# Unit - 3

01/April/2019

## Transition from classical Statistical Mechanics to Quantum Statistical Mechanics

[Two facts]

1) Physical Quantities in quantum mechanics in general are assumed to have discrete Spectra.
This fact requires that finite sums or infinite series be used in place of the usual integrals of classical mechanics.

2.) Physical Quantities, in addition to depending on the usual hamiltonian variables of classical mechanics, depend upon (Spin Variables) which are essential to quantum physics & have no analogies in classical mechanics.

Imp
- In classical mechanics the state of system is uniquely determined if all the physical quantities associated with the system are known, whereas in quantum mechanics, the state of a system defines the physical quantities only as random variables i.e it determines the laws of distributions obeyed by the Physical quantities & not values.

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A new quantum concepts of discrete exchange of energy b/w Systems & along with it a new statistics, k/a quantum statistics. In 1924, the quantum statistics was first formulated by Bose in the detection of Plank's Radiation law Einstein in the Same year employed in KE theory of gases as a substitute for the classical Boltzmann statistics, k/a Bose - einstein Statistics.

In 1926 Fermi & Dirac quigte independently modified Bose - einstein statistics in certain cases, on the basis of Pauli exclusion principle k/a Fermi-Dirac Staptistics. Thus the Quantum Statistics can be put into 2 subclasses — 1) Fermi-Dirac & 2) Bose - einstein Statistics

# Identical Particles:

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Identical Particles of any spin which are separated in the assembly which can be distinguish from one another for ex - the molecule of the gas

- Identical Particles of Zero or integral spins, which can't distinguish from one another, the particles are k/a Bose particles and Bosons. They don't obey Pauli Exclusion Principle
  For ex - Photons. $\alpha$ particles etc
- Identical Particles of half integral spins, which can't be distinguish from one another, & these particles obey Pauli's exclusion Principle are k/a Fermions
  Ex - electron, proton, etc

## Postulates of Quantum Statistical Mechanics:

The state of a quantum system at any instant of time by its wave func^n $\Psi$.

$$\Psi = \Psi(x, t)$$

where $x - x_1, x_2, x_3 \ldots$

In Hilbert space $|\Psi\rangle$.

$|\Psi\rangle$ is linear comb^n of eigen func^n of any Hamiltonian of the Hilbert space

$$|\Psi\rangle = \sum_n C_n |\phi_n\rangle \quad -① \qquad H|\phi\rangle = E_n|\phi_n\rangle$$

$$\langle A\rangle = \frac{\langle\Psi|\hat{A}|\Psi\rangle}{\langle\Psi|\Psi\rangle} = \frac{\int \Psi^* A \Psi^* \, d\tau}{\int \Psi^* \Psi}$$

$$= \frac{\sum_m\sum_n C_m C_n^* \langle\phi_n|\hat{A}|\phi_m\rangle}{\sum_n\sum_m C_n C_m \langle\phi_n|\phi_m\rangle} = \frac{\sum_n\sum_m C_n^* C_m \langle\phi_n|\hat{A}|\phi_m\rangle}{\sum_n\sum_m C_n^* C_m} \quad -③$$

using orthonormality of $|\phi_n\rangle$

where $C_n$ & $C_m$ are time-dependent constant in general.

now, microscopic system can never be considered isolated system (they continouslly interact with environment. although extremely weakly)

So, the state involved should be the state of the system + the environment combined, the state of the system will look like this

$$|\psi\rangle = \sum_n d_n |\chi_m\rangle |\phi_n\rangle$$

$\chi_n$ represent constant state of the Environment .

$$C_n \rightarrow d_n |\chi_m\rangle$$

$C_n$ will n't remain constant now but involved state of the environment

The expectation value of an observable A can be again (still be) calculate by using eqn ③ provided we identify $C_n^* C_m = d_n^* d_m \langle\chi_n|\chi_m\rangle$

however, when we measure in thermodynamics system, our measurement are never instanteous quite simply bcoz atoms & molecules move much faster then what are measuring apparatus can resolve.

what we measure really is time average value of observable The time over which average is done or rather happens is much long then typical ~~collission~~ tym of atoms & molecules

$$\langle A\rangle = \frac{\overline{\langle\psi|A|\psi\rangle}}{\overline{\langle\psi|\psi\rangle}} = \frac{\sum_n\sum_m \overline{C_n^* C_m} \langle\phi_n|\hat{A}|\phi_m\rangle}{\sum_n \overline{C_n^* C_m}} \quad - \textcircled{5}$$

④

$$= \frac{\sum_n\sum_m \overline{d_n^* d_m \langle\chi_n|\chi_m\rangle} \langle\phi_n|\hat{A}|\phi_m\rangle}{\sum_n \overline{d_n^* d_m} \langle\chi_n|\chi_m\rangle} \quad - \textcircled{6}$$

eqn (6) is very difficult to calculate as it involves all the state of environment & its interacn with system. In General this can't be calculated but one can calculated gueses arount it.

## Trace of Matrix :

03/April/19

Trace is usually used as an alternative way to write expectation values of an operator in quantum mechanics

(Postulates of Q. S Mechanics) :-

The Postulates of Quantum statistical mechanics are actually Postulates about the form $\overline{C_n^* C_n}$

① Postulate of equal a priori probability

i.e $$\overline{C_n^* C_n} = \begin{cases} 1 & (E < E_n < E + \Delta E) \\ 0 & \text{other cases} \end{cases} \quad \text{— ⑦}$$

It implies that only those states are allowed which confirm to the fixed energy const~~ant~~ raints (for fixed energy interval (E to E + ΔE)

& all such states are equally probable

② Postulate of Random Phases.

$$\overline{C_n^* C_m} = 0 \qquad (n \neq m)$$

Ex In Quantum Mechanics if $|\psi_1\rangle$ & $|\psi_2\rangle$ are 2 allowed state & the Linear Comb^n (Superpos^n of these 2) are also in allowed State i.e $\alpha_1|\psi_1\rangle + \alpha_2|\psi_2\rangle$ in Q. Mechanics.

But In Quantum Statistics mechanics this postulate implies that Quantum superpos^n of any 2 energy eigen states $|\phi_n\rangle$ & $|\phi_m\rangle$ (from eq^n ⑤) aren't allowed.

This is due to the effect of environment on the system & it grants a special status to energy eigen states.

## Density Matrix :

For a Quantum system a state defined by state func^n $|\psi\rangle$. The expectation value ~~of an~~ (observable quantity) of a quantum operator in such a state will be $\langle\psi|\hat{A}|\psi\rangle$.

$$\langle\psi|\hat{A}|\psi\rangle = \text{Trace of } \hat{A}\,|\psi\rangle|\psi\rangle \quad \text{— (7a)}$$

density can also be written as -

$\hat{\rho} = \cancel{|\Phi\rangle\langle\Psi\rangle}$, is for normalized $|\Psi\rangle$ — ⑧

$= \langle\Psi|\Psi\rangle$

$$\hat{\rho} = \frac{|\Psi\rangle\langle\Psi|}{\text{Trace}\{|\Psi\rangle\langle\Psi|\}} \quad \text{(unnormalised)} \quad — ⑨$$

—— Trace over a complete set of states

A quantum system in state $|\Psi\rangle$ can be described by a density operator $\hat{\rho}$. And expectation value $\langle\hat{A}\rangle$ can also be written in the form of density vector $\hat{\rho}$

$$\langle A\rangle = \text{Tr}\{\hat{\rho}A\}.$$

$$\langle A\rangle = \sum_{n,m} \langle\phi_n|\hat{\rho}|\phi_m\rangle\langle\phi_n|\hat{A}|\phi_m\rangle$$

$$\boxed{\langle A\rangle = \sum_{n,m} \hat{\rho}_{n,m}\langle\phi_n|\hat{A}|\phi_m\rangle} \quad — ⑩$$

where $\hat{\rho}_{n,m} = \langle\phi_n|\hat{\rho}|\phi_m\rangle$ and k/a density matrix
For a pure state, described by a single wave funcⁿ, the density matrix is always non-diagonal. It can be diagonal only when the system is in one of its energy eigen states
Comparing the above eqⁿ (10) with eqⁿ no. ⑤

$$\hat{\rho}_{n,m} = \frac{\overline{C_n^* C_m}}{\sum_n \overline{C_n^* C_n}} \quad — ⑪$$

Further more the postulates of quantum statistical mechanics ~~stated~~ ~~states~~ implies that this density matrix (in the representation of energy eigen state) is diagonal. i.e

$$\hat{\rho} = \frac{\overline{C_n^* C_n}}{\sum_n C_n^* C_n}\,\delta_{nm}.$$

The average value of observable can now be written as

$$\boxed{\langle\hat{A}\rangle = \sum_n \rho_{nm}\langle\phi_n|\hat{A}|\phi_n\rangle} \quad — ⑫$$

## The density of matrix for micro-canonical ensembles.

The eq^n ⑫ represents an average value of observable $\hat{A}$ over an ensemble which consists of copies of the system, in different microstates (quantum states) $|\phi_1\rangle |\phi_2\rangle \cdots |\phi_n\rangle$ etc. The microstates (quantum states) $|\phi_K\rangle$ occurs with a probability $\hat{\rho}_{K,K}$. Here $\rho_{n,m}$ is an example of mixed state density matrix. It represents a mixture or an ensemble of systems in different microstate occurring with different probability.

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$$\rho_{nn} = \frac{\overline{C_n^* C_n}}{\sum_K C_K^* C_K} \qquad C_n^* C_n = \begin{cases} 1 & E < E_n < E + \Delta E \\ 0 \end{cases}$$

Total no. of microstate $(\Omega)$

Density matrix for micro-canonical ensemble $\longrightarrow$

$$\boxed{\rho_{nn} = \begin{cases} \frac{1}{\Omega} & E < E_n < E + \Delta E \\ 0 \end{cases}}$$

## Density matrix for canonical ensembles

The density matrix for canonical ensembles.

$$\rho_{n,n} = \frac{e^{-\beta E}}{Z} \qquad \text{where} \quad \boxed{Z = \sum_n e^{-\beta E_n}}$$

Partition func^n

The ensemble average value of observable in this case can now be written as –

$$\boxed{\langle A \rangle = \frac{1}{Z} \sum_n e^{-\beta E_n} \langle \phi_n | \hat{A} | \phi_n \rangle}$$

## Density matrix for Grand canonical ensemble

$$\rho_{nn} = \frac{e^{-\beta[E_n - \mu N]}}{Z} \qquad \text{where} \quad Z = \sum_n e^{-\beta E_n}$$

The average value of observable in this case can now be written as –

$$\boxed{\langle A \rangle = \frac{1}{Z} \sum_{n} e^{-\beta(E_n - \mu N)} \langle \phi_n | \hat{A} | \phi_n \rangle}$$

[ Development of Quantum Statistics]

## Bose - Einstein Statistics

For particles having spin angular momentum that are zero or integral multiple of ħ. The wave function are symmetric.

And for Particles with Spin angular momentum that are odd half integral multiple of ħ. The wave function are anti-symmetric

**Bose - Einstein Statistics** :- This was developed by S.N. Bose for light quanta's called photons & generalised by Albert Einstein to describe the energy distribution among particles whose spin angular momenta are $n\hbar$, where $n = 0, 1, 2, 3$. & These particles are k/a Bosons. wave func$^n$ are symmetric i.e on interchanging any 2 bosons wave func$^n$ doesn't change.

## Pauli Exclusion Principle :

which States that in each quantum state there can't simultaneously be more than one particles.

Ex — $\alpha$-particles ($s = 0$), photons ($s = 1$) dutoron ($s = 1$)
$\pi$ - mesons ($s = 0$).

**Fermi-Dirac Statistics** - This was developed by Enrico Fermi for electrons & its rela$^n$ to quantum Mechanics was established by P.A.M Dirac (Paul Adrine Maurice Dirac) it describes the energy distribution among particles whose Spin angular momenta are $(n + \frac{1}{2})\hbar$ where $n = 0, 1, 2, 3$ $(\frac{1}{2}\hbar, \frac{3}{2}\hbar \ldots)$ & these particles are k/a Fermions wave func$^n$ are antisymmetric i.e on interchanging 2 fermions the Pauli exclusion Principle is applicable

Ex – electron ($S = 1/2$) Positron ($S = 1/2$) Proton ($S = 1/2$), Neutron ($S = 1/2$)
μ-meson ($S = 1/2$)

Consider a gas of 2 particles A & B & assume that each particle can be in one of the possible quantum state ($S = 1, 2, 3$)

Maxwell Boltzmann Statistics (The particles are considered distinguishable & any of the particle can be in anyone of the state.

| $ | 1 | 2 | 3 |
|---|---|---|---|
| | ab | — | — |
| | — | ab | — |
| | — | — | ab |
| | a | b | |
| | | a | b |
| | b | a | |
| | | b | a |
| | a | | b |
| | b | | a |

$g^{N}$

$(3)^2 = 9$

i.e. $3^N = (3)^2 = 9$

i.e. [illegible]

B.E. (Particles are Indistinguishable)

| 1 | 2 | 3 |
|---|---|---|
| $a^2$ | | |
| | $a^2$ | |
| | | $a^2$ |
| a | a | |
| | a | a |
| a | a | a |

[illegible]

Fermi-Dirac a a

(Particles are a a

indistinguishable &

follow Pauli Exclusion a a

Principle

Probability that the two particles are found in the Same State $= \mathcal{E}_c$

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Probability that the 2 particles are found in different state

$\mathcal{E}_c = -\frac{\text{Same}}{\text{state}}$

Fermi-Dirac $\mathcal{E}_c = 0$

B.E $\mathcal{E}_c = \frac{3}{3} = \frac{6}{6} \quad 1$

M.B $\mathcal{E}_c = \frac{3}{6} = \frac{1}{2}$

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Bose Einstein distribution law

Basic Postulates for B.E statistics

1.) The particles of the system are identical & indistinguishable.

2.) Any no. of particles can occupy a single cell in the phase space.

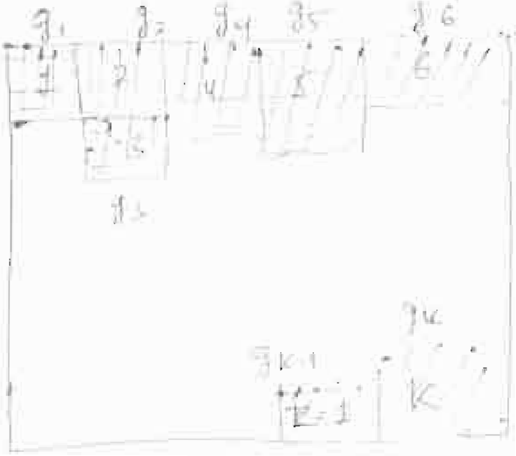
3.) The size of cell can't be small than $h^3$, where h-planck's constant

4.) The no. of Phase cells is comparable with the no. of particles i.e the occupation index $f(E_i) = \frac{n_i}{g_i} = 1$

5.) B.E statistics is applicable to the particles with spin angular momenta $\simeq n\hbar$ where $n = 0, 1, 2 \ldots$. The Particles are k/a Bosons

Take n independent particles of indistinguishable. n particles can be represented by phase pt in the phase space. In order to determine energy (momenta) distribution of these particles in the most probable state (equilibrium state), We divided the available volume in the phase space into large no. of compartments (quantum groups a) energy levels)

each compartment representing a small interval of energy (or momenta)



Let $n_1, n_2, n_3 \cdots n_i \quad n_k$ particles having mean energy $E_1, E_2, E_3 \cdots E_i \cdots E_k$ respectively in compartments numbered as $1, 2, 3 \cdots i, k-1, k$ containing $g_1 \, g_2 \, g_3 \cdots g_i \quad g_{k-1}, g_k$ cell respectively

The total no. of particles

$$n = n_1 + n_2 + n_3 + \cdots \; n_i + n_{k-1} + n_k$$

Consider $i^{th}$ compartment. It has $n_i$ indistinguishable particles distributed among $g_i$ cell

Suppose that $n_i$ particles are arranged in a row & distributed among $g_i$ quantum states among $(g_i - 1)$ partition in b/w.

The particles are indistinguishable the rearrangement of particles among themselves will n't give rise to any new distribution. The no. of such meaningless permutation factorial $n_i$ or $\underline{|n_i}$.

Hence eqn ① should be divided by $\underline{|n_i}$

$$= \frac{\underline{|n_i + g_i - 1}}{\underline{|n_i}} \qquad \text{——} ②$$

Moreover, this also ~~Indic~~ includes permutation $(g_i - 1)$ partitions among themselves. Again, these partitions also n't produce different states & hence are meaningless. Then eqn ② further divided by $\underline{|g_i - 1}$.

$$= \frac{\underline{|n_i + g_i - 1}}{\underline{|n_i} \; \underline{|g_i - 1}} \qquad \text{——} ③$$

Hence, the actual (meaningful) no. of ways in which $n_i$ particles are to be distributed in $g_i$ cells in the compartment is

$$W_{n_i} = \frac{\underline{|n_i + g_i - 1}}{\underline{|n_i} \; \underline{|g_i - 1}} \qquad \text{——} ④$$

Similar ~~to~~ expression will be obtained for other compartments

∴ the total no. of different arrangements for all n particles of the

System gives the thermodynamic probability.

$$W(n_1,n_2 \dots n_K) = \frac{\underline{|n_i+g_i-1}}{\underline{|n_i}\ \underline{|g_i-1}} \times \frac{\underline{|n_2+g_2-1}}{\underline{|n_i}\ \underline{|g_2-1}} \times \dots \frac{\underline{|n_K+g_K-1}}{\underline{|n_K}\ \underline{|g_K-1}} \quad \text{— ⑤}$$

$$W(n_1,n_2 \dots n_K) = \prod_{i=1}^{K} \frac{\underline{|n_i+g_i-1}}{\underline{|n_i}\ \underline{|g_i-1}} \quad \text{— ⑥}$$

## Most Probable microstates

The most probable microstate corresponding to the state of max$^m$ thermodynamic Probability. In eqⁿ ⑥, $n_i$ & $g_i$ both are very large no. s. Hence we can neglect the 1 in expression

$$W(n_1,n_2,n_3 \dots n_K) = \frac{\underline{|n_i+g_i}}{\underline{|n_i}\ \underline{|g_i}} \quad \text{— ⑦}$$

Taking ln of both side on eqⁿ ⑦

$$\ln W = \sum_{i=1}^{K} \left[\ln \underline{|(n_i+g_i} - \ln \underline{|n_i} - \ln \underline{|g_i}\right] \quad \text{— ⑧}$$

Using Stearling approximaⁿ

$$\ln \underline{|n} = n \ln n - n$$

$$\ln W = \sum_{i=1}^{K} \left[(n_i+g_i)\ln(n_i+g_i) - (n_i+g_i) - n_i \ln n_i + n_i - g_i \ln g_i + g_i\right].$$

$$\ln W = \sum_{i=1}^{K} \left[(n_i+g_i)\ln(n_i+g_i) - n_i \ln n_i - g_i \ln g_i\right] \quad \text{— ⑨}$$

To get the max$^m$ prob. (thermodynamic) we differentiate eqⁿ ⑨ & equal it to zero.

$$\delta(\ln W) = 0$$

$$\delta(\ln W) = \sum_{i=1}^{K} \left[\delta n_i \log(n_i+g_i) + \frac{(n_i+g_i)}{(n_i+g_i)} \cdot \delta n_i - \delta n_i \ln n_i - \frac{n_i}{n_i}\delta n_i\right]$$

$$\delta(\ln W) = \sum_{i=1}^{K} \left[\delta n_i \ln(n_i+g_i) - \delta n \ln n_i\right]$$

$$= \sum_{i=1}^{K} \left[\ln\left(\frac{n_i+g_i}{n_i}\right)\right]\delta n_i$$

$$= -\sum_{i=1}^{K} \left[\ln\left(\frac{n_i}{n_i+g_i}\right)\right]\delta n_i \quad \text{— ⑩}$$

In addition, our System must satisfy two stationary conditions

$$n = \sum_{i=1}^{k} n_i = \text{Constant}$$

$$\delta n = \sum_{i=1}^{k} \delta n_i = 0 \qquad \text{———} \ (11)$$

$$E = \sum_{i=1}^{n} n_i E_i = \text{constant}$$

$$\delta E = \sum_{i=1}^{n} E_i \, \delta n_i = 0 \qquad \text{———} \ (12)$$

now,

$$\sum_{i=1} \left[ \ln \left[ \frac{n_i}{n_i + g_i} \right] \right] \delta n_i$$

Now, we shall apply Lagrangian method of multiplier. For this multiply eqn (11) by $\alpha$ & eqn (12) by $\beta$ & add the resulting expression in eqn (10)

The eqn (10) becomes -

$$= \sum_{i=1}^{k} \left[ \ln \left( \frac{n_i}{n_i + g_i} \right) + \alpha + \beta E_i \right] \delta n_i = 0$$

The variation $\delta n_i$ are independent of eachother

$$\ln \left( \frac{n_i}{n_i + g_i} \right) + \alpha + \beta E_i = 0$$

$$\ln \left( \frac{n_i}{n_i + g_i} \right) = -\alpha - \beta E_i$$

$$\frac{n_i}{n_i + g_i} = e^{-(\alpha + \beta E_i)}$$

$$\frac{n_i + g_i}{n_i} = e^{(\alpha + \beta E_i)}$$

$$1 + \frac{g_i}{n_i} = e^{(\alpha + \beta E_i)}$$

$$\frac{g_i}{n_i} = e^{(\alpha + \beta E_i)} - 1 \qquad \Rightarrow \qquad \frac{n_i}{g_i} = \frac{1}{e^{(\alpha + \beta E_i)} - 1} \qquad \text{———} \ (13)$$

$$\boxed{n_i = \frac{g_i}{e^{(\alpha + \beta E_i)} - 1}} \qquad \text{———} \ (14)$$

• eqⁿ ⑭ represent the most probable distribution of the particles among various energy levels for a system obeying B.E statistics & is ∴ K/a Bose - einstein statistics distribution law for Boson particles, for $\beta = 1/kT$

$$\boxed{n_i = \frac{g_i}{e^{(\alpha + E_i/kT)} - 1}} \quad \text{— (15)}$$

## Bose Einstein Distribution function

The energy distribution funcⁿ $f(E_i)$ is the no. of particles per quantum state in the energy level $E_i$

$$f(E_i) = \frac{n_i}{g_i} = \frac{1}{(e^{\alpha} e^{E_i/kT} - 1)}$$

For continuous distribution

$$f(E) = \frac{1}{(e^{\alpha} e^{E/kT} - 1)}$$

## Bose Einstein distribution Law for continuous variation of energy

When the energy levels of the system are very close packed, they form Quasi continuous spectrum

If $g(E)\,dE$ is the no. of energy states b/w energy $E$ & $(E+dE)$

$$g_i = g(E)\,dE$$

If $n(E)\,dE$ is the no. of particles whose energy lies b/w $E$ & $E+dE$

The $n_i = n(E)\,dE$

$$n(E)\,dE = \frac{g(E)\,dE}{e^{\alpha} e^{E_i/kT} - 1}$$

$$\boxed{n(E)\,dE = \frac{2\pi V \left(\frac{2m}{h^2}\right)^{3/2} E^{1/2}\,dE}{(e^{\alpha} e^{E/kT} - 1)}}$$

$g(E)$ is the density of states

$$\boxed{g(E)\,dE = 2\pi V \left(\frac{2m}{h^2}\right)^{3/2} E^{1/2}\,dE}$$

This is B.E distribution law for ~~constant~~ continuous distribution of energy among free particles with no spin.

Lect 2
12/April/19

Ques-1 Three [illegible] are to be distributed in 4 energy states phase cells. Find out the possible way for such a distribution of the particle are :-
① classical ② Bosons ③ Fermi-dirac

Ques. 2 An ensembly has only two particles which are to be placed in 3 phase cells, compute the possible no. of arrangements

Sol$^n$ $n_i = 2$ $g_i = 3$

① Maxwell Boltzman ② B.E ③ F.D.

① Maxwell Boltzman

no. of possible arrangements = $(g_i)^{n_i} = (3)^2 = 9$.

② B.E

no. of possible arrangements $= \dfrac{\lfloor n_i+g_i-1}{\lfloor n_i \ \lfloor g_i-1}$

$= \dfrac{\lfloor 4}{\lfloor 2 \ \lfloor 2} = \dfrac{\overset{2}{\cancel{4}} \times 3}{\cancel{2}} = 6$

③ F.D

no. of possible arrangements $= \dfrac{\lfloor g_i}{\lfloor n_i \ \lfloor g_i-n_i} = \dfrac{3 \times \cancel{2!}}{\cancel{2!} \times 1!} = 3$

Sol$^n$ 1 1.) Classical (M.B). (Distinguishable)

$n_i = 3, \quad g_i = 4$

no. of possible arrangements $= (g_i)^{n_i} = (4)^3 = 4 \times 4 \times 4$
$= 64$

2.) B.E
no. of possible arrangements $= \dfrac{\lfloor n_i+g_i-1}{\lfloor n_i \ \lfloor g_i-1} = \dfrac{\lfloor 6}{\lfloor 3 \ \lfloor 3} = \dfrac{\overset{2}{\cancel{6}} \times 5 \times \overset{2}{\cancel{4}}}{\cancel{3} \times \cancel{2}}$

$= 20$

3) F·D

Possible arrangements $= \frac{\lfloor g_i}{\lfloor n_i \lfloor g_i - n_i} = \frac{4!}{3!\,1!} = 4$.

For indistinguishable.

① Classical $= \frac{1}{N!} \cdot 64 = \frac{1}{3!} \times 64 = \frac{32}{3}$ Ar

General form :- (Distribution function)

$$f = \frac{1}{e^{\alpha + \beta E_i} + a}$$

For M.B $a = 0$

$$f = \frac{1}{e^{\alpha + \beta E_i}}$$

For F·D $a = 1$

$$f = \frac{1}{e^{\alpha + \beta E_i} + 1}$$

For B.E $a = -1$

$$f = \frac{1}{e^{\alpha + \beta E_i} - 1}$$

Ideal Bose - einstein Gas :-

. Consider a B.E gas of N-Bosons, let these particles be distributed among states such that these are $n_1, n_2, n_3 \ldots n_i$ number of particles in quantum states whose enerergies $E, E_2, E_3$ $E_i$ respectively.

$$F(E_i) = \frac{1}{e^{\alpha + \beta E_i} - 1}$$

let the interac^n b/w the particles is assume to be negligible so that the energy may be regarded as entirely translational in character. As translational levels are closely space So we can replace $\Sigma$ by $\int$ (integration)

$$g(E)\,dE = \frac{2\pi V}{h^3} g_s (2m)^{3/2} \cancel{V} E^{1/2} dE$$

where $g_s = (2s+1)$ spin degeneracy factor.

The No. of particles having energy b/w E to E+dE

$$n(E)\,dE = \frac{g(E)\,dE}{e^{\alpha+\beta E_i}-1}$$

where, $f(E_i) = \frac{n_i}{g_i} = \frac{1}{e^{\alpha+\beta E_i}-1}$

$$n(E)\,d(E) = \frac{2\pi V g_s}{h^3}\,\frac{(2m)^{3/2}\,E^{1/2}\,dE}{e^{\alpha+\beta E_i}-1}$$

The total no. of particles in the system

$$N = \frac{2\pi V g_s (2m)^{3/2}}{h^3}\int_0^\infty \frac{E^{1/2}\,dE}{e^{\alpha+\beta E}-1} \quad — ①$$ (H.W)

where $\alpha$ is constant.

$$N = \frac{g_s Z_t}{e^\alpha}\left[1+\frac{1}{e^{\alpha}2^{3/2}}+\frac{1}{e^{2\alpha}3^{3/2}}+\cdots\right]$$

Z :

$$Z_t = V\left(\frac{2\pi m k T}{h^2}\right)^{3/2}$$

$\frac{E}{kT} = x$ ; $x^{1/2}$

Q. Average internal Energy (U) or (E)

Eq

$$E = \int_0^\infty E\,N(E)\,d(E) = \frac{2\pi g_s V (2m)^{3/2}}{h^3}\int_0^\infty \frac{E^{3/2}\,dE}{e^{\alpha+\beta E}-1}$$

Let $\frac{E}{kT} = x$

$E = xkT$

$$= \frac{2\pi g_s V (2m)^{3/2}}{h^3}\int_0^\infty \frac{x^{3/2}\cdot(kT)^{3/2}\cdot kT\,dx}{e^\alpha\cdot e^x - 1}$$

$$U = \bar{E} = \frac{2\pi g_s V}{h^3}(2mkT)^{3/2}\cdot kT\int_0^\infty \frac{x^{3/2}\,dx}{e^\alpha e^x - 1}$$

$$\int_0^\infty \frac{x^{3/2}}{e^\alpha e^x - 1}\,dx = \int_0^\infty \frac{x^{3/2}}{e^\alpha}\left(e^x - \frac{1}{e^\alpha}\right)^{-1} dx$$

$$U = \bar{E} = \frac{2\pi g_s V}{h^3}(2mkT)^{3/2}\,kT \cdot \frac{1}{e^\alpha}\int_0^\infty x^{3/2}\left(e^x - \frac{1}{e^\alpha}\right)^{-1} dx$$

$$\int_0^\infty \frac{x^{3/2}}{e^\alpha}\cdot e^{-x}\left[1 - \frac{e^{-x}}{e^\alpha}\right]^{-1} dx$$

$$e^{-kx}\,x^{n-1}\,dx = \frac{\Gamma n}{k^n}$$

$$= \frac{1}{e^\alpha}\left[\int_0^\infty x^{3/2} e^{-x}\left\{1 + \frac{e^{-x}}{e^\alpha} + \frac{e^{-2x}}{e^{2\alpha}} + \cdots\right\}\right] dx$$

$$= \frac{1}{e^\alpha}\left[\int_0^\infty x^{3/2} e^{-x}\,dx + \int_0^\infty x^{3/2}\frac{e^{-2x}}{e^\alpha}\,dx + \int_0^\infty x^{3/2}\cdot\frac{e^{-3x}}{e^{2\alpha}}\,dx + \cdots\right]$$

or

$$= \int_0^\infty \frac{x^{3/2}e^{-x}}{e^\alpha}\,dx + \int_0^\infty \frac{x^{3/2}e^{-2x}}{e^{2\alpha}}\,dx + \int_0^\infty x^{3/2}\frac{e^{-3x}}{e^{3\alpha}}\,dx + \cdots$$

Standard Gamma func$^n$

$$\boxed{\int_0^\infty e^{-ky}\,y^{n-1}\,dy = \frac{\Gamma n}{k^n}}$$

using this :-

$$= \frac{1}{e^\alpha}\left[\int_0^\infty x^{5/2-1}e^{-x}\,dx + \int_0^\infty x^{(5/2-1)}\frac{e^{-2x}}{e^\alpha}\,dx + \cdots\right]$$

$$= \frac{1}{e^\alpha}\left[\frac{\Gamma\frac{5}{2}}{1} + \frac{\Gamma 5/2}{e^\alpha\,2^{5/2}} + \frac{\Gamma 5/2}{e^{2\alpha}\,3^{5/2}} + \cdots\right]$$

$$= \frac{\Gamma 5/2}{e^\alpha}\left[1 + \frac{1}{e^\alpha\,2^{5/2}} + \frac{1}{e^{2\alpha}\,3^{5/2}} + \cdots\right]$$

$$e^{-ky}\,y^{n-1}\,dy = \frac{\Gamma n}{k^n}$$

$$= \frac{2\pi V g_s}{h^3}(2m\pi kT)^{3/2} kT \int_0^\infty \frac{E^{1/2}\,dE}{e^{\alpha+\beta E}-1}$$

$$= \frac{g_s\,2V}{\sqrt{\pi}}\left(\frac{2m\pi kT}{h^2}\right)^{3/2} kT \cdot \frac{1}{e^\alpha}\cdot\frac{3}{4}\sqrt{\pi}\left[1+\frac{1}{e^\alpha 2^{5/2}}+\frac{1}{e^\alpha 3^{5/2}}+\cdots\right]$$

$$= g_s V\left(\frac{2mk\pi T}{h^2}\right)^{3/2} kT\,\frac{1}{e^\alpha}\,\frac{3}{2}\left[1+\frac{1}{e^\alpha 2^{5/2}}+\frac{1}{e^\alpha 3^{5/2}}+\cdots\right]$$

$$\overline{E} = \frac{3}{2}kT\,\underbrace{g_s V\left(\frac{2m\pi kT}{h^2}\right)^{3/2}\frac{1}{e^\alpha}\left[1+\frac{1}{e^\alpha 2^{5/2}}+\frac{1}{e^\alpha 3^{5/2}}+\cdots\right]}_{(=N)\ (\text{no. of particles}}$$

$$\Rightarrow \overline{E} = \frac{3}{2}NkT$$

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

$$\boxed{PV = NkT}$$ Ideal gas eqn.

## 6•4. MAXWELL-BOLTZMANN STATISTICS :

Here the classical assumption that equal regions in the phase space are a priori equally probable is replaced by the assumption that each quantum state is a priori equally probable. Instead of talking about cells, we now talk about states.

Consider a system having $n$ distinguishable particles. Let these particles be divided into quantum groups such that $n_1, n_2, \ldots n_i$ particles lie in groups having energies $\varepsilon_1, \varepsilon_2 \ldots \varepsilon_i$ respectively. Let $g_i$ be the statistical weight of $i$th quantum group. The conditions in Maxwell-Boltzmann statistics are :

(1) Particles are distinguishable *i.e.*, there are no symmetry restrictions.

(2) Each eigen state $i^{th}$ quantum group may contain $0, 1, 2 \ldots n_i$ particles.

(3) The total number of particles in the entire system is always constant *i.e.*, $n = n_1 + n_2 + \ldots + n_i = \Sigma n_i =$ constant.

(4) The sum of energies of all the particles in different quantum groups, taken together, constitutes the total energy of the system.

In this distribution the particles are distinguishable and distinguishable elements are divided such that $n_1 + n_2 + \ldots + n_i = n$. Suppose first of all we choose $n_1$ particles which are to be placed in first state, this can be done in ${}^{n}c_{n_1}$ ways

$$\frac{n!}{n_1!(n-n_1)!}.$$

The remaining particles are $(n - n_1)$ and we want $n_2$ particles on second state which can be done in ${}^{n-n_1}c_{n_2}$ ways *i.e.*,

$$\frac{(n-n_1)!}{n_2!(n-n_1-n_2)!}.$$

Therefore the number of ways in which particles in different states may be exchanged, leaving the total number in each state fixed, is

$$\frac{n!}{n_1!(n-n_1)!} \times \frac{(n-n_1)!}{n_2!(n-n_1-n_2)!} \times \ldots \frac{n!}{n_1!n_2!n_3!\ldots n_i!}.$$

Now, for each group or level, $g_i$ *elementary* wavefunctions are available. Considering the $i^{th}$ group, the particles are accommodated in $g_i$ different groups. The first particle of $n_i$ can be accommodated in any of the $g_i$ groups which can be done in $g_i$ ways. The second particle can also be accommodated in $g_i$ ways because there is no restriction on this particle. In this manner all the $n_i$ particles can be occupied, in $g_i$ groups or levels in $g_i^{n_i}$ ways.

The total number of eigen states for the whole system is given by

$$G = \frac{n!\, g_1^{n_1} g_2^{n_2} g_i^{n_i}}{n_1!\, n_2! \ldots n_i!}$$

$$= n! \frac{g_1 n_1}{n_1!} \cdot \frac{g_2^{n_2}}{n_2!} \ldots \frac{g_i^{n_i}}{n_i!}$$

$$= n! \prod_i \frac{g_i^{n_i}}{n_i} \qquad \ldots(1)$$

The probability of the given state is

$$\omega = n!\,\prod_i \frac{g_i^{\,n_i}}{n_i!} \times \text{constant} \qquad \ldots(2)$$

Taking log of equation (2), we have

$$\log \omega = n \log n! + \sum_i \{n_i \log g_i - \log n_i!\} + \text{constant} \qquad \ldots(3)$$

Using Stirling approximation

$$\log \omega = n \log n + \sum_i \{n_i \log g_i - n_i \log n_i\} + \text{constant}$$

$$= \text{constant} - \sum_i (n_i \log n_i - n_i \log g_i\} \qquad \ldots(4)$$

where $n$ log $n$ has been included in the constant term. Differentiating equation (4) with respect to $n_i$, we have

$$\delta \log \omega = -\sum_i \delta(n_i \log n_i - n_i \log g_i)$$

$$= -\sum_i \left\{ \delta n_i \log n_i + \frac{n_i}{n_i}\delta n_i - \delta n_i \log g_i \right\}$$

$$= -\sum_i \left\{ \log \frac{n_i}{g_i} + 1 \right\} \delta n_i \qquad \ldots(5)$$

The condition of maximum probability gives

$$\sum_i \left\{ \log \frac{n_i}{g_i} + 1 \right\} \delta n_i = 0. \qquad \ldots(6)$$

Introducing the auxiliary conditions

$$\delta n = \Sigma \delta n_i = 0 \qquad \ldots(7)$$

$$\delta E = \Sigma \varepsilon_i \delta n_i = 0. \qquad \ldots(8)$$

and applying the Lagrange method of undetermined multipliers *i.e.,* multiplying (7) by $\alpha$ and (8) by $\beta$ and adding resulting expression to equation (6), we have

$$\sum_i \left( \log \frac{n_i}{g_i} + \alpha + \beta\varepsilon_i \right) \delta n_i = 0$$

The condition of maximum probability gives

$$\left( \log \frac{n_i}{g_i} + \alpha + \beta\varepsilon_i \right) \delta n_i = 0. \qquad \ldots(9)$$

Since $\delta n_i$'s can be treated as arbitrary, we have

$$\log \frac{n_i}{g_i} + \alpha + \beta\varepsilon_i = 0. \qquad \ldots(10)$$

$$\log \frac{n_i}{g_i} = -(\alpha + \beta\varepsilon_i),$$

and therefore

$$n_i = \frac{g_i}{e^{\alpha + \beta\varepsilon_i}} \qquad \ldots(11)$$

The result differs from that which was derived classically in only a factor namely statistical weight $g_i$.

Enrico Fermi

***ENRICO FERMI (1901–1954)*** *was born in Rome on 29 Sept. 1901. He obtained his doctorate at Pisa. Working with leading scientists in the new quantum mechanics, in 1926 at University of Rome, he investigated the statistical mechanics of those particles that obey Pauli's exclusion principle, such as electrons. Dirac independently arrived at the same conclusion shortly afterword and hence the result is finally named as Fermi-Dirac statistics. In 1933, Fermi introduced the concept of the weak interaction and used it together with Pauli's newly postulated neutrino (as named it by Fermi) to develop a theory of beta decay.*

*Later in 1930s Fermi and a group of collaborators carried out a series of experiments in which radionuclides were produced artificially by bombarding various elements with slow neutrons, which found to be most effective. This giving rise to the formation of transuranic elements. In 1938 Fermi received the Nobel Prize for this work. He then went to the United States. As a part of atom bomb project, Fermi was the leader of designing and construction of first nuclear reactor at the Chicago University. In December 1942, the nuclear reactor became operative. After second World War Fermi shifted to 'high energy particle physics'. He died of cancer in 28 Nov. 1954. An element having atomic number 100 is named as Fermium in his honour, discovered a year after his death.*

Paul Dirac

***PAUL A.M. DIRAC (1902–1984)*** *was born in Bristol on 8 Aug. 1902 in England. Dirac was basically an electrical engineer. He shifted his interest to mathematics and then to physics. He obtained his Ph. D. from Cambridge in 1926. After reading Heisenberg's first paper on quantum machanics in 1925, Dirac soon devised a more general theory and next year, Dirac formulated Pauli's exclusion principle in quantum mechanical terms. He investigated the statistical behaviour of particles like electrons which obey Pauli exclusion principle, which Fermi had investigated independently a little earlier, the result was named as Fermi-Dirac statistics, in the honour of both. In 1928 Dirac applied special relativity to quantum theory. In an attempt to explain why charge is quantized, Dirac in 1931 found it necessary to postulate the existence of magnetic monopoles, isolated N or S magnetic poles. More recent theories show that magnetic monopoles should have been created in profusion just after the Big Bang theory that marked the beginning of the universe. Dirac became Lucasian Professor of mathematics, in 1932, at Cambridge, the post Newton had held two and half centuries earlier. In 1933, Dirac shared the Nobel Prize in physics with Schrödinger. He died on Oct 20, 1984.*

## 12.8 Fermi-Dirac Distribution Law

Consider a system consisting of $n$ independent and indistinguishable particles. The particles have definite energies (or momenta) and occupy definite positions. Therefore, they can be represented by phase points in the phase space. In order to determine the energy (or momenta) distribution of these particles in the most probable state known as equilibrium state; we divide the available volume in the phase space into large numbers (say $k$) of compartments (quantum groups or energy levels), each compartment representing a small interval of energy (or momentum). Further each compartment is divided into elementary cells; each of size $h^3$, where $h$ is a Planck's constant.

Further, we suppose that the size of the compartment is very large as compared to the size of the cell so that each compartment contains a very large number of elementary cells. Let the compartments be marked 1, 2, ........ $i$, ........ $k$ and their mean energy values be represented by $E_1, E_2, \ldots\ldots E_i \ldots\ldots E_k$ containing $g_1, g_2, \ldots\ldots g_i \ldots\ldots g_k$ cells respectively in them. The total number of particles in the system is

$$n = n_1 + n_2 + \ldots\ldots + n_i \ldots\ldots + n_k$$

Our aim is to find the Fermi-Dirac distribution law *i.e.*, the distribution of $n_i$ Fermions out of the total $n$ Fermions in $g_i$ cells of the $i$th compartment. For this. the basic postulates are:

## Basic Postulates

(*i*) The particles of indistinguishable so that there is no distinction between the various ways in which $n_i$ particle are chosen.

(*ii*) The particles obey Pauli's exclusion principle according to which there can be either no particle or only one particle in a given cell. Therefore, the number of cells must be much greater than the number of particles, *i.e.*, $g_i >> n_i$.

Out of $n_i$ number of particles in the $i$th compartment with mean value $E_i$, the first particle can be placed in any one of the available $g_i$ states, *i.e.*, this particle can be assigned to any of the $g_i$ sets of quantum numbers. Thus, the first particle can be distributed in $g_i$ different ways, in accordance with Pauli's exclusion principle and the remaining $(g_i - 1)$ will remain vacant. The second particle can be arranged in $(g_i - 1)$ different ways and the process continues.

Thus, the total number of different ways of arranging $n_i$ particles among available $g_i$ states with energy level $E_i$ is given by

$$= g_i (g_i - 1)(g_i - 2)(g_i - 3) \ldots\ldots [g_i - (n_i - 1)]$$

$$= \frac{g_i\,!}{(g_i - n_i)!} \qquad \ldots(12.27)$$

Further, since the particles are indistinguishable, it would not be possible to detect any difference when $n_i$ particles are reshuffled into different ways occupied by them in the energy level $E_i$. Thus, out of these $n_i$ permutations of the indistinguishable particles among themselves will be meaningless. Therefore, the total number of different and distinguishable ways is

$$= \frac{g_i\,!}{n_i\,!(g_i - n_i)!} \qquad \ldots(12.28)$$

Therefore, the thermodynamic probability for the microstate $(n_1, n_2, \ldots\ldots n_i, \ldots\ldots n_k)$ of the system is given by

$$W(n_1, n_2 \ldots\ldots i, \ldots\ldots k) = \frac{g_1\,!}{n_1\,!(g_1 - n_1)!} \times \frac{g_2\,!}{n_2\,!(g_2 - n_2)!} \times \ldots\ldots\ldots \times \frac{g_i\,!}{n_i\,!(g_i - n_i)!} \ldots\ldots\ldots \times \frac{g_k\,!}{n_k\,!(g_k - n_k)\,!}$$

$$= \prod_{i=1}^{k} \frac{g_i\,!}{n_i\,!(g_i - n_i)!} \qquad \ldots(12.29)$$

where $\prod$ denotes multiplication of terms for various values of $i$ from 1 to $k$.

## Most Probable Microstate

Taking natural logarithm on both sides of eqn. (12.29),

$$\ln W = \sum_{i=1}^{k} \left[\ln g_i\,! - \ln n_i\,! - \ln (g_i - n_i)\,!\right]$$

As $n_i$ and $g_i$ are very large numbers, we can use Sterling approximation

$\ln n! = (n \ln n) - n$

Applying Sterling's approximation, we have

$$\ln W = \sum_{i=1}^{k} \left[g_i \ln g_i - g_i - n_i \ln n_i + n_i\right.$$

$$-(g_i - n_i)\ln(g_i - n_i) + (g_i - n_i)\Big]$$

$$= \sum_{i=1}^{k}\left[g_i \ln g_i - n_i \ln n_i - (g_i - n_i)\ln(g_i - n_i)\right]$$

Here $g_i$ is not subject to variation whereas $n_i$ varies continuously. Differentiating both sides, we have

$$\delta(\ln W) = \sum_{i=1}^{k}\left[-n_i \frac{1}{n_i}\delta n_i - \ln n_i\,\delta n_i + (g_i - n_i)\right.$$

$$\left.\frac{1}{(g_i - n_i)}\delta n_i + \ln(g_i - n_i)\,\delta n_i\right]$$

$$= \sum_{i=1}^{k}\left[\ln(g_i - n_i) - \ln n_i\right]\delta n_i$$

To get the state of *maximum thermodynamic probability*

$$\delta(\ln W) = 0$$

$$\therefore \quad \sum_{i=1}^{k}\left[\ln(g_i - n_i) - \ln n_i\right]\delta n_i = 0$$

or

$$\sum_{i=1}^{k}\left[\ln\frac{g_i - n_i}{n_i}\right]\delta n_i = 0$$

or

$$-\sum_{i=1}^{k}\left[\ln\frac{n_i}{g_i - n_i}\right]\delta n_i = 0$$

or

$$\sum_{i=1}^{k}\left[\ln\frac{n_i}{g_i - n_i}\right]\delta n_i = 0 \qquad \ldots(12.30)$$

In addition, our system must satisfy the two auxillary conditions:

(*i*) Conservation of total number of particles, *i.e.*, $n = a$ constant

$$\therefore \quad n = \sum_i n_i = \text{constant}$$

*i.e.*,

$$\delta E = \sum_i \delta n_i = 0 \qquad \ldots(12.31)$$

(*ii*) Conservation of total energy of the system, *i.e.*, $E$ = a constant.

$$\therefore \quad E = \sum_i n_i E_i \quad \text{constant}$$

*i.e.*,

$$\delta E = \sum_i E_i\,\delta n_i = 0 \qquad \ldots(12.32)$$

We shall now apply Langrangian method of undetermined multipliers. For this, let us multiply eqn. (12.31) by $\alpha$ and eqn. (12.32) by $\beta$ and add the resulting expression to eqn. (12.30),

$$\sum_{i=1}\left[\ln\left(\frac{n_i}{g_i - n_i}\right) + \alpha + \beta E_i\right]\delta n_i = 0$$

As the variations $\delta n_i$ are independent of each other, we get

$$\ln\left(\frac{n_i}{g_i - n_i}\right) + \alpha + \beta E_i = 0$$

or $$\frac{n_i}{g_i - n_i} = e^{-(\alpha+\beta E_i)}$$

or $$\frac{g_i - n_i}{n_i} = e^{\alpha+\beta E_i}$$

or $$\frac{g_i}{n_i} - 1 = e^{\alpha+\beta E_i}$$

or $$\frac{g_i}{n_i} = e^{\alpha+\beta E_i} + 1$$

or $$n_i = \frac{g_i}{e^{\alpha+\beta E_i} + 1} \qquad \text{...(12.33)}$$

This equation represents the most probable distribution of the particles among various energy levels for a system obeying Fermi-Dirac statistics and is therefore known as **Fermi-Dirac distribution law**, for an assembly of *fermions*.

The parameter $\beta = \frac{1}{kT}$, where $k$ is Boltzmann's constant, has the same role as in case of *M-B* distribution law. Substituting in equation (12.33), we have

$$n_i = \frac{g_i}{e^{\alpha+\beta E_i/kT} + 1} = \frac{g_i}{e^{\alpha} e^{E_i/kT} + 1} \qquad \text{...(12.34)}$$

**Fermi-Dirac energy distribution function.**

Since there can be a *maximum of one particle per quantum state*, the function $f(E_i)$ is the ratio of the number of quantum states of energy $E_i$ occupied by electrons to the total number of quantum states available in the energy level $E_i$. Therefore, the value of $f(E_i)$ for the Fermi-Dirac distribution at a paricular energy $E_i$ is the probability that under equilibrium a quantum state of that energy is occupied by a particle.

From equation (12.34), $f(E_i)$ is given by

$$f(E_i) = \frac{n_i}{g_i}$$

$$= \frac{1}{e^{\alpha} e^{E_i/kT} + 1} \qquad \text{...(12.35)}$$

For continuous distribution of energy at energy E, the distribution function is written as

$$f(E) = \frac{1}{e^{\alpha} e^{E/kT} + 1} \qquad \text{...(12.36)}$$

**F-D energy distribution law for continuous variation of energy**

If the energy levels are very close together, then the distribution of energy of the particles may be considered continuous. For this distribution the number of particles $n(E)dE$ whose energies lie between $E$ and $E + dE$, then $n_i = n(E)dE$ and is given by

$$n(E)dE = f(E)\, g(E)dE \qquad \text{...(12.37)}$$

where $g(E)dE$ is the number of quantum states of energy between $E$ and $E + dE$.

Substituting the value of $f(E)$ in eqn. (12.37), we have

$$n(E)dE = \frac{g(E)dE}{e^{\alpha}.e^{E/kT} + 1} \qquad \text{...(12.38)}$$

## Fermi-Dirac Distribution law

indentical

Consider a system consists of $n$-independent, & a indistinguishable Particles. The particles ~~Each~~ have a definite energies & occupy definite pos$^n$. ∴, they can be represented by Phase pt. in the phase space.

In order to determine the energy distribution of these particles in the most probable state or k/a equilibrium state we divide the phase space into large no. of compartment (says k). Further each compartment is divided into elementary cells, each of size $h^3$.

Further, we suppose a compartment consists of large no. of cells as the size of compartment is very large as compare to size of cell.

Let the compartment be marked as $1, 2, 3 \dots K$ & their mean energies are $E_1, E_2 \dots E_K$ respectively containing $g_1\, g_2 \dots g_K$ cells resp. in them

### Basic Postulates

I.) The particles are indistinguishable so, that there is no distinction b/w the various ways in which $n_i$ particles are chosen

II.) These particles obey Pauli's exclusion principle according to which there can be either no particle or only one particle in a given cell, ∴ the no. of cells must be much greater than the no. of Particles i.e $g_i >> n_i$

~~The total no. of total ways in which~~

Out of no. of $n_i$ particles in the $i^{th}$ compartment with mean Energy $E_i$, the first particle can be placed in any one of the available $g_i$ States. Thus, the first particle can be distributed in $g_i$ different ways, in accordance with Pauli's exclusion principle & remaining $(g_i - 1)$ remain vacant. The second particle can be arranged in $(g_i - 1)$ different ways & the process continues.

Thus, the total no. of different ways of arranging $n_i$ particles among available $g_i$ states with energy $E_i$ is given by

$$= g_i\, [g_i - 1]\, [g_i - 2] \dots [g_i - (n_i - 1)] = \frac{g_i!}{(g_i - n_i)!}$$

①

The total no. of different & distinguishable way is

$$= \frac{g_i!}{n_i!\,(g_i-n_i)!} \qquad \text{——— (2)}$$

∴ the ~~te~~ thermodynamic Probability for the macrostate $(n_1, n_2 \ldots n_k)$ of the system is given by

$$= \frac{g_1!}{n_1!\,(g_1-n_1)!} \times \frac{g_2!}{n_2!\,(g_2-n_2)!} \times \cdots \frac{g_k!}{n_k!\,(g_k-n_k)!}$$

$$W = \prod_{i=1}^{k} \frac{g_i!}{n_i!\,(g_i-n_i)!}$$

Taking log on both side

$$\ln W = \ln(g_i)! - \ln n_i! - \ln(g_i-n_i)!$$

using Sterling approx$^m$ $\log n! = n\log n - n$

$$\ln W = g_i \ln g_i - g_i - n_i \ln n_i + \cancel{n_i} - (g_i-n_i)\ln(g_i-n_i) + g_i - \cancel{n_i}$$

$$\ln W = g_i \ln g_i - n_i \ln n_i - (g_i-n_i)\ln(g_i-n_i)$$

differentiate this eq$^n$ w.r.t $n_i$

$$\ln(\delta W) = -n_i \times \frac{1}{n_i}\,\delta n_i - \ln n_i\,\delta n_i + (g_i-n_i) \times \frac{1}{g_i-n_i}\,\delta n_i + \ln(g_i-n_i)\,\delta n_i$$

$$\ln(\delta W) = \ln\left[\frac{g_i-n_i}{n_i}\right]\delta n_i$$

using $^{\text{The State}}$ max$^m$ thermodynamic Probability is $\ln(\delta W) = 0$

$$\sum_{i=1}^{K} \ln\left[\frac{g_i-n_i}{n_i}\right]\delta n_i = 0$$

$$\text{Or} \sum_{i=1}^{K} \ln\left[\frac{n_i}{g_i-n_i}\right]\delta n_i = 0 \qquad \text{——— (A)}$$

Using 2 auxiliary conditions

1) Conservation of total no. of particles. i.e $n = a =$ Constant

$$n = \sum_i n_i .$$

$$\delta(n) = \sum_i \delta(n_i) = 0 \quad \text{— ③}$$

2.) Conservaⁿ of total energy of System $E = a =$ constant

$$E = \sum_i n_i E_i$$

$$\delta(E) = \sum_i E_i (\delta n_i) \quad \text{— ④}$$

Multiply eqⁿ 3 with $\alpha$ & 4 with $\beta$ respectively & Add in eqⁿ Ⓐ.

$$\sum_{i=1}^{k} \ln\left[\frac{n_i}{g_i - n_i}\right] \delta n_i + \alpha\, \delta n_i + \beta E_i \delta n_i = 0$$

$$\left[\ln\left[\frac{n_i}{g_i - n_i}\right] + \alpha + \beta E_i\right] \delta n_i = 0 .$$

Or $$\ln\left[\frac{n_i}{g_i - n_i}\right] = -(\alpha + \beta E_i)$$

$$-\ln\left[\frac{g_i - n_i}{n_i}\right] = -(\alpha + \beta E_i)$$

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

$$\frac{g_i}{n_i} = e^{\alpha + \beta E_i} + 1 .$$

$$\boxed{n_i = \frac{g_i}{e^{\alpha + \beta E_i} + 1}}$$

$$\frac{g_i!}{n_i!(g_i - n_i)!}$$

$$\frac{(g_i + n_i - 1)!}{n_i!(g_i - 1)!}$$

## Fermi - Dirac energy distribution funcⁿ

Since there can be maxᵐ of one particle per quantum state, the funcⁿ $f(E_i)$ is the ratio of the no. of quantum state of energy $E_i$ occupied by the electron to the total no. of quantum states available in total Energy $E_i$

i.e $f(E_i) = \frac{n_i}{g_i}$

$$\boxed{f(E_i) = \frac{1}{e^{\alpha+\beta E_i}+1}}$$

## Fermi - Dirac distribution law for continuous variation of Energy

For this distribution the no. of particle $n(E)\,dE$ whose energies lie b/w $E$ to $E+dE$, then $n_i = n(E)\,d(E)$ is given by

$$n(E)\,dE = f(E)\,g(E)\,dE$$

$$\Rightarrow \quad n(E)\,dE = \frac{g(E)\,dE}{e^{\alpha+\beta E_i}+1}$$

$$g(E)\,dE = 2\pi V\left(\frac{2m}{h^2}\right)^{3/2} E^{1/2}\,dE$$

For the particles like electron of spin angular momentum $= \pm\frac{1}{2}\hbar$. there are 2 possible spin orientations.

$$\therefore \quad \boxed{n(E)\,dE = \frac{2 \times 2\pi V\left(\frac{2m}{h^2}\right)^{3/2} E^{1/2}\,dE}{e^{\alpha+\beta E}+1}}$$

This is the fermi - Dirac energy distribution law for continuous variation of energy among free particles with spin $\pm\frac{1}{2}$.

## Electron gas –

Metals are good conductors. The high conductivity of metals is due to the presence of free electrons. These free electrons inside a metallic conductor move freely inside the metal. They continuosly collide with fixed (localized) atoms & thus behave like an electron gas. These free electrons in a metal belongs to a most characteristic system of fermions bcoz electron obey the Pauli's exclusion principle i.e the electron have half integral spin angular momentum in unit of $\frac{h}{2\pi}$ or $\hbar$.

Energy distribution among Electrons in metal.

Consider an electron gas having $n$ free electrons in a metallic conductor whose volume is V. Let the total energy of electron to be E, practically at all temperatures, the lower level energy bands are filled with electrons. The upper level energy bands are only partially filled with electrons. The distribution of electrons is to be considered only in the upper bands called the conduction band. The zero energy level is taken at the lowest level of conduction band.

As the energy of electron in the conduction band is continuous, the term $g_i$ replaced by $g(E)\,dE$, Hence $n(E)\,dE$ electrons have energy in range E to E + dE. According to fermi - Dirac distribution law

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

$$n(E)\,d(E) = \frac{g(E)\,dE}{e^{\alpha+\beta\epsilon_i}+1}$$

$$\boxed{n(E)\,d(E) = \frac{2\times 2\pi V\left(\frac{2m}{h^2}\right)^{3/2}E^{1/2}\,dE}{e^{\alpha+\beta E}+1}}$$

at $T=0$. $f(E) = 1$

$$\therefore \quad n(E)\,dE = 2 \times 2\pi V \left(\frac{2m}{h^2}\right)^{3/2} E^{1/2}\, dE$$

$$n = 2 \times 2\pi V \left(\frac{2m}{h^2}\right)^{3/2} \frac{2}{3} E^{3/2}$$

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

$$E_f^{3/2} = \frac{3n}{8\pi V}\left(h^2 \cdot \frac{1}{2m}\right)^{3/2}$$

$$\boxed{E_f = \left(\frac{3n}{8\pi V}\right)^{2/3} \frac{h^2}{2m}}$$

# ground state energy

$$\boxed{E_0 = \frac{3}{5} n E_f}$$

# ground state Pressure

$$\boxed{P_0 = \frac{2}{5} \frac{n E_f}{V}}$$

## Ideal fermi gas –

$0 \leq z < \infty$ Ideal fermi gas

$0 < z < 1$ Ideal Bose gas.

$P = \frac{2}{3} U$

if $\frac{n\lambda^3}{g} >> 1$ → weekly degenerate fermi gase

$\frac{n\lambda^3}{g} \to \infty$ → Strongly degenerate fermi gas

## Strongly Degenerate or Completely degenerate Ideal fermi gas –

$$f(E) = \frac{1}{e^{\frac{E-\mu}{k_BT}} + 1} = 1 \quad E < \mu \quad (E = E_f)$$

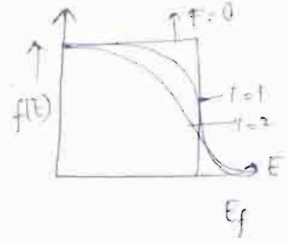
$$= 0 \quad E > \mu \quad (\mu = E_f)$$

at $T = 0$ $\quad \mu = E_f$ $\quad$ [fermi level is that level for which Occupation no. i.e $f(E) = 1/2$].

here $\mu$ is Chemical potⁿ

$$N = \int_0^{\cancel{E_f}\,\infty} f(E)\,g(E)\,dE$$

$$N = \int_0^{E_f} f(E)\,g(E)\,dE + \int_{E_f}^{\infty} f(E)\,g(E)\,dE$$



$$= \int_0^{E_f} 2 \times 2\pi V \left(\frac{2m}{h^2}\right)^{3/2} E^{1/2}\,dE$$

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

as $\frac{N}{V} = n$.

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

$$\boxed{E_F = \frac{h^2}{2m}\left(\frac{3N}{4\pi V g_s}\right)^{2/3}}$$

$g_s = 2$.

for electron or proton $g_s = 2$.

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

ef $g(s) = 2s+1$ multiplicity due to ~~g~~ spin.

$$E = \frac{p^2}{2m}$$

$$\boxed{p_F = h\left(\frac{3N}{4\pi V g_s}\right)^{1/3}}$$

as $E_F = k_B T_F$

$$\boxed{T_f = \frac{h^2}{2m k_B}\left(\frac{3N}{4\pi V g_s}\right)^{2/3}}$$

Ground state Energy ($E_0$)

$$E_0 = \int_0^{\infty} E\, f(E)\, g(E)\, dE = \int_0^{E_f} E\, f(E)\, g E\, dE + \int_{E_f}^{\infty} E\, f(E)\, g(E)\, d(E)$$

$$E_0 = 2 \times 2\pi V \left(\frac{2m}{h^2}\right)^{3/2} \int_0^{E_f} E^{3/2}\, dE$$

$$E_0 = 4\pi V \left(\frac{2m}{h^2}\right)^{3/2} \frac{2 E_f^{5/2}}{5}$$

$$E_0 = 2\pi V g_s \left(\frac{2m}{h^2}\right)^{3/2} \frac{2}{5} \cdot E_f^{5/2}$$

$$\boxed{E_0 = \frac{4}{5} \frac{\pi V g_s}{h^3} (2m)^{3/2} E_f^{5/2}}$$

Average ground state energy

$$\frac{E_0}{N} = \frac{4/5 \; \frac{\pi V g_s}{h^3} (2m)^{3/2} E_f^{5/2}}{4/3 \; \frac{\pi V g_s}{h^3} (2m)^{3/2} E_F^{3/2}}$$

$$\boxed{\frac{E_0}{N} = \frac{3}{5} E_f}$$

Ground state pressure

$$P_0 = \frac{2}{3} \frac{E_0}{V}$$

$$P_0 = \frac{2}{3} \times \frac{3}{5} \times \frac{E_f N}{V}$$

$$\boxed{P_0 = \frac{2}{5} n E_f}$$

or

$$P_0 = \frac{2}{5} n \cdot \frac{h^2}{2m} \left(\frac{3N}{4\pi V g_s}\right)^{2/3}$$

$$\boxed{P_0 \propto n^{5/3}}$$

& $P_0 = 0$ for Bose gas

## Weekly degenerate

The fermi gas at finite temp.

$$N = \frac{2 \times 2\pi V g_s}{h^2} (2m)^{3/2} \int_0^\infty \frac{E^{1/2}}{e^{(E-\mu)/kT}+1} \, dE$$

[using Taylor Series expansion]

Let $\phi(E) = E^{1/2}$

$$\int_0^\mu \phi(E)\, dE = \frac{2}{3}\mu^{3/2}$$

$$\phi'(E)\Big|_{E=\mu} = \frac{1}{2}\mu^{-1/2}$$

$$\int_0^\infty \frac{E^{1/2}}{e^{\left(\frac{E-\mu}{k_B T}\right)}+1} = \int_0^\mu \phi(E)\, dE + \frac{\pi^2}{6}\left(\frac{\partial \phi(E)}{\partial E}\right)_{E=\mu}(kT)^2$$

$$N = \frac{2 \times 2\pi V g_s}{h^2}(2m)^{3/2}\left[\frac{2}{3}\mu^{3/2} + \frac{\pi^2}{6}(kT)^2 \times \frac{1}{2}\mu^{-1/2} + \right]$$

$$N = \frac{2\pi V g_s}{h^2}(2m)^{3/2}\left[\frac{2}{3}\mu^{3/2} + \frac{\pi^2}{12}(kT)^2 \mu^{-1/2}\right].$$

$$N = \frac{3}{2}\frac{N}{E_f^{3/2}}\left[\frac{2}{3}\mu^{3/2} + \frac{\pi^2}{12}(kT)^2 \mu^{-1/2}\right]$$

$$E_f^{3/2} = \frac{3}{2}\left[\frac{2}{3}\mu^{3/2} + \frac{\pi^2}{12}(kT)^2 \mu^{-1/2}\right]$$

$$E_f^{3/2} = \frac{3}{2} \times \mu^{3/2}\left[\frac{2}{3} + \frac{\pi^2}{12}\left(\frac{kT}{\mu}\right)^2 + \cdots\right].$$

$$E_f^{3/2} = \mu^{3/2}\left[1 + \frac{\pi^2}{8}\left(\frac{k_B T}{\mu}\right)^2 + \cdots\right]$$

$$E_f = \mu \left[ 1 + \frac{\pi^2}{8} \left( \frac{k_B T}{\mu} \right)^2 + \cdots \right]^{+2/3}$$

$$\frac{\mu}{E_f} = \left[ 1 + \frac{\pi^2}{8} \left( \frac{k_B T}{\mu} \right)^2 + \cdots \right]^{-2/3}$$

$$\frac{\mu}{E_f} = 1 - \frac{1}{12} \left( \frac{\pi k_B T}{\mu} \right)^2 + \cdots$$

$$\mu = E_f \left[ 1 - \frac{1}{12} \left( \frac{\pi k_B T}{\mu} + \cdots \right] .$$

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

$$E_f(T) = E_f(0) \left[ 1 - \frac{\pi^2}{12} \left( \frac{k_B T}{E_f} \right)^2 + \cdots \right] .$$

$$\boxed{E = \frac{3}{5} n E_f \left[ 1 + \frac{5}{12} \left( \frac{\pi k T}{E_f} \right)^2 + \cdots \right]}$$

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

$$\boxed{P = \frac{2}{3} \left( \frac{n E_F}{V} \right) \left[ 1 + \frac{5}{12} \left( \frac{\pi k T}{E_f} \right)^2 + \cdots \right]} \leftarrow$$

as in case of E

$$\phi(E) = E^{3/2} \qquad \int_0^{\mu} \phi(E)\, dE = \frac{2}{5} \mu^{3/2}$$

# Ideal Bose-Einstein gas

$$f(E) = \frac{1}{e^{\alpha+\beta E} - 1}$$

$$g(E)\,dE = 2\pi V g_s \left(\frac{2m}{h^2}\right)^{3/2} E^{1/2}\,dE$$

$$N = \int_0^\infty \frac{2\pi V g_s \left(\frac{2m}{h^2}\right)^{3/2} E^{1/2}\,dE}{e^{\alpha+\beta E} - 1}.$$

$$N = 2\pi V g_s \left(\frac{2m}{h^2}\right)^{3/2} \int_0^\infty \frac{E^{1/2}\,dE}{e^{\alpha+\beta E} - 1}$$

Let $\frac{E}{kT} = x \qquad E^{1/2} = (xkT)^{1/2}$

$dE = kT\,dx$.

$$N = 2\pi V g_s \left(\frac{2m}{h^2}\right)^{3/2} (kT)^{3/2} \int_0^\infty \frac{x^{1/2}\,dx}{e^{\alpha+x} - 1}.$$

$$N = 2\pi V g_s \left(\frac{2mkT}{h^2}\right)^{3/2} \int_0^\infty \frac{x^{1/2}\,dx}{e^{x} e^{\alpha} (1 - e^{-x})}$$

$$N = 2\pi V g_s \left(\frac{2mkT}{h^2}\right)^{3/2} \frac{1}{e^{\alpha}} \int_0^\infty x^{1/2} e^{-x} \left(1 - \frac{e^{-x}}{e^{\alpha}}\right)^{-1} dx.$$

Using binomial expension.

$$N = 2\pi V g_s \left(\frac{2mkT}{h^2}\right)^{3/2} \cdot \frac{1}{e^{\alpha}} \left[\int_0^\infty x^{1/2} e^{-x} \left[1 + \frac{e^{-x}}{e^{\alpha}} + \frac{e^{-2x}}{e^{2\alpha}} + \cdots\right].\right].$$

$$N = 2\pi V g_s \left(\frac{2mkT}{h^2}\right)^{3/2} \cdot \frac{1}{e^{x}} \left[\int_0^\infty \frac{x^{1/2} e^{-x}}{e^{\alpha}}\,dx + \int_0^\infty \frac{x^{1/2} e^{-2x}}{e^{2\alpha}}\,dx + \int_0^\infty \frac{x^{1/2} e^{-3x}\,dx}{e^{2\alpha}}\right]$$

Using standard gamma func$^n$.

$$e^{-ky}\ y^{n-1}\,dy = \frac{\Gamma n}{k^{n}}.$$

$$N = 2\pi V\left(\frac{2mkT}{h^2}\right)^{3/2} g_s\left[\frac{\Gamma 3/2}{(1)^{3/2}e^{\alpha}} + \frac{\Gamma 3/2}{(2)^{3/2}e^{2\alpha}} + \frac{\Gamma 3/2}{(3)^{3/2}e^{3\alpha}} + \cdots\right]$$

$$N = 2\pi V\left(\frac{2mkT}{h^2}\right)^{3/2} g_s\,\Gamma 3/2\left[\frac{1}{e^{\alpha}} + \frac{1}{(2)^{3/2}e^{2\alpha}} + \frac{1}{(3)^{3/2}e^{3\alpha}} + \cdots\right]$$

$$N = 2\pi V\left(\frac{2mkT}{h^2}\right)^{3/2} g_s \cdot \frac{\sqrt{\pi}}{2}\left[\frac{1}{e^{\alpha}} + \frac{1}{e^{2\alpha}(2)^{3/2}} + \frac{1}{(3)^{3/2}e^{3\alpha}} + \cdots\right]$$

$$\boxed{N = 8Vg_s\left(\frac{2m\pi kT}{h^2}\right)^{3/2}\left[\frac{1}{e^{\alpha}} + \frac{1}{e^{2\alpha}(2)^{3/2}} + \frac{1}{(3)^{3/2}e^{3\alpha}} + \cdots\right]}$$

$$\bar{E} = \int_0^{\infty} f(E)E\, g(E)\,dE = \int_0^{\infty}\frac{2\pi Vg_s\left(\frac{2m}{h^2}\right)^{3/2}E^{3/2}\,dE}{e^{\alpha+\beta E}-1}$$

$$\bar{E} = 2\pi Vg_s\left(\frac{2m}{h^2}\right)^{3/2}\int_0^{\infty}\frac{E^{3/2}}{e^{\alpha+\beta E}-1}\,dE$$

Let $E/kT = x$ $dE = kT\,dx$.

$E^{3/2} = (kTx)^{3/2}$

$$E = 2\pi Vg_s\left(\frac{2m}{h^2}\right)^{3/2}(kT)^{5/2}\int_0^{\infty}\frac{x^{3/2}\,dx}{e^{\alpha}e^{x}\left(1-\frac{e^{-x}}{e^{\alpha}}\right)}$$

$$E = 2\pi Vg_s\left(\frac{2mkT}{h^2}\right)^{3/2}kT\cdot\frac{1}{e^{\alpha}}\int_0^{\infty}x^{3/2}e^{-x}\left(1-\frac{e^{-x}}{e^{\alpha}}\right)^{-1}dx.$$

using binomial expansion.

$$E = 2\pi Vg_s\left(\frac{2mkT}{h^2}\right)^{3/2}kT\left[\int_0^{\infty}\frac{x^{3/2}}{e^{\alpha}}e^{-x}\left[1+\frac{e^{-x}}{e^{\alpha}}+\frac{e^{-2x}}{e^{2\alpha}}+\cdots\right]\right]$$

$$E = 2\pi Vg_s\left(\frac{2mkT}{h^2}\right)^{3/2}kT\left[\int_0^{\infty}\frac{x^{3/2}}{e^{\alpha}}e^{-x}\,dx + \int_0^{\infty}\frac{x^{3/2}e^{-2x}}{e^{2\alpha}}\,dx + \cdots\right]$$

using standard gamma funcⁿ

$$e^{-ky}y^{n-1}\,dy = \frac{\Gamma n}{k^n}$$

$$E = 2\pi V g_s \left(\frac{2mkT}{h^2}\right)^{3/2} kT \left[\frac{\Gamma 5/2}{(1)^{5/2} e^{\alpha}} + \frac{\Gamma 5/2}{(2)^{5/2} e^{2\alpha}} + \frac{\Gamma 5/2}{(3)^{5/2} e^{2\alpha}}\right]$$

$$E = 2\pi V g_s \left(\frac{2mkT}{h^2}\right)^{3/2} kT \, \Gamma\frac{5}{2} \cdot \frac{1}{e^{\alpha}} \left[1 + \frac{1}{(2)^{5/2} e^{\alpha}} + \frac{1}{(3)^{5/2} e^{2\alpha}} + \cdots\right]$$

$$E = 2\pi V g_s \left(\frac{2mkT}{h^2}\right)^{3/2} kT \, \frac{3\sqrt{\pi}}{4} \frac{1}{e^{\alpha}} \left[1 + \frac{1}{(2)^{5/2} e^{\alpha}} + \cdots\right]$$

$$E = \frac{3}{2} V g_s \left(\frac{2m\pi kT}{h^2}\right)^{3/2} kT \left[\frac{1}{e^{\alpha}} + \frac{1}{(2)^{5/2} e^{2\alpha}} + \cdots\right]$$

$$U = \frac{3}{2} NkT \left[\frac{1}{e^{\alpha}} + \frac{1}{(2)^{3/2} e^{2\alpha}} + \frac{1}{(3)^{3/2} e^{3\alpha}}\right]^{-1} \left[\frac{1}{e^{\alpha}} + \frac{1}{(2)^{5/2} e^{2\alpha}} + \cdots\right]$$

$$\boxed{U = \frac{3}{2} NkT \left[\frac{1}{e^{\alpha}} - \frac{1}{(2)^{5/2} e^{2\alpha}} - \frac{1}{(3)^{5/2} e^{2\alpha}} + \cdots\right]}$$

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

$$P = \frac{NkT}{V} \left[1 - \frac{1}{(2)^{5/2} e^{\alpha}} - \frac{1}{(3)^{5/2} e^{2\alpha}} + \cdots\right]$$

$N/V = n$.

$$\boxed{P = nkT \left[1 - \frac{1}{(2)^{5/2} e^{\alpha}} - \frac{1}{(3)^{5/2} e^{2\alpha}} + \cdots\right]}$$

$$\boxed{\frac{N\lambda^3}{V g_s} = \frac{n}{g_s}\left(\frac{h^2}{2\pi mkT}\right)^{3/2}}$$

<u>Bose - Einstein</u> <u>Condensation</u> [Strongly Degenerate Boson gas]

Chemical potⁿ for Boson gas is always negative

$$f(E) = \frac{1}{e^{\frac{E-\mu}{kT}} - 1}$$

As the total no. of particles in Boson gas is fixed. so $\mu$ must increases if $t \to$ decreases keeping volume constant. to keep $f(E)$ +ve consequently $\mu \to 0$. The no. of particles in ground state increases sharply. this macroscopical occupatⁿ of the ground state is k/a Bose-Einstein condensation

At very low temp the value of $\mu$ is very close to ground state energy i.e zero

At $T = T_B$

$$\frac{N}{V} = 2\pi g_s \left(\frac{2mkT}{h^2}\right)^{3/2} \int_0^\infty \frac{x^{1/2}\,dx}{e^{\alpha} e^{x-1}}$$

$$\int_0^\infty \frac{x^{1/2}\,dx}{e^{\alpha} e^{x-1}} = \frac{\sqrt{\pi}}{2} \zeta(3/2)$$

$$\frac{N}{V} = 2\pi g_s \left(\frac{2mkT}{h^2}\right)^{3/2} \frac{\sqrt{\pi}}{2} \zeta(3/2)$$

$$\frac{N}{V} = g_s \left(\frac{2m\pi kT}{h^2}\right)^{3/2} \zeta(3/2)$$

$$\left(\frac{N}{V}\right)\left(\frac{h^2}{2m\pi k}\right)^{3/2} \cdot \frac{1}{g_s \zeta(3/2)} = T^{3/2}$$

$$T = \left(\frac{N}{V}\right)^{2/3} \cdot \frac{h^2}{2m\pi k} \cdot \frac{1}{\left[g_s \zeta(3/2)\right]^{2/3}}$$

## Bose - Einstein Condensation [Strongly Degenerate Boson gas].

Chemical potⁿ for Boson gas is always negative

$$f(E) = \frac{1}{e^{\frac{E-\mu}{kT}} - 1}$$

As the total no. of particles in Boson gas is fixed. so $\mu$ must increases if $t \to$ decreases keeping volume constant. to keep $f(E)$ +ve consequently $\mu \to 0$. The no. of particles in ground state increases sharply. This macroscopical occupatⁿ of the ground state is k/a Bose-Einstein Condensation

At very low temp the value of $\mu$ is very close to ground state energy i.e zero

At $T = T_B$

$$\frac{N}{V} = 2\pi g_s \left(\frac{2mkT}{h^2}\right)^{3/2} \int_0^\infty \frac{x^{1/2}dx}{e^{\alpha}e^{x}-1}$$

$$\int_0^\infty \frac{x^{1/2}dx}{e^{\alpha}e^{x}-1} = \frac{\sqrt{\pi}}{2}\zeta(3/2)$$

$$\frac{N}{V} = 2\pi g_s \left(\frac{2mkT}{h^2}\right)^{3/2} \frac{\sqrt{\pi}}{2}\zeta(3/2)$$

$$\frac{N}{V} = g_s \left(\frac{2m\pi kT}{h^2}\right)^{3/2} \zeta(3/2)$$

$$\left(\frac{N}{V}\right)\left(\frac{h^2}{2m\pi k}\right)^{3/2} \cdot \frac{1}{g_s\,\zeta(3/2)} = T^{3/2}$$

$$T = \left(\frac{N}{V}\right)^{2/3} \cdot \frac{h^2}{2m\pi k} \cdot \frac{1}{\left[g_s\,\zeta(3/2)\right]^{2/3}}$$

$$\boxed{T_B = \frac{h^2}{2\pi m k_B}\left[\frac{N}{V g_s \zeta(3/2)}\right]^{2/3}}$$

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

$$T_B = 0.0834\,\frac{h^2}{m k_B}\left[\frac{N}{V g_s}\right]^{2/3}$$

This is called condensation temp., degeneracy temp or characteristic temp or Bose temperature or transition temperature. The eqn for exist of Bose-Einstein gas is

$$N = V g_s T^{3/2}\left[\frac{2\pi m k_B}{h^2}\right]^{3/2} \zeta(3/2)$$

$N = N_0 + N_e$

$N_0 \to$ no. of particle in ground state

$N_e \to$ no. of particle in excited state

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

$N_0 < N < N_e$

$$N_e = N\left[\frac{T}{T_B}\right]^{3/2}$$

At $T < T_B$ the system may be looked upon as a mixture of 2 phase

1) Normal phase consisting $N_e$ particle distributed over excited state ($\epsilon \neq 0$)

2) Condensed phase consisting $N_0$ particle distributed (accumulated) in the ground state ($\epsilon = 0$).

$$U' = \frac{3}{2} N_e k_B T \frac{\zeta(5/2)}{\zeta(3/2)}$$

$\zeta(5/2) = 1.34$

$$U = \frac{3}{2} N_e k_B T \left(\frac{1.34}{2.61}\right).$$

$$U = \frac{3}{2} N k_B T \left(\frac{T}{T_B}\right)^{3/2} (1.34/2.61)$$

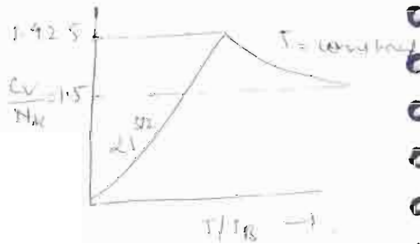
$$\boxed{U = 0.5314 \times \frac{3}{2} N k_B T \left(\frac{T}{T_B}\right)^{3/2}}$$

$$PV = \frac{2}{3} U = 0.5314\, N k_B T \left(\frac{T}{T_B}\right)^{3/2}$$

$P \propto T^{5/2}$ but independent of $n$ & $V$ only for $T < T_B$

$$\boxed{C_V = 1.925\, N k_B \left(\frac{T}{T_B}\right)^{3/2}}$$

as $C_V = \left(\frac{\partial U}{\partial T}\right)_V$



At $T < T_B$ $\mu = 0$

$$S = \frac{PV + U}{T} = \frac{5}{2} \frac{PV}{T}$$

$$S = \frac{5}{2} \times 0.53 \frac{N k_B T}{T} \left(\frac{T}{T_B}\right)^{3/2} = \frac{5}{2} N\, 0.5 k_B$$

$$S \propto \left(\frac{T}{T_B}\right)^{3/2}$$

at $T \to \infty$ all thermodynamic value approach to their classical value

## Maxwell - Boltzmann Statistics

$$W(G) = \frac{n!\,(g_1)^{n_1}(g_2)^{n_2} \cdots (g_i)^{n_i}}{n_1!\, n_2!\, n_3! \cdots n_i!}$$

$$W(G) = n! \prod_{i=1} \frac{g_i^{n_i}}{(n_i)!}$$

taking log on both side.

$$\log_e(\delta W) = \log_e n! + n_i \log_e g_i - \log_e (n_i)!$$

using Stirling app

~~$\ln(\delta W) = n\ln n - n + n_i g_i \ln g_i - n_i g_i - n_i \ln n_i + n_i$~~

~~now differentiate w.r.t $n_i$~~

~~$\ln(\delta W) = -n_i \times \frac{1}{n_i}\,\delta(n_i) + \delta n_i - g_i\,\delta n_i + g_i \ln g_i \times \delta n_i + n_i g_i \times \frac{1}{n_i g_i}\,\delta n_i$~~

~~$\ln(\delta W) = [g_i \ln g_i - g_i]\,\delta n_i$~~

~~$\ln(W) = n\ln n - n + n_i[g_i \ln g_i - g_i] - n_i \ln n_i + n_i$~~

~~$\ln(\delta W) = [g_i \ln g_i - g_i]\,\delta n_i - \delta n_i + \delta n_i$~~

$$\ln(\delta W) = n\ln n - n + n_i \ln g_i - n_i \ln n_i + n_i$$

diff w.r.t $n_i$

$$\ln(\delta W) = \ln g_i\,\delta n_i - \delta n_i - \ln n_i\,\delta n + \delta n_i$$

$$\ln(\delta W) = (\ln g_i - \ln n_i)\,\delta n_i$$

for the state of max$^m$ Probability $\delta W = 0$.

$$\sum_{i=1} \ln\left(\frac{g_i}{n_i}\right)\delta n_i = 0$$

or $\ln\left(\frac{n_i}{g_i}\right)\delta n_i = 0$. —— ①

using 2 auxiliary cond$^n$.

1.) Conservation of no. of particles i.e $n = a$ = constant

$$n = \sum_i n_i$$

$$\delta n = \sum_i \delta n_i = 0 \quad \text{——} ②$$

2) Conservat$^n$ of energy i.e $E = a$ = constant

$$E = \sum_i n_i E_i$$

$$\delta E = \sum_i E_i\,\delta n_i \quad \text{——} ③$$

Multiply eq$^n$ 2 with $\alpha$ & eq$^n$ 3 with $\beta$ and add in eq$^n$ ①

$$\left(\ln\left(\frac{n_i}{g_i}\right) + \alpha + \beta E_i\right)\delta n = 0$$

$$\ln\left(\frac{n_i}{g_i}\right) = e^{-\alpha + \beta E_i}$$

$$\frac{g_i}{n_i} = e^{\alpha + \beta E_i}$$

$$\boxed{n_i = \frac{g_i}{e^{\alpha + \beta E_i}}}$$

## Fluctuations in Energy :-

In Canonical ensemble partition func$^n$ is

$$Z = \sum_i e^{-\beta E_i} = \sum_i e^{-E_i/kT}$$

Average or mean energy is

$$\langle E \rangle = \frac{\sum_i E_i e^{-\beta E_i}}{\sum_i e^{-E_i/kT}} \quad \text{—} ①$$

$$\sum_i \langle E \rangle e^{-E_i/kT} = \sum_i E_i e^{-E_i/kT}.$$

diff.$^n$ w.r.t T both side

$$\sum_i \frac{\partial \langle E \rangle}{dt} e^{-E_i/kT} + \langle E \rangle \sum_i e^{-E_i/kT} \cdot \left(\frac{E_i}{kT^2}\right) = \sum_i \left(\frac{E_i}{kT^2}\right) E_i e^{-E_i/kT}$$

$$kT^2 \frac{\partial \langle E \rangle}{\partial t} = \frac{\sum_i (E_i)^2 e^{-E_i/kT}}{\sum_i e^{-E_i/kT}} - \frac{\sum_i \langle E \rangle \cdot (E_i) e^{-E_i/kT}}{\sum_i e^{-E_i/kT}}$$

$$kT^2 \frac{\partial \langle E \rangle}{\partial t} = \langle E^2 \rangle - \langle E \rangle^2$$

$$\frac{kT^2}{E^2} \frac{\partial \langle E \rangle}{\partial t} = \frac{\langle E^2 \rangle - \langle E \rangle^2}{\langle E \rangle^2}$$

$$\frac{kT^2}{E^2} C_V = \frac{(\langle E \rangle - E)^2}{(E)^2}$$

For
$E = nkT$.
$C_V = nk$

$$\left(\frac{\Delta E}{E}\right)^2 = \frac{kT^2}{E^2} C_V$$

$$= \frac{\cancel{k}\cancel{T^2}\, n\cancel{k}}{n^{\cancel{2}} \cancel{k^2} \cancel{T^2}} = \frac{1}{n}$$

$$\left\langle \frac{\Delta E}{E} \right\rangle = \frac{1}{n^{1/2}} \text{ or of order } n^{-1/2}.$$

For an ideal gas

$E = 3/_2\, nkT$ $\quad C_V = 3/_2\, nk$.

$$\left\langle \frac{\Delta E}{E} \right\rangle^2 = \frac{\cancel{k}\cancel{T^2}\, n\cancel{k}\, \cancel{3}/\cancel{2}}{\frac{\cancel{9}}{\cancel{4}} n^{\cancel{2}} \cancel{k^2} \cancel{T^2}} = \frac{2}{3n}$$

$$\left\langle \frac{\Delta E}{E} \right\rangle = \frac{1}{n^{1/2}} \sqrt{2/3}$$

For Bose - Einsetin gas

$$E = \frac{3}{2} nk_B \left(\frac{T}{T_B}\right)^{3/2} \times 0.5314 \times T. \quad C_V = \frac{15}{4} \times 0.5314\, nk \left(\frac{T}{T_B}\right)^{3/2}$$

$$\left\langle \frac{\Delta E}{E} \right\rangle = \frac{3.24}{\langle n \rangle} \left(\frac{T_B}{T}\right)^{3/2}$$

Fluctuation in Pressure

$$Z = e^{-E_i/kT}.$$

$$\langle P \rangle = \frac{\sum_i \left(-\frac{\partial E_i}{\partial V}\right) e^{-E_i/kT}}{\sum_i e^{-E_i/kT}}$$

$$\sum_i \langle P \rangle e^{-E_i/kT} = \sum_i \left(\frac{\partial E_i}{\partial V}\right) e^{-E_i/kT} .$$

diff$^n$ w.r.t Volume .

$$\frac{\partial \langle P \rangle}{\partial V} \sum_i e^{-E_i/kT} + \langle P \rangle \sum_i \left\langle \frac{\partial E_i}{\partial V} \right\rangle \left(\frac{-1}{kT}\right) e^{-E_i/kT} .$$

$$= \sum_i \left(\frac{\partial E_i}{\partial V}\right) e^{-E_i/kT} \cdot \left(\frac{\partial E_i}{\partial V}\right)\left(\frac{-1}{kT}\right)$$

$$+ \sum_i \left(\frac{\partial^2 E_i}{\partial V^2}\right) e^{-E_i/kT}$$

$$\frac{\partial \langle P \rangle}{\partial V} \sum_i e^{-E_i/kT} - \frac{\langle P \rangle^2}{kT} = -\frac{\langle P^2 \rangle}{kT} e^{-E_i/kT} + \sum_i \left(\frac{\partial^2 E_i}{\partial V^2}\right) e^{-E_i/kT}$$

$$kT \left[\frac{\partial \langle P \rangle}{\partial V} - \frac{\partial^2 E_i}{\partial V^2}\right] = + \langle P^2 \rangle - \langle P \rangle^2$$

$$kT \left[\frac{\partial \langle P \rangle}{\partial V} - \left\langle \frac{\partial P}{\partial V} \right\rangle\right] = \langle P^2 \rangle - \langle P \rangle^2 .$$

$$\frac{kT}{P^2} \left[\frac{\partial \langle P \rangle}{\partial V} - \left\langle \frac{\partial P}{\partial V} \right\rangle\right] = \frac{\langle P^2 \rangle - \langle P \rangle^2}{P^2} .$$

$$\left\langle \frac{\Delta P}{P} \right\rangle^2 = \frac{kT}{P^2} \left[\frac{\partial \langle P \rangle}{\partial V} - \left\langle \frac{\partial P}{\partial V} \right\rangle\right] .$$

For ideal gas

$$PV = nkT .$$

$$V\left(\frac{\partial P}{\partial V}\right) + P = 0$$

$$\frac{\partial P}{\partial V} = -P/V .$$

$\left\langle \frac{\partial P}{\partial V} \right\rangle$ must be +ve

$$\left\langle \frac{\Delta P}{P} \right\rangle^2 = \frac{kT}{P^2} \times \frac{-P}{V} = \frac{-kT}{PV} = -\frac{1}{n}.$$

## Fluctuations in Volume

$$\langle V \rangle = \sum_i \frac{V e^{-(E_i+PV)/kT}}{\sum_i e^{-(E_i+PV)/kT}}$$

~~diff w.r.t p~~

$$\langle V \rangle \sum_i e^{-(E_i+PV)/kT} = \sum_i V e^{-(E_i+PV)/kT}.$$

diff. w.r.t P

$$\frac{\partial \langle V \rangle}{\partial P} \sum_i e^{-(E_i+PV)/kT} + \langle V \rangle \sum_i \frac{V}{kT} e^{-(E_i+PV)/kT}$$

$$= \sum_i \frac{\partial V}{\partial P} e^{-(E_i+PV)/kT} \quad \sum_i \frac{V^2}{kT} e^{-(E_i+PV)/k}$$

$$kT \left[ \frac{\partial \langle V \rangle}{\partial P} - \frac{\partial V}{\partial P} \right] = \langle V^2 \rangle - \langle V \rangle^2$$

$$\frac{kT}{V^2} \left[ \frac{\partial \langle V \rangle}{\partial P} - \frac{\partial V}{\partial P} \right] = \frac{\langle V^2 \rangle - \langle V \rangle^2}{\langle V \rangle^2}$$

$$\left\langle \frac{\Delta V}{V} \right\rangle^2 = \frac{kT}{V^2} \left[ \frac{\partial \langle V \rangle}{\partial P} - \frac{\partial V}{\partial P} \right]$$

For ideal gas

$$PV = nkT.$$

$$P \frac{\partial V}{\partial P} + V = 0 \qquad \frac{\partial V}{\partial P} = -\frac{V}{P}.$$

$$\left\langle \frac{\Delta V}{V} \right\rangle^2 = \frac{kT}{V^2} \times -\frac{V}{P} = -\frac{kT}{PV} = \frac{-1}{n}.$$

Fluctuation in Enthalpy H.

$$H = E + PV$$

$$\langle H \rangle = \frac{\sum_i (E_i + PV)\, e^{-(E_i+PV)/kT}}{\sum_i e^{-(E_i+PV)/kT}}.$$

$$\langle H \rangle \sum_i e^{-(E_i+PV)/kT} = \sum_i (E_i + PV)\, e^{-(E_i+PV)/kT}.$$

diff. w.r.t t

$$\frac{\partial \langle H \rangle}{\partial t} \sum_i e^{-(E_i+PV)/kT} + \langle H \rangle \sum_i \frac{(E_i+PV)}{kT^2}\, e^{-(E_i+PV)/kT}$$

$$= \sum_i \frac{(E_i+PV)\,(E_i+PV)}{kT^2}\, e^{-(E_i+PV)/kT}$$

$$kT^2 \frac{\partial \langle H \rangle}{\partial t} + \langle H \rangle \frac{\sum_i (E_i+PV)\, e^{-(E_i+PV)/kT}}{\sum_i e^{-(E_i+PV)/kT}} = \frac{\sum_i (E_i+PV)^2\, e^{-(E_i+PV)/kT}}{\sum_i e^{-(E_i+PV)/kT}}$$

$$kT^2 \frac{\partial \langle H \rangle}{\partial t} = \langle H^2 \rangle - \langle H \rangle^2$$

$$\frac{kT^2}{H^2} \frac{\partial \langle H \rangle}{\partial t} = \frac{\langle H^2 \rangle - \langle H \rangle^2}{\langle H \rangle^2}$$

$$\left\langle \frac{\Delta H}{H} \right\rangle^2 = \frac{kT^2}{H^2} \left( \frac{\partial \langle H \rangle}{\partial t} \right)_{n,P}$$

$$\boxed{\left\langle \frac{\Delta H}{H} \right\rangle^2 = \frac{kT^2}{H^2}\, C_p}$$

$$\left\langle \frac{\Delta H}{H} \right\rangle^2 = \frac{1}{n}$$