac{\hbar\omega_{\max}}{k}.$$

The thermal capacity can then be written as

$$C_V = 9Nk \left(\frac{T}{\theta_D}\right)^3 \int_0^{\theta_D/T} \frac{x^4 e^x dx}{(e^x - 1)^2}.$$

The integral is a function of θ_D/T only and it may be calculated numerically. The function

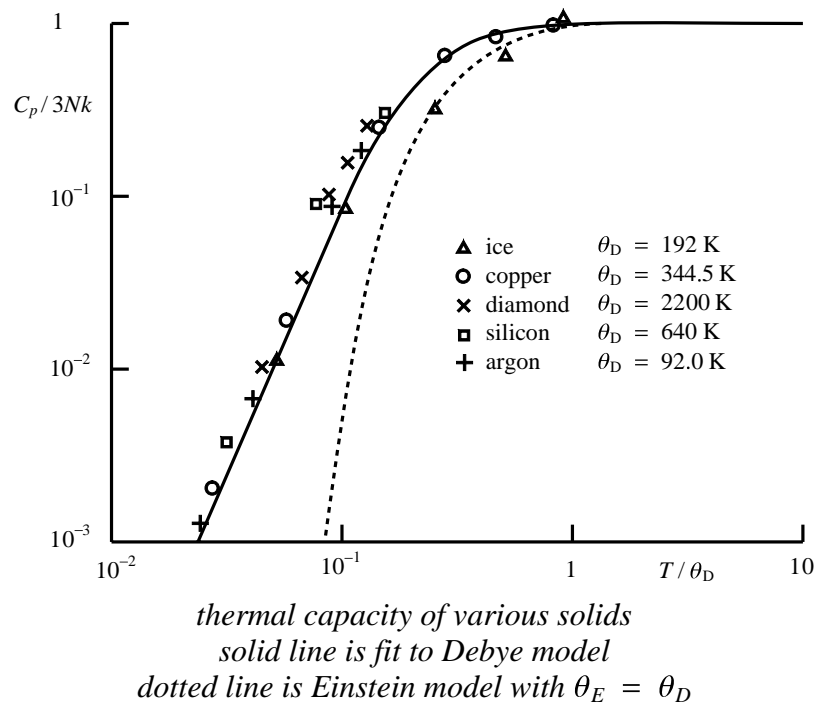
$$F_D(y) = \frac{3}{y^3} \int_0^y \frac{x^4 e^x dx}{(e^x - 1)^2}$$

is called the Debye function and it is tabulated in the American Institute of Physics handbook. In terms of this function the thermal capacity is

$$C_V = 3NkF_D\left(\frac{\theta_D}{T}\right).$$

Observe that the thermal capacity is a *universal function* of T/θ_D .

The graph shows thermal capacity against T/θ_D for a variety of substances. The fit is impressive and it supports the universality idea. (C_p is shown rather than C_V as it is easier to measure. But for solids we know that $C_p \sim C_V$.) Certainly the Debye model gives a better fit to the data than does the Einstein model.



4.4.11 Limiting forms at high and low temperatures

At high temperatures we recover the usual classical behaviour:

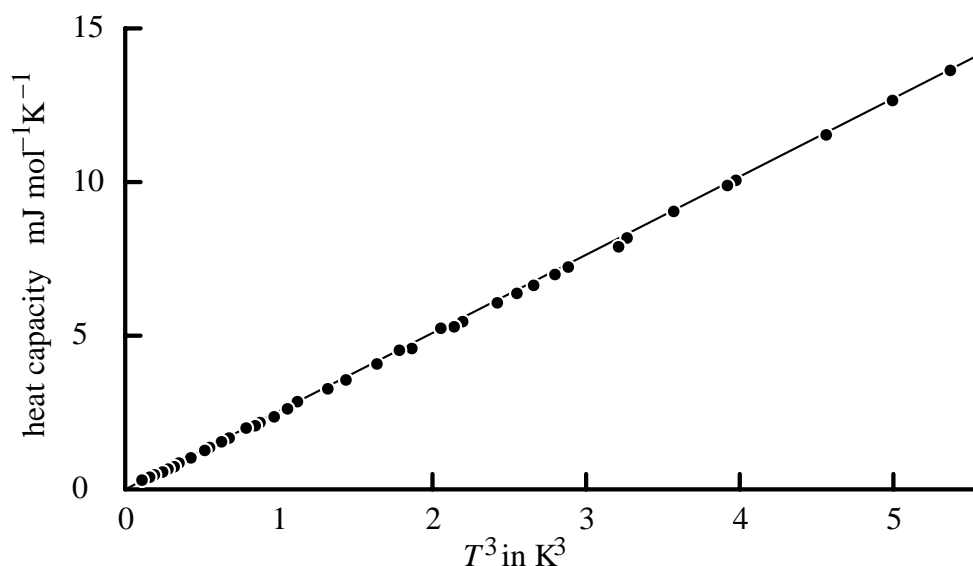
$$C_V = 3Nk \quad \text{for} \quad T \gg \theta_D.$$

As $T \rightarrow 0$ the upper limit of the integral tends to infinity and the integral tends to a constant number, just as in the photon case. The thermal capacity then has the characteristic T^3 behaviour, in this case:

$$C_V \sim \frac{12}{5}\pi^4 Nk \left(\frac{T}{\theta_D}\right)^3.$$

This is the important cubic behaviour that is observed experimentally, but which the Einstein model did not give.

The following figure shows the heat capacity of solid argon plotted against T^3 . This shows the quality of the fit at low temperatures.

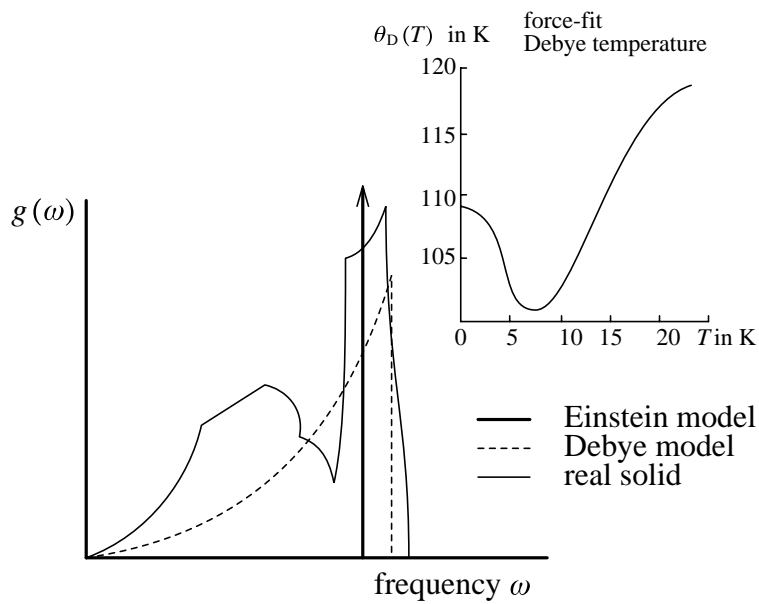


heat capacity of solid argon at low temperatures

The Debye model should be regarded as an interpolation procedure. It gives the correct behaviour at high and low temperatures. It is not quite so good in the middle range. Here the precise density of states, obtained from the correct dispersion relation, is important. Our expression for $g(\omega)$ was only an approximation, treating the solid as a continuum (linear $\omega - k$ relation), but with a frequency cutoff. In reality the equations of motion for the system must be solved to obtain the correct $\omega(k)$ relation, and from that the real density of states $g(\omega)$ – but of course that is impossible.

The figure below shows $g(\omega)$ for a real solid together with the forms predicted by the two models:

Einstein model	$g(\omega) \propto \delta(\omega - \omega_E)$
Debye model	$g(\omega) \propto (\omega/\omega_D)^2$ up to cutoff.



The real density of states contains kinks and spikes. In this respect it has some features of the Einstein model delta function. So both the Einstein model and the Debye models contain some aspects of the truth. But of course, as we have argued already, the Debye model is more appropriate at explaining the low temperature behaviour.

An alternative viewpoint is to adopt the Debye model but to force agreement with the temperature dependence of the thermal capacity by allowing the Debye temperature to vary with temperature. Such a temperature variation is shown in the inset to the figure.

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End of lecture 25