

# QUANTUM STATISTICAL MECHANICS

## Fermi-Dirac, Boson Einstein

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### Introduction:

**Boltzmann statistics Fermi-Dirac static's and Bose – Einstein statistics**

There are many important system, however in which the N-body Hamilton operator can be written assume of independent individual Hamilton and the energy of system can be written assume of individual energies.

The Boltzmann distribution law can be also be derived from Q(N,V,T) in high temperature with the First derivation the Fermi-Dirac and Bose-Einstein distribution.

### The special case of Boltzmann statistics:

The Hamilton of many body systems can be written as a sum of one body Hamilton the energy of the system is the sum of one body Hamilton, the Hamilton can be written as a sum of where the molecules are on the average far a part

$$H = H_{translation} + H_{rotational} + H_{vibrational} + H_{electronic}$$

In the quantum mechanics the fundamental concept of the quantum mechanics  $\Psi(q,t)$  the wave function where q represents set of coordination. the wave function is given the physical interpretation that the probability that of time the system is found between  $q_1$  and  $q_1+dq_1$  ,..... the uncertainly principle dictates the  $\Psi(a,t)$  is the most complete description of the system can be obtained :

$$\int \Psi^*(q,t)\Psi(q,t)dq = 1$$

$\Psi$  is said to be normalized .

The Hamilton operator is

$$\hat{H} = \hat{T} + \hat{V}$$

Where  $\hat{T} = \frac{\hat{p}^2}{2m}$

The Hamilton operator give

$$\hat{H} = \frac{\hat{p}^2}{2m} + V$$

The  $\hat{p}$  is the operator of moment give

$$\hat{p} = i \hbar \nabla$$

$$\hat{H} = -\frac{\hbar^2}{2m} \nabla^2 + V$$

The Schrödinger equation give by  $\hat{H}\Psi = E\Psi$ ,  $E$  is the scalar quantity corresponding to the energy of the system for  $\Psi(q,t)$  is the system and if apply the more  $\Psi_j(q,t)$  one more subscripts .generally then where

$$\hat{H}\Psi_j = E\Psi_j$$

1- The Hamilton in one –dimensional

$$H = -\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} + \frac{1}{2} kx^2$$

A simple harmonic oscillator and we can find by solve the equation

$$E = \hbar\omega \left( n + \frac{1}{2} \right)$$

Where  $\omega = \left( \frac{k}{m} \right)^{1/2}$

Consider the energy states of a particle in the 3-dimensional infinite we

$$\varepsilon_{n_x, n_y, n_z} = \frac{\hbar^2}{8ma^2} (n_x^2 + n_y^2 + n_z^2)$$

$n_x, n_y, n_z$  Space with coordination give

$$(n_x^2 + n_y^2 + n_z^2) = \frac{8ma^2\varepsilon}{\hbar^2} = R^2$$

We treat  $R$  a continuous variable in the volume of one in sphere of radiuses  $R$

$$\varphi(\varepsilon) = \frac{1}{8} \frac{4\pi}{3} R^3 = \frac{\pi}{6} \left( \frac{8ma^2\varepsilon}{\hbar^2} \right)^{3/2}$$

The number of sates between  $\varepsilon$  and

$$\omega(\varepsilon, \Delta\varepsilon) = \varphi(\varepsilon + \Delta\varepsilon) - \varphi(\varepsilon)$$

$$\omega(\varepsilon, \Delta\varepsilon) = \frac{\pi}{4} \left( \frac{8ma^2}{\hbar^2} \right)^{3/2} \varepsilon^{1/2} \Delta\varepsilon + O(\Delta\varepsilon^2)$$

For N-particle system

$$E = \frac{h^2}{8ma^2} \sum_{j=1}^N n_{xj}^2 + n_{yj}^2 + n_{zj}^2$$

The Hamilton can be written for a system distribution and individual energy  $\varepsilon_j^a$  where the superscript denotes the particle subscript the state

Canonical partition function become:-

$$Q(N, V, T) = \sum_j e^{-E_j / KT}$$

$$E_j = \varepsilon_i^a + \varepsilon_j^b + \varepsilon_k^c + \dots$$

$$Q(N, V, T) = \sum_{i, j, k, \dots} e^{-(\varepsilon_i^a + \varepsilon_j^b + \varepsilon_k^c + \dots) / KT} = \sum_i e^{-\varepsilon_i^a / KT} \sum_j e^{-\varepsilon_j^b / KT} \sum_k e^{-\varepsilon_k^c / KT} \dots$$

$$Q(N, V, T) = q_a q_b q_c \dots$$

The last equation very important result show that if we can write the N-particle Hamilton as a sum of independent terms the useful application of separation individual in equation is to the molecular partition function and the equation show that molecular Hamilton can be approximation the degrees of freedom of the molecule

$$Q_{mol} = q_{tran} q_{rota} q_{vibration} q_{electroin} \dots$$

$$q_{trans} = \sum_j e^{-\varepsilon_j^{trans} / kT}$$

If N-body energy

$$E_{ijkl\dots} = \varepsilon_i + \varepsilon_j + \varepsilon_k + \varepsilon_l + \dots$$

The Q(N,V,T) give portion function

$$Q(N, V, T) = \sum_{ijkl} e^{-(\varepsilon_i + \varepsilon_j + \varepsilon_k + \varepsilon_l + \dots) / kT}$$

Fermi-Dirac And Bose Einstein statistics

There are two cases to consider the evaluation the equation conical partion estimation . the resultant distribution function in the case of Fermions in called Fermi-Dirac and Bosons is called Bose- Einstein statistics the energy  $E_j(N, V)$  the system containing N-molecules and  $\varepsilon_k$  is the molecular quantum state when the system itself is in the quantum state with energy  $E_j$  the set  $\{n_k\}$  is the entire system total energy

$$E_j = \sum_k n_k \varepsilon_k$$

$$N = \sum_k n_k$$

We can write  $Q(V, T, N)$  as conical ensemble as

$$Q(V, T, N) = \sum_j e^{-\beta E_j} = \sum_j e^{-\beta \sum_k n_k \varepsilon_k}$$

This restriction turns but the be mathematics the grand canonical ensemble  $\Xi$  give

$$\Xi(V, T, \mu) = \sum_{N=0}^{\infty} Q(N, V, T) e^{\beta \mu \varepsilon_k}$$

We can write the grand conical ensemble

$$\Xi(V, T, \mu) = \sum_{N=0}^{\infty} \lambda^{\sum_k n_k} e^{-\beta \sum_k n_k \varepsilon_k}$$

$$\Xi(V, T, \mu) = \sum_{n_1}^{\infty} (\lambda e^{-\beta \varepsilon_1})^{n_1} \dots \sum_{n_k}^{\infty} (\lambda e^{-\beta \varepsilon_k})^{n_k}$$

In the finally we get

$$\Xi(V, T, \mu) = \prod_k \sum_{n_k} (\lambda e^{-\beta \varepsilon_k})^{n_k}$$

By the summation give  $(1-z)^{-1} = \sum_{k=0}^{\infty} z^k$  we can write the last equation

The Fermi – Dirac statistical and Bose – Einstein is given

$$\Xi(V, T, \mu) = \prod_k (1 + \lambda e^{-\beta \varepsilon_k})^{-1}$$

FD and BE given by

$$\Xi_{\substack{FD \\ EE}}(V, T, \mu) = \prod_k (1 \pm \lambda e^{-\beta \varepsilon_k})^{-1}$$

$$N = KT \left( \frac{\partial \ln \Xi}{\partial \mu} \right)_{V, T} = KT \left( \frac{\partial \ln \Xi}{\partial \lambda} \right)_{V, T} \left( \frac{\partial \lambda}{\partial \mu} \right)$$

We can define  $\lambda = e^{\mu \beta}$  give N by grand conical ensemble

$$N = \lambda \left( \frac{\partial \ln \Xi}{\partial \lambda} \right)_{V, T}$$

We can fin the GCE

$$\Xi(V, T, \lambda) = (1 \pm \lambda e^{-\beta \varepsilon_1})^{\pm 1} \dots (1 \pm \lambda e^{-\beta \varepsilon_k})^{\pm 1}$$

$$\ln(\Xi(V, T, \lambda)) = \ln(1 \pm \lambda e^{-\beta \varepsilon_1})^{\pm 1} + \dots + \ln(1 \pm \lambda e^{-\beta \varepsilon_k})^{\pm 1}$$

## Grand conical ensemble

$$\Xi(V, T, \lambda) = \pm \sum_k \ln(1 \pm \lambda e^{-\beta \varepsilon_k})$$

$$\frac{\partial \Xi}{\partial \lambda} = \sum_k \frac{e^{-\beta \varepsilon_k}}{1 \pm \lambda e^{-\beta \varepsilon_k}}$$

So N-particle is given by

$$N = \sum_k \frac{\lambda e^{-\beta \varepsilon_k}}{1 \pm \lambda e^{-\beta \varepsilon_k}}$$

Average number of particle in k

$$N = \sum_k n_k$$

We can find n

$$n_k = \frac{\lambda e^{-\beta \varepsilon_k}}{1 \pm \lambda e^{-\beta \varepsilon_k}}$$

We can find Energy by

$$E = N \varepsilon = \sum_k n_k \varepsilon_k = \sum_k \frac{\lambda \varepsilon_k e^{-\beta \varepsilon_k}}{1 \pm \lambda e^{-\beta \varepsilon_k}}$$

By the ideal gas equation

$$PV = NKT$$

The grand conical ensemble we show that PV is the thermodynamic function

$$PV = KT \ln \Xi(V, T, \mu)$$

We arrive no to PV give

$$PV = \pm KT \sum_k \ln(1 \pm \lambda e^{-\beta \varepsilon_k})$$

No we find the energy

$$\varepsilon_{n_x, n_y, n_z} = \frac{h^2}{8ma^2} (n_x^2 + n_y^2 + n_z^2)$$

$$n_x = \frac{a}{\pi} k_x \Rightarrow k_x^2 = \frac{\pi^2}{a^2} n_x^2$$

The same in x and y

$$n_y = \frac{a}{\pi} k_y \Rightarrow k_y^2 = \frac{\pi^2}{a^2} n_y^2$$

$$n_z = \frac{a}{\pi} k_z \Rightarrow k_z^2 = \frac{\pi^2}{a^2} n_z^2$$

$$k^2 = k_x^2 + k_y^2 + k_z^2 = \frac{\pi^2}{a^2} (n_x^2 + n_y^2 + n_z^2)$$

The moment p is given

$$P = \frac{h}{\lambda} = \frac{hk}{2\pi}$$

So the total energy is given by

$$\varepsilon_{n_x, n_y, n_z} = \frac{P^2}{2m} = \frac{h^2}{8ma^2} (n_x^2 + n_y^2 + n_z^2)$$

The basic equation associative with the two fundamental distribution laws is grand conical ensemble

$$\Xi = \prod_k (1 \pm \lambda e^{-\beta \varepsilon_k})^{\pm 1}$$

$$N = \sum_k \bar{n}_k$$

$$\bar{n}_k = \frac{\lambda e^{-\beta \varepsilon_k}}{1 \pm \lambda e^{-\beta \varepsilon_k}}$$

$$E = \sum_k \bar{n}_k \varepsilon_k$$

$$E = \sum_k \frac{\lambda \varepsilon_k e^{-\beta \varepsilon_k}}{1 \pm \lambda e^{-\beta \varepsilon_k}}$$

Where  $\lambda = e^{\mu\beta}$  and by the gas law we can find

$$PV = \pm KT \sum_k \ln(1 \pm \lambda e^{-\beta \varepsilon_k})$$

Where (+) is Fermi-Dirac and (-) is Bose-Einstein.

In this chapter we will study an ideal Fermi-Dirac gas for value of  $\lambda$  such that a series expansion the expansion useful in temperature and density region there are only small derivation from classical behavior in an ideal gas model the equation of state will no longer be  $PV=KTN$  and  $P = \rho KT$  in fact we will get the P and p is series .

**1-Weakly Degenerate ideal Fermi – Dirac gas :**

We are derive series of fermions in a region where  $\lambda$  is small enough that may represent the derivative from classical behavior by series of  $\lambda$  is small enough that we may represent the derivation from classical behavior by series of  $\lambda$  :

$$N = \sum_k \frac{\lambda e^{-\beta \varepsilon_k}}{1 + \lambda e^{-\beta \varepsilon_k}}$$

$$PV = KT \sum_k \ln(1 + \lambda e^{-\beta \varepsilon_k})$$

$\varepsilon_k$  the eigenvalue of particle in box under index  $k$

$$\varepsilon_{n_1, n_2, n_3} = \frac{h^2}{8mV^{2/3}} (n_x^2 + n_y^2 + n_z^2)$$

We get the energy state to integrals over energy levels in  $\varepsilon$  and  $\varepsilon + d\varepsilon$  give integral

$$d\omega(\varepsilon, \Delta\varepsilon) = 2\pi \left( \frac{2m}{h^2} \right)^{3/2} V \varepsilon^{1/2} d\varepsilon$$

We can write the summation by Riemannian integration in all number to be continuous and write:

$$N = 2\pi \left( \frac{2m}{h^2} \right)^{3/2} V \int_0^\infty \frac{\lambda \varepsilon^{1/2} e^{-\beta \varepsilon_k}}{1 + \lambda e^{-\beta \varepsilon_k}} d\varepsilon$$

This integration given by analysis we can write this by

$$\int_0^\infty \frac{\lambda \varepsilon^{1/2} e^{-\beta \varepsilon_k}}{1 + \lambda e^{-\beta \varepsilon_k}} d\varepsilon$$

But  $\beta\varepsilon = y \Rightarrow d\varepsilon = \frac{1}{\beta} dy$  give integral

$$\frac{1}{\beta^{3/2}} \int_0^\infty \frac{\lambda y^{1/2} e^{-\beta \varepsilon_k}}{1 + \lambda e^{-y}} d\varepsilon$$

$$\frac{1}{1+z} = 1 - z + z^2 - z^3 + \dots$$

$$\frac{1}{1+\lambda e^{-y}} = 1 - \lambda e^{-y} + (\lambda e^{-y})^2 - (\lambda e^{-y})^3 + \dots$$

$$(1 + \lambda e^{-y})^{-1} = \sum_{l=0}^{\infty} (-1)^{l+1} \lambda^l e^{-ly}$$

**By the integration**

$$\frac{1}{\beta^{3/2}} \int_0^{\infty} \lambda y^{1/2} e^{-y} \sum_{l=0}^{\infty} (-1)^{l+1} \lambda^l e^{-ly} dy$$

**By change index and give integration**

$$\frac{1}{\beta^{3/2}} \sum_k (-1)^{l+1} \lambda^{l+1} \int_0^{\infty} y^{1/2} e^{-y-ly} dy$$

**In the finally the integration**

$$(KT)^{3/2} \sum_{l=1}^{\infty} (-1)^{l+1} \frac{\lambda^l}{l^{3/2}} \Gamma 3/2$$

$$N = \left( \frac{2\pi mKT}{h^2} \right)^{3/2} V \sum_{l=1}^{\infty} (-1)^{l+1} \frac{\lambda^l}{l^{3/2}}$$

$$\Lambda = \left( \frac{h^2}{2\pi mKT} \right)^{1/2} \Rightarrow \frac{1}{\Lambda^3} = \left( \frac{2\pi mKT}{h^2} \right)^{3/2}$$

**Now we can write the N by**

$$N = \frac{1}{\Lambda^3} V \sum_{l=1}^{\infty} (-1)^{l+1} \frac{\lambda^l}{l^{3/2}}$$

**And the density we can find by p :**

$$\rho = \frac{1}{\Lambda^3} \sum_{l=1}^{\infty} (-1)^{l+1} \frac{\lambda^l}{l^{3/2}}$$

**We can write the equation like is called reversion of series and can be done in general we can write  $\lambda = a_0 + a_1\rho + a_2\rho^2 + \dots$**

**We can find  $a_0 = 0$  and**

$$\rho = \frac{1}{\Lambda^3} (a_1\rho + \dots)$$

**So that**

$$a_1 = \Lambda^3$$

$$\rho = \frac{1}{\Lambda^3} (a_1\rho + a_2\rho^2 - \frac{a_1^2\rho^2 + 2a_1a_2\rho^3 + a_2^2}{2^{3/2}})$$

$$a_2 - \frac{a_1^2}{2^{3/2}} = 0$$

And give that

$$a_2 = \frac{(\Lambda^3)^2}{2^{3/2}}$$

And can find  $a_3$

$$a_3 - \frac{2a_1a_2}{2^{3/2}} + \frac{a_2^3}{2^{3/2}} = 0$$

$$a_3 = \left[ \frac{1}{4} - \frac{1}{2^{3/2}} \right] (\Lambda^3)^3$$

$$\lambda = \Lambda^3 \rho + \frac{1}{2^{3/2}} (\Lambda^3 \rho)^2 + \left[ \frac{1}{4} - \frac{1}{2^{3/2}} \right] (\Lambda^3 \rho)^3$$

Now we want get the ratio  $\frac{P}{KT}$  by integration

$$PV = KT \sum_k (\ln(1 + \lambda e^{-\beta \varepsilon_k}))$$

$$P = KT (2\pi) \left( \frac{2m}{h^2} \right)^{3/2} \int_0^\infty \varepsilon^{1/2} \ln(1 + \lambda e^{-\beta \varepsilon}) d\varepsilon$$

$$\frac{P}{KT} = (2\pi) \left( \frac{2m}{h^2} \right)^{3/2} \int_0^\infty \varepsilon^{1/2} \ln(1 + \lambda e^{-\beta \varepsilon}) d\varepsilon$$

**Ln(1+Z)** we can find that by Taylor series around  $Z = Z_0$

$$f(z) = 1 + (z - z_0) f'(z) + \frac{(z - z_0)^2}{2!} f''(z) + \dots$$

$$\ln(1 - z) = z - \frac{z^2}{2} + \frac{z^3}{3} - \dots$$

So that

$$\ln(1 + \lambda e^{-\beta \varepsilon}) = \sum_{l=1}^k (-1)^{l+1} \frac{(\lambda e^{-\beta \varepsilon})^l}{l}$$

The integration give by the last equation

$$\int_0^\infty \varepsilon^{1/2} \ln(1 + \lambda e^{-\beta \varepsilon}) d\varepsilon = \int_0^\infty \varepsilon^{1/2} \sum_{l=1}^k (-1)^{l+1} \frac{(\lambda e^{-\beta \varepsilon})^l}{l} d\varepsilon$$

This give

$$\int_0^\infty \varepsilon^{1/2} \ln(1 + \lambda e^{-\beta \varepsilon}) d\varepsilon = \frac{1}{\beta^{3/2}} \sum_{l=1}^\infty \frac{(-1)^{l+1} \lambda^l}{l^{5/2}}$$

$$\frac{P}{KT} = \left( \frac{2m\pi KT}{h^2} \right)^{3/2} \sum_{l=1}^{\infty} \frac{(-1)^{l+1} \lambda^l}{l^{5/2}}$$

$$\frac{P}{KT} = \frac{1}{\Lambda^3} \sum_{l=1}^{\infty} \frac{(-1)^{l+1} \lambda^l}{l^{5/2}}$$

By  $\lambda$  expansion we can find the P/KT looks like

$$\frac{P}{KT} = \rho + \frac{\Lambda^3}{2^{5/2}} \rho^2 + \left[ \frac{1}{8} - \frac{2}{3^{5/2}} \right] \Lambda^6 \rho^3 + \dots$$

We can write the ratio by

$$\frac{P}{KT} = \rho + B_2(T) \rho^2 + B_3(T) \rho^3 + \dots$$

Where  $B_j(T)$  is a function of only the temperature is called the  $j$ th virial coefficient  $\Lambda$  is just the thermal DeBroglie wave length

We can find total energy with  $E=(3/2)PV$

$$E = \frac{3}{2} V K T \frac{1}{\Lambda^3} \sum_{l=1}^{\infty} \frac{(-1)^{l+1} \lambda^l}{l^{5/2}}$$

And  $\lambda$  substituted this we get

$$E = \frac{3}{2} N K T \left( 1 + \frac{\Lambda^3}{2^{5/2}} \rho + \dots \right)$$

All other thermodynamic function can be obtained the integral formula the energy obtained by the last formula where the density in large volume

### 2- Weakly Degenerate ideal Bose-Einstein gas :

We are treatment the ideal gas Bose- Einstein are define  $\lambda = e^{\beta\mu}$  and  $\beta = 1/KT$  we are expansion in  $\lambda$  as we did Fermi – Dirac we used the signs (-)

$$N = \sum_k \frac{\lambda e^{-\beta\varepsilon_k}}{1 - \lambda e^{-\beta\varepsilon_k}}$$

$$PV = -KT \sum_k \ln(1 - \lambda e^{-\beta\varepsilon_k})$$

In last equation we see that  $\lambda$  is restricted to the value  $0 \leq \lambda < e^{-\beta\varepsilon_0}$  thus if we wish our result to be valid for all of  $\lambda$  we can write N like

$$N = \frac{\lambda e^{-\beta\varepsilon_0}}{1 - \lambda e^{-\beta\varepsilon_0}} + \sum_{k \neq 0} \frac{\lambda e^{-\beta\varepsilon_k}}{1 - \lambda e^{-\beta\varepsilon_k}}$$

We can defined N by integration in summation we can write this by integration  $\varepsilon > \varepsilon_0$  give that and state in physical resultant must be independent of where one state zero of energy such that  $\varepsilon_0 = 0$  the last equation become

$$\rho = \frac{1}{V} \frac{\lambda}{1-\lambda} + 2\pi \left( \frac{2m}{h^2} \right)^{3/2} \int_{\varepsilon > \varepsilon_0}^{\infty} \frac{\lambda \varepsilon^{1/2} e^{-\beta \varepsilon_k}}{1 - \lambda e^{-\beta \varepsilon_k}} d\varepsilon$$

So we can define the PV looks like

$$PV = -KT \ln(1-\lambda) - KT \sum_{k \neq 0} \ln(1 - \lambda e^{-\beta \varepsilon_k})$$

And by integration we can write that

$$\frac{P}{KT} = -2\pi \left( \frac{2m}{h^2} \right)^{3/2} \int_{\varepsilon > \varepsilon_0}^{\infty} \varepsilon^{1/2} \ln(1 - \lambda e^{-\beta \varepsilon}) d\varepsilon - \frac{1}{V} \ln(1-\lambda)$$

The both equation  $0 \leq \lambda < 1$

Notes : the second transformation of both equation contain a factor of  $1/V$ . ordinary it is legitimate to ignore such terms since we are always interested only in the thermodynamic limited.

Where  $\lambda \rightarrow 1$   $\lambda/(1-\lambda) \rightarrow \infty$  we are get the integer of two equations and neglected the 1 in integration the result give

$$\rho = \frac{1}{\Lambda^3} \sum_{l=1}^{\infty} \frac{\lambda^l}{l^{3/2}}$$

Where

$$\rho = \frac{1}{\Lambda^3} g_{3/2}$$

And

$$\frac{P}{\rho KT} = 1 - \frac{\Lambda^3}{2^{5/2}} \rho + \dots$$

Look the second terms in this equation must be neglects and the energy

$$E = \frac{3}{2} PV = \frac{3}{2} NKT \left( \frac{P}{\rho KT} \right)$$

$$E = \frac{3}{2} NKT \left( 1 - \frac{\Lambda^3}{2^{5/2}} + \dots \right)$$

Where

$$E = \frac{3}{2} NKT \left( 1 - \Lambda^3 g_{5/2} + \dots \right)$$

And

$$g_n = \sum_{l=1}^{\infty} \frac{\lambda^l}{l^n}$$

All other thermodynamic function for a weakly degenerate ideal gas of Bosons following in similar way in thermodynamics function useful only for small  $\lambda$  or small  $\rho$  and represent small quantum correction to the limited classical result

### 3- A strongly Degenerate ideal Fermi – Dirac gas

First we shall treat the case of ideal Fermi – Dirac at low temperature and or height density we get

$$\bar{n}_k = \frac{\lambda e^{-\beta \varepsilon_k}}{1 + \lambda e^{-\beta \varepsilon_k}}$$

Where  $\lambda = e^{\beta \mu}$

$$\bar{n}_k = \frac{1}{1 + e^{\beta(\varepsilon_k - \mu)}}$$

As in the pervious section  $\varepsilon_k$  is essentially a continuous parameter and we can write f by

$$f(\varepsilon) = \frac{1}{1 + e^{\beta(\varepsilon - \mu)}}$$

Where  $f(\varepsilon)$  is the probability that a given state in occupied this equation the number of states with energy between  $\varepsilon$  and  $\varepsilon + d\varepsilon$  give

$$\omega(\varepsilon)d\varepsilon = 4\pi \left( \frac{2m}{h^2} \right)^{3/2} V \varepsilon^{1/2} d\varepsilon$$

We can define  $\mu_0$  immediately from the fact that all the states below  $\varepsilon = \mu_0$  are occupied and all these above are unoccupied this if N is the number of valence electrons

$$N = 4\pi \left( \frac{2m}{h^2} \right)^{3/2} V \int_0^{\mu_0} \varepsilon^{1/2} d\varepsilon$$

$$N = \frac{8\pi}{3} \left( \frac{2m}{h^2} \right)^{3/2} V \mu_0^{3/2}$$

And we can get  $\mu_0$

$$\mu_0 = \frac{h^2}{2m} \left( \frac{3}{8\pi} \right)^{2/3} \left( \frac{N}{V} \right)^{3/2}$$

The distribution  $f(\varepsilon)$  still essentially a step function a  $T=0$  compared to characterize temperature  $\mu_0 / K$  room temperature may be consider to be zero and it is an excellent first approximation use distribution

$$\begin{aligned} f(\varepsilon) &= 1 \Rightarrow \varepsilon < \mu_0 \\ &= 0 \Rightarrow \varepsilon > \mu_0 \end{aligned}$$

At room temperature the quantity  $\mu_0 / K$  is called Fermi temperature and denote by  $T_F$ . Fermi temperature are typically of the order of thousands and degrees Kelvin

$$E_0 = 4\pi \left( \frac{2m}{h^2} \right)^{3/2} V \int_0^{\mu_0} \varepsilon^{3/2} d\varepsilon$$

$$E_0 = \frac{2}{5} 4\pi \left( \frac{2m}{h^2} \right)^{3/2} V \varepsilon^{3/2} \varepsilon \Big|_0^{\mu_0}$$

$$E_0 = \frac{2}{5} N \mu_0$$

Where we have written  $E_0$  to emphasize that this  $T=0K$  result the equation give in zero temperature distribution but not difficult to calculate correction to be these zero temperature and we are expansion in power of parameter  $\eta = KT / \mu_{e0}$ . now we can write all thermodynamic quantities N, E, P,..... can be written by

$$I = \int_0^{\infty} f(\varepsilon) h(\varepsilon) d\varepsilon$$

Where  $I=N$  give h by

$$h(\varepsilon) = 4\pi \left( \frac{2m}{h^2} \right)^{3/2} V \varepsilon^{3/2}$$

And we derive the E and N by the I by integral by part give

$$I = f(\varepsilon) H(\varepsilon) \Big|_0^{\infty} - \int_0^{\infty} f'(\varepsilon) h(\varepsilon) d\varepsilon$$

Now we can find the I give

$$I = - \int_0^{\infty} f'(\varepsilon) h(\varepsilon) d\varepsilon$$

Where

$$H(\varepsilon) = \int_0^{\varepsilon} h(\varepsilon) d\varepsilon$$

We using the fact  $f(\varepsilon) = 0$  and  $f'(\varepsilon)$  is nonzero only for some small region around  $\varepsilon = \mu$  and we can find  $H(\varepsilon)$  by Taylor around  $\varepsilon = \mu$

$$H(\varepsilon) = H(\mu) + (\varepsilon - \mu) \left( \frac{dH}{d\varepsilon} \right)_{\varepsilon=\mu} + \frac{1}{2} (\varepsilon - \mu)^2 \left( \frac{d^2H}{d\varepsilon^2} \right)_{\varepsilon=\mu} + \dots$$

$$I = H(\varepsilon) = H(\mu) + \left( \frac{dH}{d\varepsilon} \right)_{\varepsilon=\mu} L_0 + \frac{1}{2} \left( \frac{d^2H}{d\varepsilon^2} \right)_{\varepsilon=\mu} L_1 + \dots$$

Where

$$L_j = -\int_0^{\infty} (\varepsilon - \mu)^j f'(\varepsilon) d\varepsilon$$

The first integral  $L_1 = 1$

And we can find  $L_1, L_2, \dots$  we may replace the lower limited  $-\infty$  so we can write the probability function like

$$f'(\varepsilon) = \frac{\beta e^{\beta(\varepsilon - \mu)}}{(1 + \beta e^{\beta(\varepsilon - \mu)})^2}$$

But  $\beta(\varepsilon - \mu) = x$  and  $d\varepsilon = dx / \beta$

$$L_j = -\frac{1}{\beta^j} \int_0^{\infty} \frac{x^j e^x}{(1 + e^x)^2} dx, j = 0, 1, 2, \dots$$

Now we can find  $L_1 = 0$

$$L_2 = -\frac{1}{\beta^2} \int_0^{\infty} \frac{x^2 e^x}{(1 + e^x)^2} dx = \frac{\pi^2}{3\beta^2}$$

Now we can write the I by

$$I = H(\mu) + \frac{\pi^2}{6} (KT)^2 \left( \frac{d^2 H}{d\varepsilon^2} \right)_{\varepsilon=\mu}$$

Now we can defined  $H(\varepsilon) = \int_0^{\varepsilon} h(\varepsilon) d\varepsilon$  and we calculate N in this case

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

$$H(\mu) = \frac{8\pi}{3} \left( \frac{2m}{h^2} \right)^{3/2} V \mu^{3/2}$$

$$\frac{d^2 H}{d\varepsilon^2} \Big|_{\varepsilon=\mu} = 2\pi \left( \frac{2m}{h^2} \right)^{3/2} V \mu^{-1/2}$$

By replace I by N and give N now

$$N = \frac{8\pi}{3} \left( \frac{2m}{h^2} \right)^{3/2} V \mu^{3/2} \left[ 1 + \frac{\pi^2}{8} (\beta\mu)^{-2} \right]$$

By equation

$$\mu_0 = \frac{h^2}{2m} \left( \frac{3}{8\pi} \right)^{2/3} \left( \frac{N}{V} \right)^{3/2}$$

$$\mu_0 = \mu \left[ 1 + \frac{\pi^2}{8} (\beta\mu)^{-2} \right]^{2/3}$$

$$\mu = \mu_0 \left[ 1 + \frac{\pi^2}{8} (\beta\mu)^{-2} \right]^{-2/3}$$

$$\mu = \mu_0 \left[ 1 - \frac{\pi^2}{12} (\beta\mu)^{-2} \right]$$

**This equation show that  $\mu$  change slowly with temperature and is approximately  $\mu_0$  throughout the entire solid state range of a metal  
Now we can calculate E by the I looks like**

$$h(\varepsilon) = 4\pi \left( \frac{2m}{h^2} \right)^{3/2} V \varepsilon^{3/2}$$

**so we can write**

$$H(\varepsilon) = \frac{4\pi}{5} \left( \frac{2m}{h^2} \right)^{3/2} V \varepsilon^{5/2}$$

$$\frac{d^2 H}{d\varepsilon^2} = 6\pi \left( \frac{2m}{h^2} \right)^{3/2} V \varepsilon^{1/2}$$

**In the finally we get on E by series**

$$E = \frac{8\pi}{5} \left( \frac{2m}{h^2} \right)^{3/2} V \mu^{5/2} \left[ 1 + \frac{5\pi^2}{8} (\beta\mu)^{-2} \right]$$

$$E = E_0 \left( \frac{\mu}{\mu_0} \right)^{5/2} \left[ 1 + \frac{5\pi^2}{8} (\beta\mu)^{-2} \right]$$

**By the ratio we fin E**

$$E = E_0 \left[ 1 + \frac{5\pi^2}{12} (\beta\mu)^{-2} \right]$$

**The last equation give the energy in power series**

#### **4-A strongly Degenerate ideal Bose-Einstein :**

**we consider the situation when  $\lambda$  not necessarily small let us to return equation in weakly Bose –Einstein**

$$\rho = 2\pi \left( \frac{2m}{h^2} \right)^{3/2} \int_0^\infty \frac{\lambda \varepsilon^{1/2} e^{-\beta \varepsilon}}{1 - \lambda e^{-\beta \varepsilon}} d\varepsilon + \frac{\lambda}{V(1-\lambda)}$$
$$\frac{P}{KT} = -2\pi \left( \frac{2m}{h^2} \right)^{3/2} \int_0^\infty \varepsilon^{1/2} \ln(1 - \lambda e^{-\beta \varepsilon}) d\varepsilon - \frac{1}{V} \ln(1 - \lambda)$$

**Where  $0 \leq \lambda < 1$  and we write equation by  $g_n(\lambda)$  is give**

$$\rho = \frac{1}{\Lambda^3} g_{3/2}(\lambda) + \frac{\lambda}{V(1-\lambda)}$$
$$\frac{P}{KT} = \frac{1}{\Lambda^3} g_{5/2}(\lambda) - \frac{1}{V} \ln(1 - \lambda)$$

**Where**

$$g_n(\lambda) = \sum_{\lambda=1}^{\infty} \frac{1}{\lambda^n}$$

**we can define Riemann zeta function**

$$\xi(n) = \sum_{l=1}^{\infty} \frac{1}{l^n}$$

**By the average number of particle in their ground state**

$$\bar{n}_k = \frac{\lambda}{1-\lambda}$$

**So it is clear that  $0 \leq \lambda < 1$  in order to determine the equation of state now we need determine  $\lambda, \rho$  by solving equation can find that by graphs like that**

$$\rho \Lambda^3 = g_{3/2}(\lambda) + \frac{\Lambda^3}{V} \frac{\lambda}{1-\lambda}$$

**And notes Riemann zeta function**

$$\xi(3/2) = 2.612....$$

**The rang of  $\rho \Lambda^3$  give  $0 < \rho \Lambda^3 < 2.612$  by**

$$a = \frac{\Lambda^3}{\rho \Lambda^3 - g_{3/2}(\lambda)} \Rightarrow \rho \Lambda^3 > g_{3/2}(\lambda)$$

**Is a continuous function of  $\lambda$**

$$\lambda = 1 - \frac{a}{V}$$

In this equation where  $V \rightarrow \infty$  give  $\lambda = 1$  clearly the point  $\rho\Lambda^3 = \rho \left( \frac{h^2}{2\pi mKT} \right)^{3/2}$  to be a function of the T and we can find the number of particle in their ground state

$$\bar{n}_k = \frac{\lambda}{1 - \lambda} = \frac{V}{a}$$

$$\bar{n}_k = \frac{V}{\Lambda^3} (\rho\Lambda^3 - g_{3/2}(l))$$

We can write their in a more interactive form by define temperature  $T_0$

$$\rho\Lambda_0^3 = \rho \left( \frac{h^2}{2\pi mKT_0} \right)^{3/2} = g_{3/2}(l)$$

In this terms then

$$\bar{n}_0 = V \left( \rho - \frac{g_{3/2}(l)}{\Lambda^3} \right)$$

It can be seen that where  $T > T^0$  the fraction of molecular in their ground state is essentially zero. This is the normal situation. Where the molecular can distribution smoothly over the many molecular quantum states available to each one. However as the temperature is lowered past T . Sadly the ground state begins to be appreciably population.

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