

Statistical Mechanics Lecture Notes 3 - Quantum statistics and its applications

Sankalpa Ghosh, Physics Department, I I T Delhi

April 8, 2008

This part has been mostly taken from Amit and Verbin, Bhattacharjee, Pathria and Reif and some updating to correct the innumerable typos and to supplement some portion will go on and students will be informed.

1 Grand Canonical Ensemble

$$\begin{aligned} Q(T, V, \mu) &= \sum_N e^{\beta\mu N} \sum_i e^{-\beta E_i} \\ &= \sum_N e^{\beta\mu N} Z(T, V, N) \\ &= e^{\beta[\mu N - F(T, V, N)]} \end{aligned}$$

Following relations are useful

$$P = \frac{1}{\beta} \frac{\partial \ln Q}{\partial V}$$
$$N = \frac{1}{\beta} \frac{\partial \ln Q}{\partial \mu}$$

We also define the thermodynamic potential for the Grand canonical ensemble namely

$$\Omega = -kT \ln Q$$

which is the generalization of the relation

$$F = -kT \ln Z$$

for the canonical ensemble

We also have the standard thermodynamic relations from the following relation for Ω

$$d\Omega = -SdT - PdV - Nd\mu$$

2 Introduction

The passage to the statistical mechanics of systems identical quantum particles is achieved in two steps. First step is the appearance of the quantum states. These are generally obtained from stationary or time dependent equations that controls the dynamics of the quantum state. For example, in the well known framework of non-relativistic quantum mechanics, such states correspond to the solutions of the Schrödinger equations. The second step is how the particles are distributed in these quantum states. This is where quantum statistics comes into the picture. This two steps also has to be consistent with each other since the quantum description of any entity (call it particles or whatever) is very different from its classical description.

In the first step one takes into consideration that quantum particles cannot be described by full specifications of their co-ordinate and momentum, because of the uncertainty principle. Instead particles are described by wave functions which satisfy by container to which are they are confined. If the particles are non-interacting, then they are independent of each other and each particle is described by its own wave function.

We shall take a particular example. The wave function of a particle in a rectangular box is a standing in each of the three perpendicular directions. As we know, the wave function of a particle in a rectangular box is a standing wave in each of the three perpendicular directions. Such a state is specified by three integers n, p, q which determine the allowed wavelengths, or wave numbers along the three perpendicular directions and the corresponding three components of the De Broglie momentum. Such a set of three integers that determine the state of the particle, we denote it schematically as a single index k .

The principal effect of quantum Mechanics on the thermodynamic properties of the systems of identical particles is brought about by the quantum mechanical constraints on the identification of allowed, distinguishable microscopic state of the system. Such constraints follow from the symmetry properties that must be obeyed by wave function of many identical particles. The discussion of the underlying wavefunction requires more advanced introduction of the quantum mechanics. Here it suffices to mention that all

possible quantum particles may be divided into two types

- Fermi Dirac particles or (Fermions) No single particle states can be occupied by more than one particle. This is Pauli's exclusion principle. Here the states are characterized by the occupation numbers that can be either 0 and 1. The any set of $\{0, 1\}$ occupation numbers correspond to a microscopic state of the system. Fermions are found to possess half-integer spins
- Bose- Einstein particles (or bosons) single particle states can be occupied by any number of particles, but for any distribution of occupation numbers there is a single microscopic state of the system.

Let us now briefly mention about two different ways of identifying the microscopic state of a system of many particles. Both ways use single particle states denoted by $\{k\}$. In the first way we can only treat distinguishable particles by labeling the microscopic states with N numbers with $\{k_j\}$ with $j = 1, \dots, N$. It leads to a partition function which is the N -th power of the partition function of a single particle.

This way is incompatible with the indistinguishability of the identical particles and leads to the Gibbs paradox and is remedied by introducing the factor $\frac{1}{N!}$ in the partition function.

The alternative way of specifying the microscopic states uses occupation numbers $\{n_k\}$. The partition sum will be then over all possible sets of the occupation numbers over all possible single particle states respecting the constraint on the total number of particles. This can be carried out to reproduce the classical result for the partition function, provided one keeps in mind that the number of N -particle states that correspond to a given distribution of n_k 's is

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

On the other hand in quantum statistics a state with a given set of $\{n_k\}$ corresponds to a single microscopic state. This makes computing the canonical partition sum for the systems of particles impossible.

2.1 Thermodynamics of Fermions and Bosons

The partition function of an ideal gas of identical particles is a sum over all values of n_k as follows:

$$Z = \sum_{n_1, n_2, \dots, n_k, \dots} e^{\beta E(n_1, n_2, \dots, n_k, \dots)}$$

If we neglect the forces between the particles, the total energy of the states is the sum of single particles energy and is given by

$$E = \sum_k n_k \epsilon_k$$

Thus we have

$$Z = \sum_{n_1, n_2, \dots, n_k, \dots} \exp[-\beta(n_1 \epsilon_1 + n_2 \epsilon_2 + \dots + n_k \epsilon_k + \dots + \dots)]$$

The above sum cannot be written as a product of independent sums over each occupation number because of the constraint

$$\sum_k n_k = N$$

and therefore,

$$Z \neq \sum_{n_1} (e^{-\beta \epsilon_1 n_1}) \left(\sum_{n_2} e^{-\beta \epsilon_2 n_2} \right) \dots \left(\sum_{n_k} e^{-\beta \epsilon_k n_k} \right) \dots$$

Since what is blocking the factorization of the canonical partition function, is the constraint implied by the fixed number of particles, we turn to grand canonical ensemble. The constraint is removed at the expense of the chemical potential μ .

We turn to eq. where a microscopic state α is characterized by all the occupation number $\{n_k\}$. The set $\{n_k\}$ determines the total number of particles via the above mentioned constraints. Hence the Grand canonical partition function or the grand partition function

$$\begin{aligned} Q(T, V, \mu) &= \sum_{\alpha} [\beta(\mu N - E_i)] \\ &= \sum_{\{n_k\}} \exp \left[\sum_{k=1}^{\infty} n_k (\mu - \epsilon_k) \right] \end{aligned}$$

Now there is constraint on the occupation numbers. They take on independent values, provided those are consistent with the particles statistics. Hence it is possible to write Q as

$$Q = \prod_k \sum_{n_k} e^{\beta(\mu - \epsilon_k)n_k}$$

We now need to calculate the summations in the above product, namely

$$Q_k = \sum_{n_k} e^{\beta(\mu - \epsilon_k)n_k}$$

Quantum statistics dictates two options, either $n_k = 0, 1$, for a gas of **fermions** or $n_k = 0, 1, \dots, \infty$ for **bosons**.

$$\begin{aligned} Q_k^F &= \sum_{n_k=0}^1 \\ &= 1 + e^{\beta(\mu - \epsilon_k)} \end{aligned}$$

while for bosons the right hand side is an infinite geometric series

$$\begin{aligned} Q_k^B &= \sum_{k=0}^{\infty} e^{\beta(\mu - \epsilon_k)} \\ &= (1 - e^{\beta(\mu - \epsilon_k)})^{-1} \end{aligned}$$

Note that the above summation converges only when μ is lower than all energy levels of the system including the ground level. If the ground level is $\epsilon_1 = 0$, then the chemical potential is 0.

Conversely for the fermions the summation consists only of two terms and thus there is no such constraint and thus there is no such constraint on the chemical potential of a gas of fermions.

Next step is to calculate the thermodynamic potential which is the equivalent of the free energy for a grand canonical potential.

The Thermodynamic potential can be readily calculated from the grand partition function.

$$\begin{aligned} \Omega^F &= -\frac{1}{\beta} \sum_k \ln(1 + e^{\beta(\mu - \epsilon_k)}) \\ \Omega^B &= -\frac{1}{\beta} \sum_k \ln(1 - e^{\beta(\mu - \epsilon_k)}) \end{aligned}$$

From these expressions for Ω , and given the energy we can proceed to calculate all the thermodynamic properties of the system, as function T , V and μ .

In the grand canonical ensemble the number of particles are not fixed. However the probability distribution of the different states is such that the number actually fluctuates very little around an average number that is determined by T, V, μ .

This average is given by

$$N^F = -\left(\frac{\partial \Omega^F}{\partial \mu}\right)_{V,T} = \sum_k \frac{1}{e^{\beta(\epsilon_k - \mu)} + 1}$$

$$N^B = -\left(\frac{\partial \Omega^B}{\partial \mu}\right)_{V,T} = \sum_k \frac{1}{e^{\beta(\epsilon_k - \mu)} - 1}$$

Now N^F and N^B are actually average number of particles in states at thermodynamic equilibrium and in principle should be denoted by $\langle N \rangle$. But since the fluctuation is very small we retain the notation without $\langle \rangle$.

Since N is a sum over all single particle states each term of the sum corresponds to a given single particle state k , the average number of particles in the state. For a state k with energy ϵ_k .

$$\langle n_k^{(F)} \rangle = \frac{1}{e^{\beta(\epsilon_k - \mu)} + 1}$$

$$\langle n_k^{(B)} \rangle = \frac{1}{e^{\beta(\epsilon_k - \mu)} - 1}$$

The above quantities are also known as the occupation number for fermions and bosons.

The average number of bosons in a given state looks familiar. In the derivation of the specific heat of solid the average number of excitation of a harmonic oscillator is given exactly by the same expression with $\mu = 0$. The connection between them becomes clear if the excited states of the harmonic oscillator is treated as particles **phonons with energy $\hbar\omega$** . Then the average number of phonons with a frequency ω in the crystal is the average degree of excitation of the oscillator that was discussed in the earlier case.

The average occupation number for the fermions is consistent with the Pauli exclusion principle. The denominator is always greater than 1. If the variable $n_k^{(F)}$ takes the value 0 and 1 only, then its thermal average must

be less than 1 and hence the average $\langle n_k^{(F)} \rangle < 1$. Bosons on the other hand do not obey Pauli exclusion principle and at low temperature try to accumulate at the ground state.

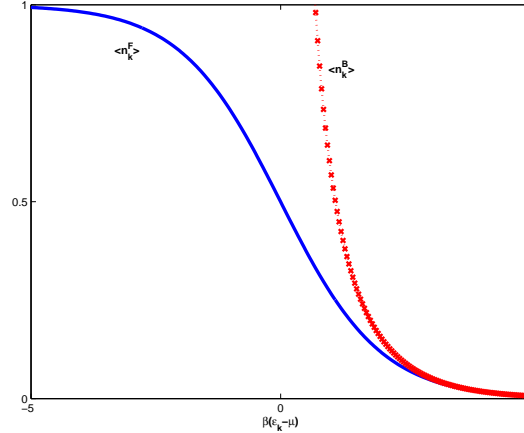


Figure 1: *The Fermi and Bose occupation number. Lower part of the both curves are identical and same as Maxwell Boltzman statistics*

Only the thermal fluctuation stop them all ending up in the ground state. In fact that the above form of $\langle n_k^B \rangle$ reveals that indeed the occupation number increases with decreasing ϵ_k and diverges for $\epsilon_k \rightarrow \mu$

In the figure we have plotted the occupation number as a function of $\beta(\epsilon - \mu)$. This allows us to study the behavior on ϵ at constant T , or alternatively the dependence of temperature T at fixed energy T .

As can be seen from the above plot, for large values $\beta(\epsilon - \mu)$ the two graphs merge, since the exponential dominates the denominator. . This is where the both distribution tends towards the classical approximation. - the **Maxwell Boltzmann** distribution.

3 Ideal gas in the classical limit—Derivation using quantum statistics

3.1 Quantum states of a single particle

Consider a free particle . The wave function (probability amplitude) of the free particle is just plane wave

$$\Psi = A e^{i(\boldsymbol{\kappa} \cdot \mathbf{r} - \omega t)}$$

The energy and the momentum of the particle follows

$$\begin{aligned}\epsilon &= \hbar\omega \\ \mathbf{p} &= \hbar\boldsymbol{\kappa} \\ \epsilon &= \frac{\mathbf{p}^2}{2m} = \frac{\hbar^2\mathbf{k}^2}{2m}\end{aligned}$$

All these can be systematically derived from the Schrödinger equation which is

$$i\hbar\frac{\partial\Psi}{\partial t} = H\Psi$$

Where

$$H = \frac{1}{2m}\mathbf{p}^2 = -\frac{\hbar^2}{2m}\nabla^2$$

Solving these equation we can generate all the above results. Now we shall worry about the boundary conditions.

We use the following set of boundary condition, by assuming an ideal gas in a three dimensional box, namely

$$\begin{aligned}\Psi(x + L_x, y, z) &= \Psi(x, y, z) \\ \Psi(x, y + L_y, z) &= \Psi(x, y, z) \\ \Psi(x, y, z + L_z) &= \Psi(x, y, z)\end{aligned}\tag{1}$$

For obvious reasons, such set of boundary conditions are called periodic boundary conditions.

The solutions of the Schrödinger equation with these boundary conditions straightforwardly yields

$$\begin{aligned}\Psi &= e^{i\boldsymbol{\kappa}\cdot\mathbf{r}} = e^{i\kappa_x x + i\kappa_y y + i\kappa_z z} \\ \kappa_x &= \frac{2\pi}{L_x}n_x \\ \kappa_y &= \frac{2\pi}{L_y}n_y \\ \kappa_z &= \frac{2\pi}{L_z}n_z \\ \epsilon &= \frac{2\pi^2\hbar^2}{m}\left(\frac{n_x^2}{L_x^2} + \frac{n_y^2}{L_y^2} + \frac{n_z^2}{L_z^2}\right)\end{aligned}$$

The number of translational states that lies in the range of the wave-vector $\boldsymbol{\kappa}$ and $\boldsymbol{\kappa} + d\boldsymbol{\kappa}$

Since

$$\delta n_x = \frac{L_x}{2\pi} dk_x$$

we get

$$\begin{aligned} \rho d^3 \boldsymbol{\kappa} &= \delta n_x \delta n_y \delta n_z \\ &= \frac{L_x L_y L_z}{(2\pi)^3} dk_x dk_y dk_z \\ &= \frac{V}{(2\pi)^3} d^3 \mathbf{k} \end{aligned}$$

The quantity ρ is called the density of states and plays a very important role in the calculation of various quantities.

We can also use the expression $\mathbf{p} = \hbar \boldsymbol{\kappa}$ and or $\epsilon = \frac{\hbar^2}{2m} \kappa^2$ to rewrite the density of states in terms of either momentum or energy

$$\begin{aligned} \rho_p d^3 \mathbf{p} &= V \frac{d^3 \mathbf{p}}{h^3} \\ \rho_\epsilon d\epsilon &= \frac{V}{4\pi^2} \frac{(2m)^{\frac{3}{2}}}{\hbar^3} \epsilon^{\frac{1}{2}} d\epsilon \end{aligned}$$

3.2 Evaluation of the Canonical partition function

As we have noted the major difficulty in evaluating the canonical partition function for a non-interacting set of indistinguishable quantum particles which

$$Z(N) = \sum_{\{n_r\}} e^{-\beta(n_1 \epsilon_1 + n_2 \epsilon_2 + \dots)}$$

where $n_r = 0, 1, 2, \dots$, comes from the constraint

$$\sum_r n_r = N$$

This problem is avoided by going to the Grand canonical ensemble where the number of particles can be varied. Here we will show that once we know the Grand partition function it is possible to recover the partition function. The scheme comes from the observation that in a thermodynamic system the fluctuation around the number of particles about the mean number of particles vanishes. The grand partition function can be thought of as a sum

of some function of canonical partition functions (for classical system this is obvious) of subsystems each of which has a definite number of particles. Now it is clear that we are interested in the value of $Z(N')$ only at $N' = N$ which corresponds to the most probable configuration of the system under equilibrium condition. This $Z(N)$ can be evaluated by finding out the sharp maxima of the function $Z(N') \exp(-\alpha N')$ which in turn will determine the parameter N' from the equilibrium condition

Since a sum of this functions $Z(N') \exp(-\alpha N')$ over all possible values of N' thus selects only those term of interest near $N' = N$ and hence we can write

$$\sum_{N'} Z(N') e^{-\alpha N'} = Z(N) e^{-\alpha N} \Delta^* N'$$

Now the Grand partition function(Q) and canonical partition function (Z) are related by

$$Q = \sum_{N'} Z(N') e^{-\alpha N'}$$

Using the fact that $Z(N')$ has a sharp maxima we can actually write

$$\ln Z(N) = \alpha N + \ln Q \tag{2}$$

where we have neglected terms of order $\ln \Delta^* N'$ which is utterly negligible compared to other terms of the order N .

For fermions and bosons

$$\ln Q = \pm \sum_r \ln(1 \pm e^{-\alpha - \beta \epsilon_r})$$

This

$$\ln Z(N) = \alpha N \pm \sum_r \ln(1 \pm e^{-\alpha - \beta \epsilon_r})$$

Maximization of $Z(N') \exp(-\alpha N')$ will then determine $\alpha = -\frac{\mu}{kT}$

The first important thing is to note the behavior of the partition function in the classical limit

For that we shall go to the limit of sufficiently low density or sufficiently high temperature when the classical limit is valid

As we have just noted that the canonical partition function of the gas may be given (to a very good approximation) given by

$$\ln Z = -\beta \mu N \pm \sum_k \ln(1 \pm e^{\beta(\mu - \epsilon_k)})$$

Consider the gas when N is very small with a given volume. The constraint of total number of particles then immediately imply that $\langle n_k \rangle$ is also small for any k or $\exp(\beta(\epsilon_k - \mu)) \gg 1$ for all states k . Under this situation the distribution is like Maxwell Boltzmann.

Another limit is to keep the number of particles same, but to go to a very high temperature. Since $\beta \leftarrow 0$ and increasing number of terms with large value ϵ_k will only contribute to the partition function. To prevent this sum to exceed some given $N - \beta\mu$ has to be sufficiently large so that each term is sufficiently small. This again mean $\exp(\beta(\epsilon_k - \mu)) \gg 1$, the limit where the distribution behaves in a classical way. Thus one arrives at a conclusion that if the concentration is made sufficiently low or the temperature is made sufficiently high then we can think of classical limit.

Here in what will follow we shall calculate the canonical partition function in this classical limit

4 Ideal Gas in the classical limit

We introduce the notation

$$-\beta\mu = \alpha$$

In the classical limit, both FD and BE statistics reduces to

$$\langle n_k \rangle = e^{-\alpha - \beta\epsilon_k}$$

Now by definition

$$\sum_k e^{-\alpha - \beta\epsilon_k} = N$$

Since chemical potential does not depends on k summation, we therefore have

$$e^{\beta\mu} = e^{-\alpha} = N \left(\sum_k e^{-\beta\epsilon_k} \right)^{-1}$$

Thus we get

$$\langle n_k \rangle = N \frac{e^{-\beta\epsilon_k}}{\sum_k e^{-\beta\epsilon_k}}$$

Hence it follows that in the classical limit of sufficiently low density or sufficiently high temperature the quantum distribution laws whether *FD* or *BE* reduce to MB distribution.

Now in the classical limit

$$\begin{aligned}
\ln Z &= \alpha N \pm \sum_r \ln(1 \pm e^{-\alpha - \beta \epsilon_r}) \\
&\approx \alpha N \pm \sum_r (\pm e^{-\alpha - \beta \epsilon_r}) \\
&\approx \alpha N + N \\
\Rightarrow \alpha &= -\ln N + \ln\left(\sum_r e^{-\beta \epsilon_r}\right)
\end{aligned}$$

This gives

$$\ln Z = -N \ln N + N + N \ln\left(\sum_r \exp(-\beta \epsilon_r)\right)$$

Now this is indeed not equal to the partition function Z_{MB} of a classical gas of N identical particles evaluated earlier where

$$\ln Z_{MB} = N \ln\left(\sum_r e^{-\beta \epsilon_r}\right)$$

This readily gives

$$\begin{aligned}
\ln Z &= \ln Z_{MB} - (N \ln N - N) \\
&= \ln Z_{MB} - \ln N!
\end{aligned} \tag{3}$$

Thus we have

$$Z = \frac{Z_{MB}}{N!}$$

So finally we have

$$\ln Z = N(\ln \xi - \ln N + 1)$$

with

$$\xi = \sum_k e^{-\beta \epsilon_k}$$

Now for an ideal monatomic gas as we have computed

$$\xi = \sum_{\kappa_x, \kappa_y, \kappa_z} \exp\left[-\frac{\beta \hbar^2}{2m}(\kappa_x^2 + \kappa_y^2 + \kappa_z^2)\right]$$

The exponential term factors out giving

$$\xi = \left(\sum_{\kappa_x} e^{-\frac{\beta\hbar^2}{2m}\kappa_x^2} \right) \left(\sum_{\kappa_y} e^{-\frac{\beta\hbar^2}{2m}\kappa_y^2} \right) \left(\sum_{\kappa_z} e^{-\frac{\beta\hbar^2}{2m}\kappa_z^2} \right)$$

Successive terms in the the sum like over $\kappa_x = \frac{2\pi n_x}{L_x}$ correspond to a very small increment $\Delta\kappa_x = \frac{2\pi}{L_x}$ in κ_x and therefore differ very little for each other.

Thus we get

$$\left| \frac{\partial}{\partial\kappa_x} \left(e^{-\frac{\beta\hbar^2}{2m}\kappa_x^2} \right) \left(\frac{2\pi}{L_x} \right) \right| \ll \left(e^{-\frac{\beta\hbar^2}{2m}\kappa_x^2} \right)$$

Provided this condition is satisfied it is an excellent approximation replace the sum in the partition function by the corresponding integral, namely,

$$\begin{aligned} \sum_{\kappa_x=-\infty}^{\infty} e^{-\frac{\beta\hbar^2}{2m}\kappa_x^2} &= \int_{-\infty}^{\infty} \left(\frac{L_x}{2\pi} d\kappa_x \right) e^{-\frac{\beta\hbar^2}{2m}\kappa_x^2} \\ &= \frac{L_x}{2\pi} \left(\frac{2\pi m}{\beta\hbar^2} \right)^{\frac{1}{2}} \end{aligned}$$

Therefore we get

$$\xi = \frac{V}{h^3} (2\pi m k T)^{\frac{3}{2}}$$

Exercise; Show that the above continuum approximation is valid if the de Broglie wavelength (thermal) is much smaller than inter-particle separation.

Then we can immediately get

$$\ln Z = N \left(\ln \frac{N}{V} - \frac{3}{2} \ln \beta + \frac{3}{2} \ln \frac{2\pi m}{h^2} + 1 \right)$$

This reproduces

$$\bar{E} = -\frac{\partial \ln Z}{\partial \beta} = \frac{3}{2} N k T$$

And accordingly

$$\begin{aligned} S &= k(\ln Z + \beta \bar{E}) \\ &= N k \left(\ln \frac{V}{N} + \frac{3}{2} \ln T + S_0 \right) \end{aligned}$$

The constant

$$S_0 = \frac{3}{2} \ln \frac{2\pi mk}{h^2} + \frac{5}{2}$$

is now not arbitrary like in the classical case and has been determined in terms of the Planck's constant.

Exercise; Explicitly generalize the above calculate for the entropy where the ideal monatomic gas has J possible spin states.

The above Quantum Mechanical calculation has the following important consequences

- The correct dependence of $\ln Z$ on N , the factor $N!$ is an automatic consequence of the theory. Thus the Gibb's paradox does not arise and $\ln Z$ behaves properly like an extensive quantity under simultaneous change of scale N and V
- Also the constant S_0 is now determined correctly in terms of the Planck constant

These modifications are all due to the introduction of the new quantity called chemical potential , namely

$$\mu = \left(\frac{\partial F}{\partial N}\right)_{V,T} = -kT \left(\frac{\partial Z}{\partial N}\right)_{V,T}$$

Based on the above derivation we can see that

$$= \frac{1}{\beta} \ln \frac{\xi}{N}$$

Chemical potential particularly determined the equilibrium between various phases and control the number of transferred particles from one phase to another. . It also depends on various quantities N and \hbar for example (for large N , however N dependence is negligible).

4.1 Average occupation per state

4.1.1 Fermions

We know that

$$\langle n_k \rangle^F = \frac{1}{e^{\beta(\epsilon_k - \mu)} + 1}$$

It is instructive to picture the average occupation per state for different temperature.

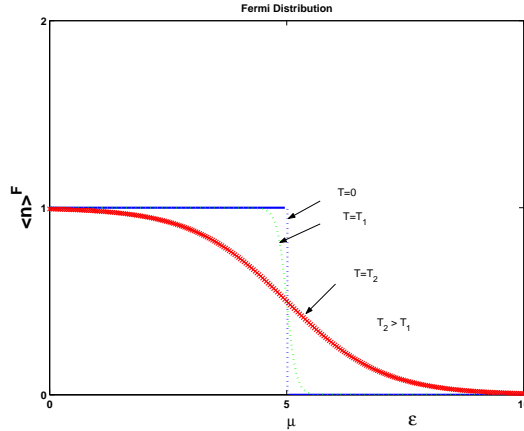


Figure 2:
The Fermi Distribution at different temperature

For $T = 0$, $\beta = \infty$. Here for $\epsilon_k < \mu$, $\exp(\beta(\epsilon_k - \mu)) \leftarrow 0$ and hence on average there is one particle state in this energy range. On the other hand for $\epsilon_k > \mu$, $\exp(\beta(\epsilon_k - \mu)) \leftarrow \infty$ and hence $\langle n_k \rangle \leftarrow 0$. Thus all particles are accommodated in the states below the chemical potential μ and distribution is like that of step function. The chemical potential μ at $T = 0$ is called the Fermi energy ϵ_F . For temperature $T > 0$ the distribution develops a tail for $\epsilon_k > \mu$ with $\langle n_k \rangle = \frac{1}{2}$ at $\epsilon_k = \mu$. As the temperature increases the tail becomes more and more pronounced.

4.1.2 Bosons

In the case of the Bosons

$$\langle n_k \rangle^B = \frac{1}{e^{\beta(\epsilon_k - \mu)} + 1}$$

Here the important point to note is that since $\langle n_k \rangle$ must exist for $\epsilon_k = 0$, one must have $\exp(-\beta\mu) \geq 1$ or $\mu \leq 0$. Thus the chemical potential for bosons must be less than or equal to 0. This is same as the condition that ensures sum appears in the grand partition function should converge for all $\epsilon_k \geq 0$. For those bosons which do not obey the particle conservation, the chemical potential is identically 0. This is due to the fact total number of particles is now a variable which is fixed in equilibrium by the condition of minimum free energy and hence $\mu = \left(\frac{\partial F}{\partial N}\right)_{V,T} = 0$. For those bosons where

the chemical potential vanishes at a finite temperature, the phenomenon of Bose-Einstein condensation occurs.

Now we have already seen that for a collection of free particles (no interaction and no confinement the number of quantum states per unit energy interval is given by

$$\rho(\epsilon) = (2S + 1) \frac{2\pi}{h^3} (2m)^{\frac{3}{2}} \epsilon^{\frac{1}{2}}$$

Thus the number of particles $\rho(\epsilon)d\epsilon$ in the energy range is

$$\rho(\epsilon)d\epsilon = (2S + 1) \frac{2\pi V}{h^3} (2m)^{\frac{3}{2}} \frac{\epsilon^{\frac{1}{2}}}{e^{\beta(\epsilon-\mu)} \pm 1} d\epsilon$$

4.2 Equation of state

For a Grand canonical ensemble (Look at the earlier notes on Grand canonical ensemble)

$$\begin{aligned} PV &= k_B T \sum_k \ln Q_k^{F,B} \\ &= \pm k_B T (2s + 1) \frac{2\pi V (2m)^{\frac{3}{2}}}{h^3} \times \\ &\quad \int_0^\infty \ln(1 \pm e^{-\beta(\epsilon-\mu)}) \epsilon^{\frac{1}{2}} d\epsilon \end{aligned}$$

The upper sign holds for the fermion and the lower sign holds for the bosons. Integrating by parts the integral on the right hand side of the above equation, we arrive at

$$\begin{aligned} PV &= \pm k_B T (2s + 1) \frac{2\pi V (2m)^{\frac{3}{2}}}{h^3} \\ &\quad \left[\left(\frac{2}{3} \epsilon^{\frac{3}{2}} \ln(1 \pm e^{-\beta(\epsilon-\mu)}) \Big|_0^\infty \right) \right. \\ &\quad \left. + \frac{2}{3} \int_0^\infty \left(\frac{\pm \epsilon^{3/2} e^{-\beta(\epsilon-\mu)}}{1 \pm e^{-\beta(\epsilon-\mu)}} \right) d\epsilon \right] \\ &= \frac{2}{3} (2s + 1) \frac{2\pi V (2m)^{\frac{3}{2}}}{h^3} \int_0^\infty \frac{\epsilon^{\frac{3}{2}} d\epsilon}{e^{\beta(\epsilon-\mu)} \pm 1} \\ &= \frac{2}{3} \int_0^\infty \epsilon \rho(\epsilon) d\epsilon \\ &= \frac{2}{3} E \end{aligned}$$

Where E is the average energy of the system. The above result, as should be clear from the derivation is true both for the bosons and the Fermions. In fact, this also holds for the classical gas.

5 Examples of Fermi distribution

5.1 Degenerate Fermi Gas

A collection of independent fermions is called degenerate if it is at very low temperature or if its density is very high. The characteristic of the degenerate Fermi Gas is that distribution function $f(\epsilon) = 1$ if $\epsilon < \mu$ and 0 if $\epsilon > 0$. This is because temperature of the gas can be considered to be absolute 0 and the limiting form of the Fermi distribution discussed earlier is obtained. Let us consider spin $\frac{1}{2}$ fermions (for example, electron). Then the density of state is

$$\begin{aligned}\rho(\epsilon)d\epsilon &= 2 \cdot 2\pi V \left(\frac{2m}{h}\right)^{\frac{3}{2}} \epsilon^{\frac{1}{2}} d\epsilon, \text{ for } \epsilon < \mu \\ &= 0, \text{ for } \epsilon > \mu\end{aligned}$$

If the total number of fermions is N then,

$$\begin{aligned}N &= \int_0^{\mu} \rho(\epsilon)d\epsilon \\ &= 4\pi V \left(\frac{2m}{h}\right)^{\frac{3}{2}} \frac{2}{3} \cdot \mu^{\frac{3}{2}} \\ &= \frac{8\pi}{3} V \left(\frac{2m}{h}\right)^{\frac{3}{2}} \epsilon_F^{\frac{3}{2}}\end{aligned}$$

Where we identify the chemical potential μ at absolute 0 as the Fermi energy ϵ_F . In terms of the number density $n = \frac{N}{V}$ the fermi energy can be written as

$$\epsilon = \left(\frac{3n}{8\pi}\right)^{\frac{2}{3}} \frac{\hbar^2}{2m}$$

The Fermi temperature T_F is defined through

$$\epsilon_F = k_B T_F$$

The Fermi velocity

$$\nu_F = \sqrt{\frac{2\varepsilon_F}{m}}$$

and the Fermi momentum as $p_F = m\nu_F$. Since the Fermi temperature is proportional to the two-third power of density and hence a high density Fermi density gas has a high Fermi temperature. The Fermi gas is called degenerate if its temperature is much lower than T_F . This is generally the criterion if the limiting form of the distribution for the degenerate gas is applicable in a given situation or not.

The total energy of non relativistic degenerate is given by

$$\begin{aligned} E &= \int \epsilon \rho(\epsilon) d\epsilon \\ &= 4\pi V \left(\frac{2m}{h^2}\right)^{\frac{3}{2}} \int_0^{\varepsilon_F} \epsilon^{\frac{3}{2}} d\epsilon \\ &= \frac{8}{3} \pi V \left(\frac{2m}{h^2}\right)^{\frac{3}{2}} \varepsilon_F^{\frac{3}{2}} \frac{3}{5} \varepsilon_F \\ &= \frac{3}{5} N \varepsilon_F \end{aligned}$$

The pressure exerted by a Fermi Gas is found from the general expression

$$P = \frac{2}{3} \frac{E}{V}$$

Thus we get the well know formulae for the pressure exerted by a degenerate Fermi Gas known as Fermi pressure

$$P = \frac{2}{3} n \cdot \varepsilon_F = \frac{2}{5} n k T_F$$

Thus one pictures the degenerate Fermi gas as being at absolute zero with all levels below $\epsilon = \varepsilon_F$ occupied, the occupancy factor being $(2s + 1)$, where s is the spin of the fermions. The number of fermions and the zero point kinetic energy coming from the uncertainty principle allows the gas to exert pressure which is given by the above equation. One natural manifestation of such intense Fermi pressure is the white dwarf stars, which we shall describe now.

5.2 White Dwarf and Chandrasekhar Limit

The brightness of a star diminishes as the color become redder and in the brightness against color plot most of the stars lie in a strip. Certain stars

are brighter than their red colour warrants - these are known as red giants and certain stars are than their white color would suggest- these are white dwarfs. The reason for their dimness is the absence of hydrogen. The mass of the star is provided by the helium nuclei while the stability is provided by the ionized electrons. The mass of star will try to drive its towards gravitational collapse- this is prevented by the zero point pressure exerted by electrons which can be considered as degenerate Fermi gas.

We consider Fermi Gas electrons to consist of N particles. The number of nucleons is then $2N$ and the mass of the star is approximately $2Nm_n$, where the M_n is the nucleon mass . Knowing the approximate mass of the star we can estimate N and from the approximate size estimate , the volume V . Thus the density $n = \frac{N}{V}$ is known and hence the Fermi temperature of the star. It turns out to be $T_F = 10^{11}K$, the temperature of the star 10^7K . Hence the electron gas can be taken to be at zero temperature and thus completely degenerate.

The role of nucleons is to provide the mass while the role of the electrons is to exert the pressure. The typical energy of the electrons is much large than the rest mass of the electrons and hence we need the relativistic expression for energy in calculating the pressure of the degenerate electron gas.

$$\begin{aligned}
 E &= V \cdot \frac{8\pi}{h^3} \int_0^{p_F} \sqrt{(p^2c^2 + m^2c^4)} p^2 dp \\
 &= V \frac{8\pi}{h^3} \cdot c \int_0^{p_F} \left(1 + \frac{m^2c^2}{2p^2} + \dots\right) \cdot p^3 dp \\
 &= V \frac{8\pi}{h^3} \cdot c \left(\frac{p_F^4}{4} + \frac{m^2}{c^2} 4p_F^2 + \dots\right) \\
 &= V \frac{8\pi}{h^3} \cdot \frac{m^4c^5}{4} (X_F^4 + X_F^2 + \dots)
 \end{aligned}$$

where $X_F = \frac{p_F}{mc}$.

Here E is the free energy The Pressure can be obtained by differentiating E with respect to V , as

$$\begin{aligned}
 P &= -\left(\frac{\partial E}{\partial V}\right)_T \\
 &= -\frac{2\pi}{h^3} m^4 c^5 (X_F^4 + X_F^2 + V \frac{\partial X_F^2}{\partial V} (2X_F^2 + 1) + \dots)
 \end{aligned}$$

The important thing to note is that E is here free energy. Rest of the part are the details of derivation from the book of Bhattacharjee. It is basically

equating the Fermi pressure exerted by the degenerate gas of electrons to expand the system against the gravitation pull generated by the mass of the nucleons and from that the calculation of the mass limit beyond which the gravitational pull will be too high to be counterbalanced by the Fermi pressure. Very few natural phenomenon brings together such an interplay between the classical gravitational effect and quantum Fermi pressure effect demonstrated first time by Chandrasekhar

Now

$$\begin{aligned}
 V \cdot \frac{\partial}{\partial V} X_F^2 &= 2V \frac{\partial}{\partial V} \frac{\varepsilon_F}{mc^2} \\
 &= \frac{2}{mc^2} V \cdot \frac{\partial \varepsilon_F}{\partial V} \\
 &= \frac{2}{mc^2} V \cdot \frac{\partial}{\partial V} \left[\frac{h^2}{2m} \left(\frac{3N}{8\pi V} \right)^{\frac{2}{3}} \right] \\
 &= -\frac{4}{3} \frac{m\varepsilon_F}{m^2 c^2} = -\frac{2}{3} X_F^2
 \end{aligned}$$

Thus we get the following expression for the pressure

$$\begin{aligned}
 P &= -\frac{2\pi m^4 c^5}{h^3} (X_F^4 + X_F^2 - \frac{4}{3} X_F^4 - \frac{2}{3} X_F^4) \\
 &= \frac{2\pi m^4 c^5}{3h^3} (X_F^4 - X_F^2)
 \end{aligned}$$

In terms of the mass and the radius of the star, we can write

$$M = 2Nm_n, V = \frac{4}{3}\pi R^3$$

leading to

$$2m_n \cdot n = \frac{3M}{4\pi R^3}, \text{ or, } n = \frac{3M}{8\pi m_n} R^3$$

and

$$X_F = \bar{M}^{\frac{1}{3}} \bar{R}$$

Where dimensionless mass and radius are respectively given by

$$\bar{M} = \frac{9\pi}{8} \frac{M}{m_n}$$

and

$$\bar{R} = \frac{R}{\frac{h}{mc}}$$

Therefore in terms of \bar{M} and \bar{R} , we have

$$P = K \left(\frac{\bar{M}^{\frac{4}{3}}}{\bar{R}^4} - \frac{\bar{M}^{\frac{2}{3}}}{\bar{R}^2} \right)$$

with

$$K = \frac{2\pi}{3} mc^2 \left(\frac{mc}{h} \right)^3$$

The equilibrium radius is found by equating the work done against the pressure to the gravitational potential energy. The gravitational potential energy of a system of total mass M and radius R is

$$V(R) = -\frac{\alpha GM^2}{R} = -\alpha G \left(\frac{8m_n}{9\pi} \right)^2 \frac{mc}{h} \frac{\bar{M}^2}{R}$$

where α is a number of order unity and can be fully determined only when the density is known as function of the radial distance. The work done against the pressure is

$$\begin{aligned} W &= \int_{\infty}^R P 4\pi r^2 dr \\ &= 4\pi \left(\frac{h}{mc} \right)^3 \int_{\infty}^{\bar{R}} P(\bar{r}) 4\pi \bar{r}^2 d\bar{r} \end{aligned}$$

which must be equated to the potential energy $V(R)$. Differentiating both these terms with respect to R we get

$$4\pi \bar{R}^2 p(\bar{R}) = \alpha G \left(\frac{8m_n}{9\pi} \right)^2 \left(\frac{mc}{h} \right)^4 \frac{\bar{M}^2}{\bar{R}^2}$$

Thus we finally get

$$K \left(\frac{\bar{M}^{\frac{4}{3}}}{\bar{R}^4} - \frac{\bar{M}^{\frac{2}{3}}}{\bar{R}^2} \right) = K' \frac{\bar{M}^2}{\bar{R}^4}$$

with

$$K' = \frac{\alpha g}{4\pi} \left(\frac{8\pi m_n}{9\pi} \right)^2 \left(\frac{mc}{h} \right)^4$$

Solving the equation we get

$$\bar{R}^2 = \bar{M}^{\frac{2}{3}} \left(1 - \left(\frac{\bar{M}}{\bar{M}_0} \right)^{\frac{2}{3}} \right)$$

where

$$\begin{aligned}
\bar{M}_0^{\frac{2}{3}} &= \frac{K}{K'} \\
&= \frac{\frac{2\pi}{3} m c^2 \left(\frac{m c}{h}\right)^3}{\frac{\alpha G}{4\pi} \left(\frac{8m_n}{9\pi}\right)^2 \left(\frac{m c}{h}\right)^4} \\
&= \frac{27\pi}{64\alpha} \frac{h c}{G m_n^2}
\end{aligned}$$

Clearly for \bar{R} to exist, we must have $\bar{M} \leq \bar{M}_0$. Thus \bar{M}_0 is the upper limit of a mass of a white dwarf star. The dimensionless number $\frac{h c}{G m_n^2}$ is 10^{39}

For $\alpha = 1$, the corresponding dimensionless mass \bar{M} is almost M_{sun} . When proper estimate of α is taken it can be shown the upper limit is $1.4 M_{sun}$, the famous **Chandrasekhar limit**.

6 Specific heat of electron gas

So far we have discussed only the case of $T = 0$, namely the highest occupied energy state. We now consider the case of finite temperature when it is possible to populate the energy above the chemical potential μ and consequently the chemical potential is now going to be a function of the total number of particles N and the temperature T . Here that temperature dependent chemical potential will be determined.

The way we proceed is to use the following equation of state

$$PV = \frac{2}{3} E = \frac{2}{3} \frac{2V}{4\pi^2} \left(\frac{2m}{h^2}\right)^{\frac{3}{2}} \int_0^\infty \frac{\epsilon^{\frac{3}{2}} d\epsilon}{\exp(\beta(\epsilon - \mu)) + 1}$$

For spin s fermions the factor 2 associated with fermions is replaced by $2s + 1$. we need to evaluate the above integral.

We note

$$\begin{aligned}
\int_0^\infty \int_0^\infty \frac{\epsilon^{\frac{3}{2}} d\epsilon}{\exp(\beta(\epsilon - \mu)) + 1} &= (k_B T)^{\frac{5}{2}} \int_{-\beta\mu}^\infty \frac{(x + \mu\beta)^{\frac{3}{2}}}{e^x + 1} dx \\
&= (k_B T)^{\frac{5}{2}} I(\mu\beta)
\end{aligned}$$

If we now use even more compact notation $\alpha = \mu\beta$, then we get to solve the integral

$$I(\alpha) = \int_{-\alpha}^\infty \frac{(x + \alpha)^{\frac{3}{2}}}{e^x + 1} dx$$

The full evaluation of this integral in term of known analytic function is not possible and hence a perturbation approach is taken.

The full details is there in Bhattacharjee. The basic idea is that though one considers a finite temperature nevertheless we only consider low temperature.

Hence $\alpha = \frac{\mu}{k_B T} \gg 1$ and thus a perturbation expansion is possible

$$\begin{aligned}
I(\alpha) &= \int_{-\alpha}^{\infty} \frac{(x + \alpha)^{\frac{3}{2}}}{e^x + 1} dx \\
&= \int_{-\alpha}^0 \frac{(x + \alpha)^{\frac{3}{2}}}{e^x + 1} dx + \int_0^{\infty} \frac{(x + \alpha)^{\frac{3}{2}}}{e^x + 1} dx \\
&= \int_0^{\alpha} \frac{(\alpha - x)^{\frac{3}{2}}}{e^{-x} + 1} dx + \int_0^{\infty} \frac{(x + \alpha)^{\frac{3}{2}}}{e^x + 1} dx \\
&= \int_0^{\alpha} (\alpha - x)^{\frac{3}{2}} \frac{e^x}{e^x + 1} dx + \int_0^{\infty} \frac{(x + \alpha)^{\frac{3}{2}}}{e^x + 1} dx \\
&= \int_0^{\alpha} \frac{(\alpha - x)^{\frac{3}{2}}}{d} x - \int_0^{\alpha} (\alpha - x)^{\frac{3}{2}} \frac{1}{e^x + 1} dx \\
&\quad + \int_0^{\infty} \frac{(x + \alpha)^{\frac{3}{2}}}{e^x + 1} dx \\
&= \frac{2}{5} \alpha^{\frac{5}{2}} + \int_0^{\infty} dx \frac{(\alpha + x)^{\frac{3}{2}} - |(\alpha - x)|^{\frac{3}{2}}}{e^x + 1} \\
&\quad + \int_{\alpha}^{\infty} \frac{|\alpha + x|^{\frac{3}{2}}}{e^x + 1} dx \dots
\end{aligned}$$

It can be shown that

$$(\alpha + x)^{\frac{3}{2}} - |(\alpha - x)|^{\frac{3}{2}} = 3\alpha^{\frac{1}{2}}x + 0\left(\frac{1}{\sqrt{\alpha}}\right)$$

After sum algebra (see Bhattacharjee) we finally arrive

$$I(\alpha) = \frac{2}{5} \alpha^{\frac{5}{2}} + \frac{\pi^2}{4} \alpha^{\frac{1}{2}} + O\left(\frac{1}{\alpha^{\frac{1}{2}}}\right)$$

We shall now substitute the above formula in the equation

$$PV = \frac{2}{3}E$$

Again remember, here E is the Free energy (normally written as F) and not the internal energy.

This gives us immediately

$$\begin{aligned} PV &= \frac{V}{3\pi^2} \left(\frac{2m}{h^2}\right)^{\frac{3}{2}} (k_B T)^{\frac{5}{2}} \left[\frac{2}{5} \left(\frac{\mu}{k_B T}\right)^{\frac{5}{2}} + \frac{\pi^2}{4} \left(\frac{\mu}{k_B T}\right)^{\frac{1}{2}} + \dots \right] \\ &= \frac{V}{3\pi^2} \left(\frac{2m}{h^2}\right)^{\frac{3}{2}} \left[\frac{2}{5} \mu^{\frac{5}{2}} + \frac{\pi^2}{4} (k_B T)^2 \mu^{\frac{1}{2}} + \dots \right] \end{aligned}$$

Now since $N = \frac{\partial E}{\partial \mu}|_{T,V}$

Therefore we can get immediately,

$$N = \frac{V}{4\pi^2} \left(\frac{2m}{h^2}\right)^{\frac{3}{2}} \left[\mu^{\frac{3}{2}} + \frac{\pi^2}{8} (k_B T)^2 \frac{1}{\mu^{\frac{1}{2}}} + \dots \right]$$

As $T \rightarrow 0$, the first term correctly reproduces the zero temperature result $N = \frac{8\pi}{3} V \left(\frac{2m}{h^2}\right)^{\frac{3}{2}} \varepsilon_F^{\frac{3}{2}}$. The Fermi energy ε_F is given now and eliminating $\frac{N}{V}$ in favor of ε_F we get

$$\begin{aligned} \mu &= \varepsilon_F \left[1 + \frac{\pi^2}{8} \left(\frac{k_B T}{\mu}\right)^2 + \dots \right]^{\frac{2}{3}} \\ &= \varepsilon_F \left[1 - \frac{\pi^2}{12} \left(\frac{k_B T}{\varepsilon_F}\right)^2 + \dots \right] \end{aligned}$$

Students are asked to do a detailed derivation how they will get the above equation from the one before it

to the leading order in temperature T . This result does go with the expectation that very high temperature the chemical potential of a fermionic system (classical limit) is negative and thus the first correction to the positive zero temperature chemical potential is to decrease it.

Substituting this form in the expression of the energy we find

$$\begin{aligned} E &= \frac{V}{2\pi^2} \left(\frac{2m}{h^2}\right)^{\frac{3}{2}} \left[\frac{2}{5} \mu^{\frac{5}{2}} + \frac{\pi^2}{4} (k_B T)^2 \mu^{\frac{1}{2}} + \dots \right] \\ &= \frac{V}{2} \left(\frac{2m}{h^2}\right)^{\frac{3}{2}} \left[\frac{2}{5} \varepsilon_F^{\frac{5}{2}} + \frac{\pi^2}{6} (k_B T)^2 \varepsilon_F^{\frac{1}{2}} + \dots \right] \end{aligned}$$

Differentiating the energy E with respect to T at constant volume we get the specific heat

$$\begin{aligned}
C_V &= \left. \frac{\partial E}{\partial T} \right|_V \\
&= \frac{V}{2\pi^2} \left(\frac{2m}{h^2} \right)^{\frac{3}{2}} \frac{\pi^2}{3} k_B^2 \varepsilon_F^{\frac{1}{2}} T + \dots \\
&= \frac{\pi^2}{2} N k_B \frac{k_B T}{\varepsilon_F} + \dots
\end{aligned}$$

In deriving the last line we have used the relation between N and ε_F . Thus as $T \leftarrow 0$, we have

$$C_V = \frac{\pi^2}{2} N k_B \frac{k_B T}{\varepsilon_F}$$

which vanishes linearly with T as T tends to zero. This is to be contrasted with the T^3 dependence of the contribution to the vibration of the nuclei forming the crystal lattice. The full specific heat will be given by both contribution. At very low temperature the linear part dominates whereas at very high temperature the cubic part will dominate. The results are in surprisingly good agreement with a wide variety of metal.

6.1 Emission of electrons from a metal surface

This is not covered in the lecture but has been provided as a tutorial problem We consider a metal in equilibrium with a dilute electron gas at very low temperature. The periodic distribution of the ions which produces the periodic potential in which the electrons move is interrupted at the surface giving rise to a potential barrier which is needed to be overcome if an electron is to leave the surface. We model this barrier by giving an electron at the bottom of the conduction band an energy $-V$. The maximum kinetic energy of the of an electron is, to a good extent, if the temperature is sufficiently low, is equal to the Fermi energy ε_F . The minimum energy required to eject a metal is therefore

$$W = V - \varepsilon_F$$

which is called the workfunction of the metal. Now to calculate the chemical potential of this electron gas inside the metal, we note that the Fermi distribution for particles having momentum between \mathbf{p} and $\mathbf{p} + d\mathbf{p}$ is given by

$$\langle n^F \rangle = \frac{1}{e^{\beta(\frac{p^2}{2m} + V - \mu)} + 1}$$

and at very low temperature the standard calculation of the Fermi energy yields

$$\varepsilon_F = V + \mu$$

thus giving the expect result

$$\mu = -W$$

inside the metal.

Generally outside the metal the density of the electron gas is very low and hence corresponds to a situation where the Fermi distribution will reduce to the classical distribution and thus the number of electrons between \mathbf{p} and $\mathbf{p} + d\mathbf{p}$ will be given by $e^{\beta(\frac{p^2}{2m} - \mu_0)}$ whereas μ_0 is the chemical potential outside the metal. If the total number of electron is N and the volume is V then outside the metal

$$N = 2 \cdot V \frac{4\pi}{h^3} \int_0^\infty p^2 e^{-\frac{p^2}{2mkT}} e^{\frac{\mu_0}{k_B T}} dp$$

The factor 2 comes because of the two available spin states.

Solving the integral we get the density of the electrons in terms of the chemical potential

$$n = 2 \cdot \left(\frac{2\pi mkT}{h^2} \right)^{\frac{3}{2}} e^{\frac{\mu_0}{k_B T}}$$

For equilibrium between the metal and the electron Gas, the chemical potentials must be equal and hence

$$\mu_0 = \mu = -W$$

Thus we get

$$n = 2 \left(\frac{2\pi mkT}{h^2} \right)^{\frac{3}{2}} e^{-\frac{W}{k_B T}} = \frac{W}{\lambda^3}$$

The equilibrium here achieved is a dynamical one. In that, in every unit time interval, a certain number of electrons strike the metal surface per unit area per unit time and a fraction of them are absorbed. To keep the number of electrons fixed an equal number of electrons must energy from the metal surface per unit area per unit time. This gives the emission current from

the metal surface. The number of electrons with momentum between p_z and $p_z + dp_z$ (the surface is at $z = 0$) and with the density already mentioned striking a unit area of metal in unit time

$$\frac{2n\lambda^3}{h^3} \int_{-\infty}^{\infty} dp_x \int_{-\infty}^{\infty} dp_y \int_{-\infty}^{\infty} dp_z v_z e^{-\frac{p^2}{2mkT}}$$

And hence the total number of electrons striking the metal surface per unit area is

$$\begin{aligned} \bar{N} &= 2 \frac{e^{-\frac{W}{k_B T}}}{h^3} \int_{-\infty}^{\infty} dp_x \int_{-\infty}^{\infty} dp_y \int_{-\infty}^{\infty} dp_z \frac{p_z}{m} e^{-\frac{p^2}{2mkT}} \\ &= 2 \cdot \frac{2\pi m k_B T}{h^2} \frac{k_B T}{h} e^{-\frac{W}{k_B T}} \end{aligned}$$

If the reflection coefficient of the metal surface is r , then the number of electrons absorbed on the metal surface per unit area per unit time is $(1-r) \frac{4\pi m k_B T}{h^2} \frac{k_B T}{h} e^{-\frac{W}{k_B T}}$ and this must equal to the emission rate. Thus the emission current is given by the formulae

$$I = (1-r) \frac{4\pi m k_B T}{h^2} \frac{k_B T}{h} e^{-\frac{W}{k_B T}}$$

The factor $e^{-\frac{W}{k_B T}}$ reflects the depletion of the current due to potential barrier.

7 Bose Einstein Condensation

From the last part we have the relation

$$PV = \frac{3}{2}E$$

Now by definition

$$N = \frac{\partial(PV)}{\partial\mu}$$

The last equation follows from the fact

$$\begin{aligned}
N &= \sum_i \langle n_i \rangle \\
&= kT \sum_i i \frac{1}{e^{\beta(\epsilon_i - \mu)} - 1} \\
&= kT \sum_i \frac{\partial}{\partial \mu} \ln Q_{B,F}^i \\
&= \frac{\partial}{\partial \mu} (kT \ln Q)|_{T,V} \\
&= \frac{\partial}{\partial \mu} (PV)|_{T,V}
\end{aligned}$$

Thus we get

Substituting the result for E we finally get,

$$N = \pm(2s + 1) \frac{2\pi V}{h^3} (2m)^{\frac{3}{2}} \int_0^\infty \frac{\pm \epsilon^{\frac{1}{2}} d\epsilon}{e^{\beta(\epsilon - \mu)} \pm 1}$$

The idea is eliminate the chemical potential with the help of the above equation and getting an equation of state of the form

7.1 Bose Einstein condensation

The chemical potential of system of spinless bosons ($s = 0$) is related to the number of particles through the equation

$$N = V \cdot 2\pi \left(\frac{2m}{h^2}\right) \int_0^\infty \frac{\epsilon^{\frac{1}{2}} d\epsilon}{e^{\beta(\epsilon - \mu)} - 1}$$

For a dilute Bose gas, that is the classical limit $\exp(-\beta\mu) \gg 1$. This means the chemical potential is a large negative value. Now we shall consider a limit where $\exp(-\beta\mu) \approx 1$. For a given chemical potential, as we decrease the temperature, the value of $\exp(-\beta\mu)$ will decrease and will approach unity. Now let us look at this following puzzling behavior,

According to the previous formulation

$$n(\mu) = \frac{N}{V} = 2\pi \left(\frac{2m}{h^2}\right) \int_0^\infty \frac{\epsilon^{\frac{1}{2}} d\epsilon}{e^{\beta(\epsilon - \mu)} - 1}$$

We are interested in the behavior of the Boson gas at the low temperatures. Since the Pauli principle does not apply to Boson, they tend to

concentrate to the lowest energy level and it is only the thermal fluctuation that will prevent them all occupying the ground state of the system. At low temperature, when the thermal fluctuation will be less, we can thus expect that a macroscopic number of boson to occupy the ground level of the system, namely $\epsilon = 0$. Accordingly we find that at low temperature number of order of bosons in the ground state is N then

$$N \approx \frac{1}{\exp(-\beta\mu) - 1}$$

$$\mu \approx -\frac{kT}{N}$$

- At first sight such a behavior makes sense because it is consistent with the tendency that chemical potential to decrease with the high temperature and also consistent with the requirement that the chemical potential should be negative (since the lowest energy available is 0).
- However this formulae is in direct contradiction with the expression of the density given before it. This equation gives the density of particles as a sum of the contribution from all energies. We find there the contribution to the integral coming from the region near $\epsilon = 0$ is 0. Thus the occupation of the ground level which is very large at low temperature
- This difficulty leads to a paradox which is a consequence of relation between the density of particles and the chemical potential. As we can see the integral on the right hand side is an increasing function of μ since the integrand at a given value of μ is an increasing function of μ . But the integral cannot become larger than its value at $\mu = 0$ since μ cannot become positive. Consequently the right hand side of this equation has an upper bound which is its value at $\mu = 0$. This would imply that the density n at a given temperature, of our non-interacting boson gas cannot rise above a certain maximum value, determined by the maximum on the right hand side.
- This conclusion is, of course, unreasonable, since it is impossible for there to be a restriction on the number of non-interacting bosons in a given volume. Even fermions which obey the Pauli principle do not resist the addition of fermions. They only force the new fermions to occupy the higher energy levels. Now suppose a system is prepared at a density and temperature for which there exist a solution for μ , as T

is lowered the solution disappears. Moreover at $T = 0$ the equation will allow only 0 density which is clearly absurd. So the question is what went wrong?

7.2 The rationale for condensation

In order to clarify the reason for this inconsistency we look at the calculation of various quantities using the density of states. Namely calculation of the Thermodynamic potential Ω (the analogue of free energy for grand partition function) and its derivatives which gives us various thermodynamic quantities.

As we know we do all these calculations by invoking the notion of density of states, namely the number of states that lies in between energy ϵ and $\epsilon + d\epsilon$, denoted by $n(\epsilon)d\epsilon$. We then multiply any quantity by this density of states after taking into consideration their bosonic or the fermionic character and obtain the thermodynamic value of that quantity. For example the thermodynamic potential Ω itself for an ideal gas of bosons with spin 0

$$\Omega_B = \frac{4\pi V kT}{h^3} \int_0^\infty \ln [1 - \exp(\beta(\mu - \frac{p^2}{2m}))] p^2 dp$$

and then differentiating with respect to μ we get the average number of bosons, namely which is given at the beginning of this section. All these have been obtained by replacing the summation over a discrete momentum states k by an integration over a continuous momentum. But since $n(\epsilon) \propto \epsilon^{\frac{1}{2}}$, this means that density of states goes to 0 as we approach the ground state since $n(0) = 0$. Thus we are losing the huge contribution that goes into the ground state.

If the temperature is not too low (or the density is not too high) the occupation of the ground level does not differ greatly from that of the other levels. In that condition, each of the term entering in the expression of the thermodynamic potential is of the order N , where as sum is of the order N . Hence the error introduced in neglecting the ground level is insignificant.

But at low temperature the chemical potential tends to 0 as $\frac{1}{N}$ since $\mu \approx -\frac{kT}{N}$ and the terms corresponding the the ground level in the various sum must be examined more closely. For example in the sum for Ω , the contribution from ground state

$$\begin{aligned}
\Omega_0 &= k_B T \ln(1 - e^{\beta\mu}) \\
&\approx k_B T \ln(1 - e^{-\frac{a}{N}}) \\
&\approx k_B T \ln\left(\frac{a}{N}\right)
\end{aligned}$$

This term can be neglected since $\ln N$ is negligible compared to N as $N \leftarrow \infty$. In contrast, at low T the ground level term in the sum for N is

$$N_0 = \frac{1}{e^{-\beta\mu} - 1} \approx \frac{1}{e^{\frac{a}{N}} - 1} \approx \frac{N}{a}$$

. This sum is of the order of the magnitude as the entire sum, despite the fact that it originates from the negligible ground level term in Ω . Neglecting it gives the contradiction we have just encountered.

Thus we write

$$\Omega = \Omega_0 + k_B T V \int_0^\infty n(\epsilon) \ln(1 - e^{\beta(\mu-\epsilon)}) d\epsilon,$$

and

$$N = N_0(\mu) + 2\pi V \left(\frac{2m}{h^2}\right)^{\frac{3}{2}} \int_0^\infty \frac{\epsilon^{\frac{1}{2}} d\epsilon}{e^{\beta(\epsilon-\mu)} - 1}$$

where

$$N_0 = \frac{1}{\exp(-\beta\mu) - 1}$$

is the ground state occupancy

Now say at $T = T_c$ $\exp(\beta\mu)$ reaches its minimum value 1. Thus to obey the conservation of number of particle and the fact the positive values of the chemical potential is not allowed such that $e^{-\beta\mu} < 1$ we arrive at the following solution for a given total number of particles N . The ground state occupation $N_0(\mu)$ starts varying to maintain $\mu = 0$ at $T < T_c$ and letting $N_0(\mu)$ vary to keep the equation

$$N = N_0(\mu) + 2\pi V \left(\frac{2m}{h^2}\right)^{\frac{3}{2}} \int_0^\infty \frac{\epsilon^{\frac{1}{2}} d\epsilon}{e^{\beta(\epsilon-\mu)} - 1}$$

satisfied with $e^{-\mu\beta} = 1$. Writing $e^{\beta\mu} = z$ and $\beta\epsilon = x$ we now have

$$\begin{aligned}
N &= N_0 + 2\pi V \frac{2mk_B T}{h^2} \int_0^\infty \frac{zx^{\frac{1}{2}}e^{-x}}{1 - ze^{-x}} dx \\
&= N_0 + V \left(\frac{2\pi mk_B T}{h^2} \right)^{\frac{3}{2}} \zeta_{3/2}(z)
\end{aligned}$$

Where the function

$$\zeta_{3/2}(z) = \sum_{k=0}^{\infty} \frac{z^{k+1}}{(k+1)^{\frac{3}{2}}}$$

The algebra is the following

$$\begin{aligned}
\int_0^\infty dx \frac{zx^{\frac{1}{2}}e^{-x}}{1 - ze^{-x}} &= \int_0^\infty dx \sum_{k=0}^{\infty} z^{k+1} x^{\frac{1}{2}} e^{-(k+1)x} \\
&= \sum_{k=0}^{\infty} \frac{z^{k+1}}{(k+1)^{3/2}} \frac{1}{2} \sqrt{\pi}
\end{aligned}$$

This is clearly a monotonically increasing function for $z > 0$ and rises from 0 at $z = 0$ to 2.612 at $z = 1$ and the derivative is discontinuous at $z = 1$. indicating a phase transition.

Now we can write

$$N_0 = N - V \left(\frac{2\pi mk_B T}{h^2} \right)^{\frac{3}{2}} \zeta_{3/2}(z)$$

The highest T at which N_0 is not equal to 0 is given by T_c which satisfies

$$\left(\frac{2\pi mk_B T_c}{h^2} \right)^{\frac{3}{2}} \zeta_{3/2}(1) = \frac{N}{V} = n$$

For the $T < T_c$, z have already reached unity and cannot change any more and hence the particle density in the ground state has to change accordingly as

$$\begin{aligned}
n_0 = \frac{N_0}{V} &= \frac{N}{V} - \left(\frac{2\pi mk_B T}{h^2} \right)^{\frac{3}{2}} \zeta_{3/2}(1) \\
&= n \left(1 - \left(\frac{T}{T_c} \right)^{\frac{3}{2}} \right)
\end{aligned}$$

This phenomenon is known as Bose Einstein condensation. Beyond a critical temperature the occupation of the ground state is macroscopic

7.3 Thermodynamic quantities below $T = T_C$

When $T < T_C$; In this range the total energy is obtained by noting that $\mu = 0$ and only the particles outside the condensate contribute. We have originally,

$$N = N_0(\mu) + 2\pi V \left(\frac{2mk_B T}{h^2} \right)^{\frac{3}{2}} \int_0^\infty \frac{x^{\frac{1}{2}} dx}{e^{-\mu\beta}(e^x - 1)}$$

Now it is clear that the part N_0 does not have any contribution to the energy. Consequently, the energy is given by

$$E = \int_0^\infty d\epsilon \epsilon n(\epsilon)$$

Following the same steps as before, namely expanding the denominator in a power series and using the properties of the Gamma function $\Gamma(n+1) = n\Gamma(n)$

$$\begin{aligned} E &= 2\pi V \left(\frac{2mk_B T}{h^2} \right)^{\frac{3}{2}} \int_0^\infty \frac{x^{\frac{3}{2}} dx}{(e^x - 1)} \\ &= 2\pi V \left(\frac{2mk_B T}{h^2} \right)^{\frac{3}{2}} k_B T \frac{1}{2} \cdot \frac{3}{2} \sqrt{\pi} \zeta_{\frac{5}{2}} \\ &= \frac{3}{2} V \left(\frac{2\pi mk_B T}{h^2} \right)^{\frac{3}{2}} k_B T \zeta_{\frac{5}{2}} \\ &= \frac{3}{2} N k_B T \left(\frac{T}{T_C} \right)^{\frac{3}{2}} \frac{\zeta_{\frac{5}{2}}}{\zeta_{\frac{3}{2}}} \\ &= \frac{3}{2} \frac{1.341}{2.312} N k_B T \left(\frac{T}{T_C} \right)^{\frac{3}{2}} \\ &= 0.770 N k_B T \left(\frac{T}{T_C} \right)^{\frac{3}{2}} \end{aligned}$$

The equation of state follows as

$$PV = \frac{3}{2} E = 0.513 N k_B T \left(\frac{T}{T_C} \right)^{\frac{3}{2}}$$

Or, the pressure is given by

$$P = \left(\frac{2\pi mk_B T}{h^2} \right)^{\frac{3}{2}} k T^{\frac{5}{2}} \zeta_{\frac{5}{2}}$$

Differentiating the energy E with respect to T will give the specific heat at constant volume as

$$C_V = 1.925Nk_B \left(\frac{T}{T_C}\right)^{\frac{3}{2}}$$

The entropy is obtained by integrating $\frac{C}{T}$ and hence

$$S = 1.282Nk_B \left(\frac{T}{T_C}\right)^{\frac{3}{2}}$$

When $T > T_C$; Now $N_0 = 0$ and $z = \exp(\beta\mu)$ has to be fixed from the equation

$$N = N_0(\mu) + 2\pi V \left(\frac{2m}{h^2}\right)^{\frac{3}{2}} \int_0^\infty \frac{\epsilon^{\frac{1}{2}} d\epsilon}{e^{\beta(\epsilon-\mu)} - 1}$$

This immediately yields,

$$N = V \left(\frac{2\pi mk_B T}{h^2}\right)^{\frac{3}{2}} \zeta_{\frac{3}{2}}(z)$$

The energy is given by

$$\begin{aligned} E &= 2\pi V \left(\frac{2\pi mk_B T}{h^2}\right)^{\frac{3}{2}} \int_0^\infty \frac{x^{\frac{3}{2}} dx}{\frac{1}{z} e^x - 1} \\ &= \frac{3}{2} V \left(\frac{2\pi mk_B T}{h^2}\right)^{\frac{3}{2}} \zeta_{\frac{5}{2}}(z) k_B T \end{aligned}$$

To find out the entropy we note that in the grand canonical ensemble

$$E - TS - \mu N = -PV = -\frac{3}{2}E$$

Thus

$$\begin{aligned} TS &= \frac{5}{3}E - \mu N \\ S &= \frac{5}{2}k_B V \left(\frac{2\pi mk_B T}{h^2}\right)^{\frac{3}{2}} \zeta_{\frac{5}{2}}(z) - Nk_B \ln Z \end{aligned}$$

$$\begin{aligned} C &= \frac{15}{4}k_B V \left(\frac{2\pi mk_B T}{h^2}\right)^{\frac{3}{2}} \zeta_{\frac{5}{2}} \\ &\quad + \frac{3}{2}V k_B T \left(\frac{2\pi mk_B T}{h^2}\right)^{\frac{3}{2}} \times \frac{d}{dz} \zeta_{\frac{5}{2}}(z) \cdot \frac{\partial z}{\partial T} \Big|_{N,V} \end{aligned}$$

To find out the derivative $\frac{\partial z}{\partial T}$ we use the relation

$$\frac{N}{V} = \left(\frac{2\pi m k_B T}{h^2} \right)^{\frac{3}{2}} \zeta_{\frac{3}{2}}(z)$$

Since the *LHS* is a constant, we get after differentiating

$$\begin{aligned} 0 &= \frac{3}{2} T^{\frac{1}{2}} \zeta_{\frac{3}{2}} + T^{\frac{3}{2}} \frac{d}{dz} \zeta_{\frac{3}{2}}(z) \cdot \frac{\partial z}{\partial T} \\ \frac{\partial z}{\partial T} &= -\frac{3}{2T} \left[\frac{d}{dz} \zeta_{\frac{3}{2}} \right]^{-1} \zeta_{\frac{3}{2}}(z) \end{aligned}$$

Using the definition of $\zeta_n = \sum_{k=0}^{\infty} \frac{z^{k+1}}{(k+1)^n}$ we finally get

$$\frac{1}{z} \frac{\partial z}{\partial T} = -\frac{3}{2T} \frac{\zeta_{\frac{3}{2}}(z)}{\zeta_{\frac{1}{2}}(z)}$$

Thus we finally get

$$C = \frac{15}{4} k_B V \left(\frac{2\pi m k_B T}{h^2} \right)^{\frac{3}{2}} \zeta_{\frac{3}{2}}(z) - \frac{9}{4} N k_B \frac{\zeta_{\frac{3}{2}}(z)}{\zeta_{\frac{1}{2}}(z)}$$

Thus if we consider the Thermodynamic quantities like E and S and C above and below the critical temperature $T = T_C$ we found that they are continuous at $T = T_C$. However we have noted (also given as a tutorial problem) that in the low temperature phase the pressure is independent of volume and hence studying the isotherms. If we hold T fixed and vary V from large values to smaller one going from dilute classical to the degenerate gas then at a critical V given by

$$\left[\frac{2\pi m k_B T_C}{h^2} \right]^{\frac{3}{2}} \zeta_{\frac{3}{2}}(1) = \frac{N}{V_C}$$

The condensate phenomenon will set at $V = V_c$ implying that there will be a finite condensate N determined by

$$N_0 = N \left(1 - \frac{V}{V_c} \right)$$

In the $P - V$ diagram the pressure does not change in the range $0 < V < V_C$ and then decreases with increasing V .

For higher temperature the critical V_C occurs at smaller and smaller values. The flat part of each curve can be thought of the co-existence of two phases, a standard feature of first order transition.

Since the pressure in this regime is solely dependent on temperature, we found the slope of the vapor pressure curve as

$$\frac{dP}{dT} = \frac{5}{2} \zeta_{\frac{5}{2}}(1) \left[\frac{2\pi m k_B T_C}{h^2} \right]^{\frac{3}{2}} \cdot k_B$$

Now for an isotherm at temperature T , the specific volume are zero and $\frac{V_c}{N}$ for the condensate and the gas phase respectively. From that, using the Clausius Clapeyron equation we can calculate the latent heat of transition per particle as

$$\begin{aligned} L &= T \left(\frac{V_c}{N} - 0 \right) \cdot \frac{dP}{dT} \\ &= \frac{5}{2} \frac{\zeta_{5/2}(1)}{\zeta_{3/2}(z)} \cdot k_B T \end{aligned}$$

Thus the condensation has certain features of first order phase transition.

7.4 Behavior of the chemical potential near the transition

We are interested how the chemical potential behaves (how it goes to 0 from a large negative value) as the transition temperature $T = T_C$ is approached from the top (from the side $T > T_c$

To find out that we note that at $T > T_c$, for fixed N and V we have

$$T^{\frac{3}{2}} \zeta_{\frac{3}{2}}(z) = \frac{N}{V} = \text{constant}$$

Now $\mu = 0$ implies $z = \exp(\beta\mu) = 1$

Therefore, taking the differential near $z = 1$ at $T = T_C$, we have

$$\frac{3}{2} \zeta_{\frac{3}{2}}(1) \frac{\delta T}{T_c} = - \left. \frac{d\zeta_{\frac{3}{2}}(z)}{dz} \right|_{z=1} \delta z$$

However $\left. \frac{d\zeta_{\frac{3}{2}}(z)}{dz} \right|_{z=1}$ is a divergent quantity and hence we should inspect this divergence more carefully

We can write

$$\left. \frac{d\zeta_{\frac{3}{2}}(z)}{dz} \right|_{z=1} \delta z = \zeta_{\frac{3}{2}}(1 + \delta z) - \zeta_{\frac{3}{2}}(1)$$

We can provide the integral representation of the above expression by writing

$$\begin{aligned}\frac{d\zeta_{\frac{3}{2}}(z)}{dz}\Big|_{z=1}\delta z &= \frac{1}{\Gamma(\frac{3}{2})} \int_0^\infty \left[\frac{1}{\frac{e^x}{1+\delta z} - 1} - \frac{1}{e^x - 1} \right] \\ &= \frac{1}{\Gamma(\frac{3}{2})} \int_0^\infty \frac{dx x^{\frac{1}{2}} \delta z e^x}{(e^x - 1) \left(\frac{e^x}{1+\delta z} - 1 \right)}\end{aligned}$$

The following features are important

- $\delta Z \leftarrow 0$, the integral is completely dominated by the small x -regime
The denominator becomes 0 if we set $\delta z = 0$ and $x = 0$. Hence to retain the leading order correction in δz it suffices to linearize e^x .
- The integral is well defined only for negative δz which is as it should be since the maximum value of z ($z = 1$) is achieved at $T = T_c$ and z has to decrease as T increases above T_c .

We thus set $\delta z = -\varepsilon$ and upon linearizing e^x we get

$$\begin{aligned}\varepsilon \frac{d}{dz} \zeta_{\frac{3}{2}}(z)\Big|_{z=1} &= \frac{\varepsilon}{\Gamma(3/2)} \int_0^\infty \frac{dx}{\sqrt{\varepsilon}} \cdot \frac{1}{x + \varepsilon} \\ &= \frac{\pi \sqrt{\varepsilon}}{\Gamma(\frac{3}{2})}\end{aligned}$$

Substituting this in the equation

$$\frac{3}{2} \zeta_{\frac{3}{2}}(1) \frac{\delta T}{T_c} = - \frac{d\zeta_{\frac{3}{2}}(z)}{dz}\Big|_{z=1} \delta z$$

we get

$$\begin{aligned}\sqrt{\varepsilon} &= \frac{3}{2} \frac{\zeta_{\frac{3}{2}} \Gamma(3/2)}{\pi} \frac{\delta T}{T_c} \\ \varepsilon &= \frac{9}{4} \left(\frac{\zeta_{\frac{3}{2}} \Gamma(3/2)}{\pi} \right)^2 \left(\frac{\delta T}{T_c} \right)^2 \\ z \left[\frac{\delta \mu}{k_B T} - \frac{\mu}{k_B T} \frac{\delta T}{T} \right] \Big|_{T=T_c, \mu=0, z=1} &= \frac{9}{4} \left(\frac{\zeta_{\frac{3}{2}} \Gamma(3/2)}{\pi} \right)^2 \left(\frac{\delta T}{T_c} \right)^2 \\ \delta \mu &= \frac{9}{4} k_B T_c \left(\frac{\zeta_{\frac{3}{2}} \Gamma(3/2)}{\pi} \right)^2 \left(\frac{\delta T}{T_c} \right)^2\end{aligned}$$

The slope of the chemical potential is consequently discontinuous at $T = T_C$.

This leads to interesting consequences for the slope of the specific heat. If we go back to the physical meaning of chemical potential this is obvious.

We can now expand the energy as a function of z and T near $z = 1$ and $T = T_C$ in a Taylor series (keeping N and V fixed).

Then we have

$$E(T, z) = E(T_C, 1) + \left(\frac{\delta E}{\delta T}\right)_{T_C, 1} \delta T + \left(\frac{\delta E}{\delta z}\right)_{T_C, 1} \delta z + \frac{1}{2} \left(\frac{\delta^2 E}{\delta T^2}\right)_{T_C, 1} (\delta T)^2 + \dots$$

We do not need any further terms since $\delta z \sim O((\delta T)^2)$.

Now using the value of the derivatives it can be easily shown that the slope of the specific heat as T approached T_C from above is given by

$$\left(\frac{dC_V}{dT}\right)_{T \rightarrow T_C^+} = -0.776 \frac{Nk_B}{T_C}$$

Using the expression of specific heat when T_C is approached from below one can show

$$\left(\frac{dC_V}{dT}\right)_{T \rightarrow T_C^-} = 2.89 \frac{Nk_B}{T_C}$$

The specific heat thus has maximum at $T = T_C$ (kink) and slope discontinuity of $3.66 \frac{Nk_B}{T}$.

- All the above derivations are true only for a non-interacting Bose gas will change drastically even in the presence of any interaction.
- Another important thing is in all these derivations we have assumed that the total number of particles is conserved. This is essential for condensation and hence in a system with no such conservation law, for example, photon or phonon gas, it is not possible to have Bose Einstein condensation.
- The system of cold atoms where all the recent experiments of BEC took place is harmonically trapped and very weakly interacting. The Bose Einstein condensation happens in such system have its own characteristics (some of them will come out upon solving the tutorial problems)

8 Examples for the Bose Einstein systems

We shall basically discuss two examples. One that of a photon gas. Because of the zero chemical potential of a photon gas, which means there is no conservation of the photon number, photons cannot condense. A gas of photons behaves otherwise like the ideal gas of atoms except that its chemical potential is 0 and rest mass is also zero and energy momentum relation is relativistic (linear). With these inputs one can just get Planck's distribution straightforwardly from the expression of occupation number of photons. One must compare the derivations with the derivation of the kinetic theory of gases from canonical distribution function. One here gets distribution of Intensity as a function of frequency and wavelength and verify various well known laws, like Rayleigh Jeans, Stefan Boltzman, or Wien displacement law straightforwardly.

9 Planck's theory of Black Body radiation; Derivation from BE statistics

Black Body radiation is modeled as a cavity enclosed by matter such that the electromagnetic radiation inside that cavity is in thermal equilibrium with the matter that encloses it. Radiation in the cavity can have different frequencies and different wavelength. The distribution of the energy as a function of the wavelength is what we like to evaluate. To begin with, classically the e.m. radiation can be described by the electric field that satisfies the Maxwell's equation

$$\nabla^2 \vec{\mathcal{E}} = \frac{1}{c^2} \frac{\partial^2 \vec{\mathcal{E}}}{\partial t^2}$$

The solutions of the above equation can be written in the form of plane waves, namely

$$\vec{\mathcal{E}} = \vec{A} e^{i(\mathbf{k} \cdot \mathbf{r} - \omega t)} = \vec{\mathcal{E}}_0(\mathbf{r}) e^{-i\omega t}$$

with

$$\kappa = \frac{\omega}{c}, \kappa = |\boldsymbol{\kappa}|$$

Now, as according to Planck's such electromagnetic waves are quantized, then the associated quanta, known as photons is described in familiar way as a

relativistic particle with momentum p and energy ϵ such that

$$\begin{aligned}\epsilon &= \hbar\omega = h\nu \\ \mathbf{p} &= \hbar\mathbf{k}\end{aligned}$$

Since an electromagnetic wave also have to satisfy the Maxwell's equation (there is no charge inside the cavity)

$$\vec{\nabla} \cdot \vec{\mathcal{E}} = 0$$

This gives, with the help of plain wave solutions that we have mentioned

$$\boldsymbol{\kappa} \cdot \vec{\mathcal{E}} = 0$$

Thus for each κ there are only two perpendicular directions of the electric field that can be specified. In terms of photons this means there are two possible directions of polarizations.

Now since photons are particles, according to the quantum mechanics, not all possible values of $\boldsymbol{\kappa}$ is allowed and only certain discrete values which will reflect the boundary conditions are allowed. Let us take an enclosure in the form of a parallelepiped with edges with length L_x , L_y and L_z . Suppose the smallest of these length, call it $L \gg \lambda$, where the $\lambda = \frac{2\pi}{\kappa}$ is the longest wavelength of significance in this discussion.

Then we can again neglect the situation at the boundary and describe the radiation in terms of simple traveling waves. As we have already learned from the calculation from the density of states, that to eliminate the effect of the walls, we just put the periodic boundary condition. The enumeration of possible states of the photon are then same as possible values of κ of a particle in a box with **periodic boundary condition**.

Now rest of the calculation will be very similar to the derivation of the kinetic theory of gases using classical statistical mechanics. Here only the enumeration of the states and the distribution function will take into consideration quantum mechanical nature of the photons.

$$\begin{aligned}\rho(\mathbf{k})d^3\boldsymbol{\kappa} &= \text{the mean number of states} \\ &\text{per unit volume with} \\ &\text{one specified direction of polarization} \\ &\text{when wavevector lies in between} \\ &\kappa \text{ and } \kappa + d\kappa \\ &= \frac{n_\epsilon}{(2\pi)^3}d^3\mathbf{k}\end{aligned}$$

Each of this state has energy

$$\epsilon = \hbar\omega = \hbar c\kappa$$

The quantum statistics or more specifically the bosonic nature of photon enters in the fact that the mean number photon with a definite value of κ is given by,

$$\bar{n}_\epsilon = \frac{1}{e^{\beta\epsilon} - 1}$$

Calculating the average occupation number for photon is simple since it has 0 chemical potential. namely, Let us consider the photon is in the state s with energy ϵ_s . Then the average occupation number of photon in that case which we shall denote as \bar{n}_s is given by

$$\begin{aligned} \bar{n}_s &= \frac{\sum_{n_1, n_2, \dots} n_s e^{-\beta(n_1\epsilon_1 + n_2\epsilon_2 + \dots + n_s\epsilon_s + \dots)}}{\sum_{n_1, n_2, \dots} e^{-\beta(n_1\epsilon_1 + n_2\epsilon_2 + \dots + n_s\epsilon_s + \dots)}} \\ &= \frac{-\frac{1}{\beta} \frac{\partial}{\partial \epsilon_s} \sum e^{-\beta n_s \epsilon_s}}{\sum e^{-\beta n_s \epsilon_s}} \\ &= -\frac{1}{\beta} \frac{\partial}{\partial \epsilon_s} \ln\left(\sum e^{-\beta n_s \epsilon_s}\right) \end{aligned}$$

The particles being boson n_s can take any integer value between 0 and ∞ . Thus the above sum is a G.P. series given by

$$\sum e^{-\beta n_s \epsilon_s} = (1 - e^{-\beta \epsilon_s})^{-1}$$

Thus we have

$$\bar{n}_s = \frac{1}{e^{\beta \epsilon_s} - 1}$$

Thus the corresponding mean number of photons is simply

$$f(\mathbf{k}) d^3\mathbf{k} = \frac{1}{e^{\beta \hbar \omega} - 1} \frac{d^3\mathbf{k}}{(2\pi)^3}$$

Note $f(\mathbf{k})$ depends on $|\mathbf{k}| = \kappa$ only. Now \mathbf{k} is a vector (wave number along three different direction) where as ω is a scalar, related with each other through the relation

$$\omega = c|\mathbf{k}|$$

Then the mean number of photons per unit volume with both direction of polarization with angular frequency in the range ω and $\omega + d\omega$, is given by

summing over all the volumes in the $\boldsymbol{\kappa}$ space contained within the spherical shell of radius $\kappa = \frac{\omega}{c}$ and $\kappa + d\kappa$ (basically we are eliminating the angular dependence of $\boldsymbol{\kappa}$ through integration since the energy density is independent of it). This is just

$$2f(\kappa)4\pi\kappa^2 d\kappa = \frac{8\pi}{(2\pi c^2)^3} \frac{\omega^2 d\omega}{e^{\beta\hbar\omega} - 1}$$

Let $\bar{u}(\omega; T)$ be the mean energy per unit volume in the frequency range between ω and $\omega + d\omega$ with both direction of polarization. This will be obtained by simply multiplying the above quantity with the energy $\hbar\omega$. Thus we have

$$\bar{u}(\omega; T) = \frac{\hbar}{\pi^2 c^3} \frac{\omega^3 d\omega}{e^{\beta\hbar\omega} - 1}$$

The significant dimensionless parameter is

$$\eta = \beta\hbar\omega = \hbar\omega k_B T$$

In terms of this

$$\bar{u}(\omega, T) = \frac{\hbar}{\pi^2 c^3} \left(\frac{k_B T}{\hbar}\right)^4 \frac{\eta^3 d\eta}{e^\eta - 1}$$

If we now plot the function $\frac{\pi^2 c^3 \hbar^3}{k_B^4} \frac{\bar{u}}{T^4}$ as a function of η we shall find that it is peaked at $\eta \approx 3$.

Now this peak will remain at the same η even at a different temperature. Thus we get a simple scaling relation. If the peak occurs at a frequency ω_1 at temperature T_1 , it will occur at different frequency ω_2 at temperature T_2 such that

$$\begin{aligned} \frac{\hbar\omega_1}{k_B T_1} &= \frac{\hbar\omega_2}{k_B T_2} \\ \frac{\omega_1}{T_1} &= \frac{\omega_2}{T_2} \end{aligned}$$

This result is known as Wein's displacement law.

The mean energy density is given by by

$$\begin{aligned} \bar{u}_0(T) &= \int_0^\infty \bar{u}(T; \omega) d\omega \\ &= \frac{\hbar}{\pi^2 c^3} \left(\frac{k_B T}{\hbar}\right)^4 \int_0^\infty \frac{\eta^3 d\eta}{e^\eta - 1} \\ &= \frac{\pi^2}{15} \frac{(k_B T)^4}{(c\hbar)^3} \end{aligned}$$

In the last line we have used

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

This is Stefan Boltzman law.

We can also calculate the radiation pressure. The pressure contribution to a photon in the state s with energy ϵ_s is given by $-\frac{\partial \epsilon_s}{\partial V}$

Hence the mean pressure due to all the photons is given by

$$\bar{p} = \sum_s \bar{n}_s \left(-\frac{\partial \epsilon_s}{\partial V} \right)$$

Now

$$\begin{aligned} \epsilon_s &= \hbar\omega \\ &= \hbar c(\kappa_x^2 + \kappa_y^2 + \kappa_z^2)^{\frac{1}{2}} \\ &= \hbar c \frac{2\pi}{L}(n_x^2 + n_y^2 + n_z^2)^{\frac{1}{2}} \end{aligned}$$

Here we take $L_x = L_y = L_z = L$.

Thus

$$\epsilon_s = CL^{-1} = CV^{-1/3}$$

here C is some constant. Thus substituting this volume in the formula of the pressure we get

$$\bar{p} = \frac{1}{3V} \sum_s \bar{n}_s \epsilon_s = \frac{1}{3} \bar{u}_0$$

The radiation pressure can be also calculated in the following different ways

$$\bar{p} = \frac{1}{\beta} \left(\frac{\partial \ln Z}{\partial V} \right)$$

Also we can use the detail kinetic argument. For example photons impinging on an area dA of the container wall normal to the z direction impart to it in unit time a mean z component of the momentum G_z^+ . In equilibrium an equal number of photons leaves the wall and gives rise to an equal momentum flow $-G_z^+$ in the opposite direction. Hence the net force per unit area, or pressure is given by

$$\bar{p} = \frac{1}{dA} [G_z^+ - (-G_z^+)] = \frac{2G_z^+}{dA}$$

Now

$$G_z^+ = \frac{1}{dt} \int_{\kappa_z > 0} [2f(\kappa) d^{\mathbf{\kappa}} (cdt dA \cos \theta) (\hbar \kappa_z)]$$

From that one can easily find the same expression for the radiation pressure.

Thus all the conclusions of Planck's law can be reestablished using Bose Einstein distribution.

9.1 Superfluidity of liquid Helium

The second example is that of the superfluidity of liquid Helium. Which we shall discuss rather phenomenologically, I mean without going in to rigorous derivations and same procedure will be followed for the Bose Einstein condensation of cold atomic gases. Historically this was also the first case where a condensate has been formed had been suspected by F. London as an explanation of certain peculiar behavior of Liquid behavior.

Basically after having found that an ideal boson gas behaves at low temperature very differently from a Boltzman gas, the following question arises:; In what physical conditions does this behavior manifests itself.

First we need to have an estimate of the critical temperature T_C . For example for the lightest element hydrogen , the atomic mass being $1 - .7 \times 10^{-24}$ gr , we obtain a critical temperature $7K$. For heavier elements the critical temperature is even less.

The problem of seeing the Bose Einstein condensation in nature is that at this extremely low temperature , all substances are either solid and liquid and hence cannot ne further cooled. However liquid Helium liquefies at $4.2K$ and does not freeze at even absolute 0. Particularly liquid Helium He^4 have bosonic atoms and may be treated as an ideal candidate for Bose Einstein condensation.

A very interesting properties of the He^4 around this region of low temperature is its extremely low viscosity $20\mu P$. In fact it has been known from twenties from the work of Kapitza and others that at the temperature $2.17K$ the liquid helium changes its properties drastically and has been characterized by two different phases above and below this temperature.

Particularly in the phase Helium *II* He^4 shows a frictionless flow through the capillary. This is known as superfluidity. It also has an enormously high thermal conductivity $10^4 - 10^5$. All these properties particularly lead to F. London to think of this phase transition of Helium at $2.17K$ as a manifestation of Bose Einstein condensation.

According to London's explanation at this temperature a macroscopic number of atoms populate the ground state while the other half populate the excited state, both being behaving as different phases. The ground state atoms behave like a superfluid where as the the excited atoms behave like a normal fluid. This is known as two fluid theory of Helium and obtained experimental support. For example, because of these two fluid the measurement of viscosity can give very different result depending on the method of measuring the viscosity. For example it has been shown the Helium can crawl along a capillary immersed in it. This happens mostly due to the superfluid phase. The viscosity of the normal components keeps it away from taking part in this crawling. On the other hand if the entire fluid is rotated in a bucket, then it is only the normal fluid that takes part. Superfluid can rotate only through the creation of vortices. Thus in this type of measurements only the normal fluid takes part as a result the viscosity is very high.

The huge thermal conductivity is also a reflection of fact that *HeII* consists of two different components. The heating of a certain region *A* with respect to a nearby region *B* leads to a difference of concentration of the atoms of the superfluid component, since their number decreases with increasing temperature. As a result the concentration of the superfluid component in the region of *A* is lowered and a current has to flow from the region *B* to *A*. The current causes an increase in the total density and total pressure in the region *A* which in turn gives rise to a current of the normal component from the region *A* to *B*. In a steady state in which temperature gradient is created $T_A > T_B$ between the two regions a super-current will flow from *A* to *B* and a normal current will flow from *B* to *A*.

Since the atoms of the superfluid component are all in the ground level they cannot carry heat. On the other hand the normal component can carry heat and the temperature difference that is created is accompanied by a flow of heat from the hot region to the cold region. This mechanism of heat transfer is very efficient. For example because of this *HeII* boils without creating bubble. Any local temperature rise near the boiling point does not lead to the evaporation of the boiling area and to the appearance of a bubble since the heat is immediately carried to the edge of the liquid causing the surface to evaporate.

9.2 Critical temperature

If the phase transition of the Helium is related to the Bose Einstein condensation then the transition temperature should be very close to T_C . And

indeed substituting the approximate values of the parameter for Helium we found T_C $3K$ which is close to the transition temperature $2.17K$ (given the crudity of the calculation of T_c where He^4 is treated as ideal gas whereas in reality it is strongly interacting.)

The next issue is the specific heat. In the earlier calculation we have calculated the specific heat below and above the transition temperature.

As we have learned that the specific heat at T_C when approached from the above and below of T_C shows different slope. That is very clearly demonstrated in the experimental behavior of the liquid Helium

9.3 How Bose Einstein condensation leads to superfluidity: Landau

We consider the motion of a body in a liquid. The viscosity of the liquid is expressed as a frictional force acting on the moving body, originating in the collisions between the body and the molecules of the liquid. Therefore it is possible to give a satisfactory account of viscosity of gases considering there molecules as free particles colliding from time to time with the body. However in a liquid since the molecules are correlated the the effect of such collision is collective. Therefore a body moving through a liquid and losing energy due collision with the molecules will loose the energy to the liquid as a whole and not to a single molecule as in the case of a Gas. This was also the spirit behind the evaluation of the specific heat of a crystal by assuming that the crystal vibrate in a collective manner. However because of the periodicity of the crystal it is much easier there to evaluate the frequency of these collective modes of the vibration and to find out the dispersion of these modes . However we can take clues about this modes from the experimental facts.

Added with these facts that liquid Helium is a quantum liquid. . We therefore assume that sound waves excited by a moving body through such liquid He^4 may be treated as quantum harmonic oscillators where each oscillator is characterized by its wave vector \mathbf{q} and frequency ω . We thus model liquid helium at very low temperature a a collection of such collective excitations above a quantum mechanical ground state. These excitations are bosonic and are at Thermodynamic equilibrium (T fixed) with the rest of the quantum liquid and a body moving through the He^4 will basically excite such low temperature collective modes. We call them phonons.

If the body moves through the liquid excites a phonon with momentum $\hbar\mathbf{q}$ and energy $\epsilon(\mathbf{q})$ then we get from the conservation laws

$$\begin{aligned}\mathbf{p} &= \mathbf{p}' + \hbar\mathbf{q} \\ \frac{p^2}{2M} &= \frac{p'^2}{2M} + \epsilon(q)\end{aligned}$$

It turns out that above two equations can be satisfied only within a narrow range of velocities. If these condition is not satisfies then the body will move through the liquid cannot gives rise to the excitation of phonons and hence superfluidity follows.

Solving these two equation simultaneously we get

$$\hbar\mathbf{q} \cdot \mathbf{v} = \frac{(\hbar q)^2}{2M} + \epsilon(q)$$

The right hand side of this equation is positive. Hence the angle θ between \mathbf{v} and \mathbf{q} has to be acute. The most efficient case is $\theta = 0$ In this case the velocity of the body will attains the minimum value which will still allow the phonon to be excited with momentum $\hbar q$. Thus the body has to move with a minimum velocity (known as Landau's critical velocity) given by

$$v_{min} = \frac{\epsilon(q)}{\hbar q}$$

For phonons

$$\epsilon(q) = c_s q$$

where c_s is the velocity of sound in liquid helium which is $237ms^{-1}$. Thus a body that will move through liquid Helium at very low temperature with a speed less than $237ms^{-1}$ will face no friction.

For an ideal Bose gas excitation are like free particles. Show that in that case the critical velocity can be 0. Thus an ideal Bose gas does not show superfluidity even though it can be condensed.

(For more details please read D. J. Amit 497 – 503)

9.4 A short note on the Bose Einsetin condensation

As we all know Bose Einstein condensation happens in three dimension due to the saturation of the number of particles in the higher levels (all levels except one for which $\epsilon = 0$)

So how one will calculate the number of particles in these exited levels. This is somewhat mathematically delicate. We call this number N'_{max}

As we have discussed

$$N'_{max} = \int_0^{\infty} \frac{d\epsilon n(\epsilon)}{e^{\beta(\epsilon-\mu)} - 1} \quad (4)$$

Now we are concerned with the lower limit of this integral.

At low temperature and very close to the $\epsilon = 0$, we can separate contribution due to the region near lower limit of the integral in the following way

$$\lim_{\delta \rightarrow 0} \int_{\delta}^{\lambda_1} \frac{d\epsilon n(\epsilon)}{e^{\beta(\epsilon-\mu)} - 1}$$

The integrand of this integrand, near its lower limit at very low temperature upon expansion gives

$$\frac{\delta^{\frac{1}{2}}}{(\beta\delta) + (\beta\delta)^2 + \dots - 1}$$

If we retain only the first term (since $\delta \rightarrow 0$) the integral becomes $\approx \int \delta^{-\frac{1}{2}} d\delta$. After performing this integral then we set $\delta = 0$ to see that the contribution due to the lower limit of the integral vanishes. If one set $\delta = 0$ within the integral itself one will get a spurious divergence. Therefore the way to take the limit is very delicate here.

One can employ the similar technique in $2D$ and $1D$ where one gets logarithmic and power law like divergence.

Russel-Hertzprung (RH) plot

Figure 3:

Figure 4: T