UNIT-II
CLASSICAL STATISTICS AND QUANTUM STATISTICS

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Statistical Physics: Studying the macroscopic parameters of system in equilibrium from knowledge of microscopic properties of constituents particles

Classical Statistics : Employs classical results of Maxwell's law of molecular velocities distribution and Boltzmann theorem.

Known as Maxwell Boltzmann statistics

Quantum Statistics : Employs quantum theory and developed by Bose, Einstein, Fermi and Dirac like scientist

Known as BE and FD statistics

Phase Space

Degree of Freedom :System involve f coordinates of position and f coordinates of momentum.

System with one molecule has f degree of freedom and with N molecule N f

Position Space : In static system,three dimensional space in which location of a particle is completely given by three position co-ordinates

A small element in position space denoted by volume element $dV = dx\,dy\,dz$

Momentum Space :In dynamic system,system can be specified by three components of momentum $p_x=mv_x$, $p_y=mv_y$, $p_z=mv_z$

P_x p_y and p_z in 3D space known as momentum space

Small volume element in momentum space is given by dp_x ,dp_y ,dp_z

Phase space

Phase Space

Phase space : Combination of position space and momentum space is known as phase space

Phase space has six dimensions

All six coordinates are mutually perpendicular to each other

Complete information about any particle in dynamic system obtained from phase space

Small element in a phase space is $d\tau = (\mathbf{dx\ dy\ dz})\ (\boldsymbol{dp_x dp_y dp_z})$

Phase cell :Phase space can be divided into large number of cells known as

Maxwell Boltzmann's Distribution Law

Suppose total amount of energy is to be distributed among system of n particles

System consisting of *n* identical particles

Widely separated just like molecules of gas

Particles be distributed among *s* cells and designated by $A_1, A_2, A_3, \ldots$

These cells accommodate $n_1, n_2, n_3 \ldots\ldots$ particles respectively

Let n_1 particles in cell A_1 with energy u_1, n_2 in A_2 with u_2 and so on

To distribute total energy – how many particles have energy u_1, how many u_2

Priori probability g_i that particle will occupy i^{th} cell is

$$g_i = \frac{v_i}{V} \quad \text{----} \quad (1)$$

v_i is volume of i^{th} cell, V is total volume

$g_i \propto$ Volume of cell

Maxwell Boltzmann's Distribution Law

Priori probability that n particles will occupy i^{th} cell = $g_i^{n_i}$

Probability of distribution of n particles among s cells is

$$W = \frac{n!}{n1!\ n2!\ n3!}(g_1)^{n_1}(g_2)^{n_2}\dots(g_s)^{n_s} \quad \text{---------(2)}$$

When cells of equal size , g_1, g_2, ...g_s are each equal to 1/s then eq 2 reduced to

$$W = \frac{n!}{n_1!\ n_2!\ n_3!}(s)^{-n} \quad \text{----(3)}$$

Eq. 2 can be rewriting in the form

$$W = \frac{n!}{\pi\, n_s!}\pi\, {g_s}^{n_s} \quad \text{-----(4)}$$

Here $\pi\, n_s! = n_1!\ \ n_2!\ \ n_3! \dots n_s!$ -------(5)

$\pi\, gs^{n_s} = (g_1)^{n_1}(g_2)^{n_2}\dots(g_s)^{n_s}$--------(6)

Maxwell Boltzmann's Distribution Law

Taking logarithm of both sides of eq.(6)

$\boldsymbol{log\ W = log\ n! + log\ (\pi\ gs^{n_s}) - \log\ (\pi\ n_s)!}$----(7)

Using Stirling's approximation formula

$\boldsymbol{log\ n! = n\ log\ n - n}$ --------(8)

$\boldsymbol{log\ (\pi\ gs^{n_s})} = \log \boldsymbol{g_1}^{\boldsymbol{n_1}} + \boldsymbol{log\ g_2}^{\boldsymbol{n_2}} + \cdots . + \boldsymbol{log(g_s)^{n_s}}$

$= \boldsymbol{n_1\ log\ g_1 + n_2\ log\ g_2 + \cdots . + ns\ log\ \ gs}$

$= \sum \boldsymbol{n_s\ log\ \ gs}$ ------(9)

$\boldsymbol{\log\ (\pi\ n_s)!}$ $= \log \boldsymbol{n_1! + log\ n_2! + . \ldots . + logns!}$

$= \boldsymbol{n_1\ log\ n_1\ \_\ n_1 + n_2\ log\ n_2 - n_2 + \cdots .. + ns\ log\ ns\ - ns}$

$= (\boldsymbol{n_1\ log\ n_1 + n_2\ log\ n_2} + \ldots + \boldsymbol{n_s\ log\ ns}) - (\boldsymbol{n_1 + n_2 + \cdots + ns})$

$= \sum \boldsymbol{n_s\ log\ ns - ns = \sum n_s\ log\ ns - n}$ -----(10)

Maxwell Boltzmann's Distribution Law

$$= \sum n_s \log ns - ns = \sum n_s \log ns - n \text{ -----(10)}$$

Using eq. 7,8 , 9 and 10 eq. 7 yields

$$\log W = n \log n + \sum n_s \log gs - \sum n_s \log ns \text{----(11)}$$

Condition for maximum probability

i) $\delta(\log W) = 0$ ii) $\delta \sum n_s = 0$ and $\sum n_s u_s = 0$ ---(12)

Differentiating eq 11 we get

$$\delta(\log W) = \sum \log gs\, \delta ns - \sum (1 + \log ns)\, \delta ns \text{ ----(13)}$$

Using eq 12 ,eq 13 yields

$$\sum(\log gs - \log ns)\, \delta ns - \sum \delta ns = 0$$

$\sum \log\left(\frac{gs}{ns}\right) \delta ns = o$ ----(14) since $\sum \delta ns = 0$

Maxwell Boltzmann's Distribution Law

Rewriting eq 13 and using $\sum \delta\, ns = 0\; and\; \sum u_s\, \delta ns = 0$

And combining with eq 14 by the method of Lagrange's method of underdetermined multiplier ie. We multiply

$$\sum \delta\, ns = 0\; by\; -\alpha \quad and \sum u_s\, \delta ns = 0\; by\; -\beta$$

and then adding with eq 14 we obtain

$$\sum \left(log\, \frac{g_s}{n_s} - \alpha - \beta us \right) \delta\, ns = 0 \text{ ---(15)}$$

$\alpha\; and\; \beta$ are Lagrange's multiplier

Eq. 15 holds good for all values of *s* *bracket quantity vanishes*

Maxwell Boltzmann's Distribution Law

$$log\left(\frac{g_s}{n_s}\right) - \alpha - \beta\, u_s = 0$$

Or $$g_s = ns\; exp\,(\alpha + \beta us)$$

Or

$$ns = \frac{gs}{f}\; exp\,(-\beta\, us) \text{ ---(16)}$$

Here

$$f = exp(\alpha)\text{----------(17)}$$

Eq. 16 is called Maxwell-Boltzmann distribution law

β are Distribution modulus β=1/Kt

f is degeneracy parameters

Maxwell Boltzmann's Distribution Law

$\boldsymbol{\beta}$ are Distribution modulus $\boldsymbol{\beta}$=1/Kt gives number of particles possessing energy u_s

$$\boldsymbol{From\ eq\ 16}$$

1) gi depends upon size of cell
2) Cells of equal size having lower energy will filled first then cells having higher energy
3) Number of particles decreases with exponentially with energy.

Bose –Einstein Distribution Law

Particles are identical and indistinguishable

Interchange of two particles between two energy state give new complexation or micro state

system of n indistinguishable particles

Divided into quantum levels such as $n_1, n_2, n_3 \ldots n_i$ number of particles in groups approximate energies are $\varepsilon_1, \varepsilon_2, \varepsilon_3 \ldots \varepsilon_i$

g_i – degeneracy or no. of eigen states or statistical weights of i^{th} quantum level

Bose –Einstein Distribution Law

condition for distribution of ni indistinguishable particles in g_i states

1) As indistinguishable, no distinction bet'n different ways of choosing n_i particles

2) Each eigen states of i^{th} quantum state may contain 0,1,2…n_i identical particles

3) Sum of energies of all particles in different quantum groups together as total energy of the system

A box containing g_i sections or cells and n_i particles to be distributed

Box is divided into g_i sections by (g_i-1) partitions

Bose –Einstein Distribution Law

Permutation of n_i and (g_i-1) partitions simultaneously=$(\boldsymbol{ni}+\boldsymbol{gi}-\mathbf{1})!$
As groups are internally indistinguishable required number of ways in which n_i particles are to be distinguished in gi sublevels of i^{th} quantum group= $\boldsymbol{(ni+gi-1)!}$

= $\boldsymbol{ni\,!\,(gi-1)!}$

Thermodynamic probability

$$\boldsymbol{W=\frac{(n_1+g_1-1)!}{n_1\,!\,(g_i-1)!}\cdot\frac{(n_2+g_2-1)!}{n_2\,!\,(g_2-1)!}\dots\dots\dots\frac{(ni+gi-1)!}{n_i\,!\,(g_i-1)!}}$$

$$\boldsymbol{W=\Pi_i\frac{(ni+gi-1)!}{n_i\,!(gi-1)!}}\text{ ....(1)}$$

Bose –Einstein Distribution Law

Since ni and gi are large, neglecting 1

$$W = \Pi_i \frac{(ni+gi)!}{n_i\,!(gi)!} \text{ ....(2)}$$

Using Striling's approximation

$$logW = \sum (n_i + gi) log\,(n_i + gi) - nilogni - gi\,log\,gi$$

Bose –Einstein Distribution Law

n_i varies continuously and g_i not subject to variation

Differentiation of eq. 2 leads

$$\delta(\log W) = \sum\{\log(n_i + gi) - \log n_i\}\delta ni$$

$$= -\sum_i \left\{\log \frac{n_i}{n_i + gi}\right\} \delta ni \text{ ....(3)}$$

For most probable distribution W=W max

$\delta(\log Wmax) = 0$ and gives

$$\sum_i \left\{\log \frac{n_i}{n_i + gi}\right\} \delta ni = 0 \text{........(4)}$$

Bose –Einstein Distribution Law

Two conditions are there

1) Total number of particles in a system is constant

ie $\boldsymbol{n = \sum_i n_i = constant} \quad ,\boldsymbol{\delta n = \sum_i \delta n_i = 0}$.....(5)

2) Total energy of system is constant

$\boldsymbol{E = \sum_i \epsilon_i n_i = constant \quad , \delta E = \sum_i \epsilon_i \delta ni = 0}$ ......(6)

using Lagranngian method and multiplying eq,5 by α and 6 by β and then adding the resulting expression to eq 4

$$\sum_{ì} \left[\boldsymbol{log \left(\frac{ni}{ni+gi}\right) + \alpha + \beta\, \varepsilon_i} \right] \boldsymbol{\delta ni = 0} \quad ....(7)$$

Bose –Einstein Distribution Law

Since variation of δ ni are independent of each other

$$\left[\log\left(\frac{ni}{n_i+gi}\right)+\ \alpha+\beta\epsilon_i\right]=0$$

OR $$\frac{ni}{ni+gi}=exp\,(\alpha+\beta\epsilon_i)$$

OR

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

OR $$n_i=\frac{g_i}{[e^{\alpha+\beta\epsilon_i-1}]}$$

Bose –Einstein Distribution Law

$$ni = \frac{gi}{[e^{\alpha+\beta\epsilon_i-1}]} \text{--------}(8)$$

Equation 8 represent most probable distribution of particles among various energy levels for a system obeying B-E statistics known as B-E Distribution law

Fermi-Dirac Distribution Law

System having n indistinguishable particles

Particles divided into quantum levels such that there are $n_1, n_2, \ldots, n_i$ number of particles with energy $\epsilon_1, \epsilon_2, \ldots, \epsilon_i$ respectively

g_i be degeneracy or statistical weight

Conditions:

1) Particles are indistinguishable so that there is no distinction between different ways in which n_i particles chosen

2) Fermi particles obey Pauli exclusion principle –each cell or sub level may contain 0 or 1 particles i.e. g_i must be greater or equal to n_i

Fermi-Dirac Distribution Law

3) sum of energies of all particles in different level taken together is the total energy of system.

According to Pauli exclusion principle no cell can occupy more than one particle

Therefore among gi cells only ni cells will occupied by one each

Remaining (g_i- n_i) cells are empty

Number of arrangement of ni particles in gi cells are

$$\frac{g_i\,!}{n_i\,!(g_i - ni)!} \quad .....(1)$$

Fermi-Dirac Distribution Law

Total number of eigen states for entire system is

$$G = \prod_i \frac{g_i\,!}{n_i\,!(g_i - ni)!} \; .....(2)$$

The probability of system is

$$W = \prod_i \frac{g_i\,!}{n_i\,!(g_i - ni)!} \times constant \; .....(3)$$

Taking log of eq. 3

$$\log W = \left[\Pi_i \; \frac{g_i\,!}{n_i\,!(g_i - ni)!} \times constant\right]$$

Fermi-Dirac Distribution Law

$$= \sum_i [\log gi\,! - \log ni\,! - \log (g_i - ni)! + constant] \quad ..(4)$$

Using Stirling approximation

$$\log n! = n \log n - n \quad ....(5)$$

Eq. 4 reduces to

$$\log W = \sum_i g_i \log gi - gi - ni \log ni + ni - (g_i - ni)\log (g_i - ni) + (g_i - ni) + const$$

$$= \sum_i [(n_i - gi)\log (g_i - ni) + gi\log gi - ni\log ni] + const \quad ..(6)$$

Since gi is not subject to variation and ni varies continuously

Fermi-Dirac Distribution Law

Differentiating eq. 6

$$\delta \log W = \sum_i \{\log(g_i - ni) - \log ni\}\delta ni$$

$$= -\sum_i \left\{\log \frac{ni}{gi-ni}\right\}\delta ni \;\ldots\ldots(7)$$

For most probable distribution $W = Wmax$ and $\delta(logWmax) = 0$

$$\sum_i \left\{\log \frac{ni}{gi-ni}\right\}\delta ni = 0 \quad \ldots..(8)$$

Fermi-Dirac Distribution Law

Two subsidiary conditions are

1) Total number of particles of system are constant

$\boldsymbol{n = \sum_i n_i = const}$ i.e. $\boldsymbol{\delta\, n = \sum \delta\, ni = 0}$ ---(9)

2) Total energy of the system is constant

$\boldsymbol{E = \sum_i \epsilon_i n_i = \mathbf{const}}$ i.e. $\boldsymbol{\delta E = \sum_i \epsilon_i \delta n_i = 0}$ ...(10)

using Lagranngian method and multiplying eq,9 by α and 10 by β and then adding the resulting expression to eq 8

$$\boldsymbol{\sum_i \left[log\left(\frac{n_i}{g_i - ni}\right) + \alpha + \beta\epsilon_i \right] \delta ni = 0} \text{ ...(11)}$$

Fermi-Dirac Distribution Law

Since variation of $\boldsymbol{\delta ni}$ are independent of each other , one obtain

$$\boldsymbol{log\ \frac{n_i}{g_i - ni} + \alpha + \beta\epsilon_i = 0}$$

On simplification

$$\boldsymbol{ni = \frac{g_i}{e^{\alpha+\beta\epsilon_i + 1}}} \quad ....(12)$$

Equation 12 is F.D. Distribution law

COMPARISION OF THE THREE STATISTICS:

Maxwell-Boltzmann	Bose-Einstein	Fermi-Dirac
1. Particles are distinguishable	Particles are indistinguishable	Particles are indistinguishable
2. Only particles are taken into consideration	Only quantum states are taken into consideration	Only quantum states are taken into consideration
3. No restriction on number of particles in a given state	No restriction on number of particles in a given quantum state	There is restriction on number of particles in a given quantum state

COMPARISION OF THE THREE STATISTICS:

Maxwell-Boltzmann	Bose-Einstein	Fermi-Dirac
4.Volume of state in six dimensional space is not given	Phase space is known $V=h^3$	Phase space is known $V=h^3$
5. Number of distinguishable ways $W = \prod_i \frac{{g_i}^{n_i}}{n_i!}$	Number of distinguishable ways $\boldsymbol{W = \prod_i \frac{(ni + gi - 1)!}{n_i!(gi - 1)!}}$	Number of distinguishable ways $\boldsymbol{W = \prod_i \frac{g_i!}{n_i!(g_i - ni)!}}$
6 Maximum Probability distribution $\propto \frac{1}{e^{(\alpha+\beta\epsilon_i)}}$	Maximum Probability distribution $\propto \frac{1}{[e^{(\alpha+\beta\epsilon_i)}] - 1}$	Maximum Probability distribution $\propto \frac{1}{[e^{(\alpha+\beta\epsilon_i)}] + 1}$

COMPARISION OF THE THREE STATISTICS:

Maxwell-Boltzmann	Bose-Einstein	Fermi-Dirac
7.	At high temp.BE statistics approaches to MB statistics	At high temp.FD statistics approaches to MB statistics
8.Applicable to ideal gas molecules	8.Applicable to photons and symmetrical particles known as bosons	8.Applicable to electrons and antisymmetrica particles known as Fermions
9. Internal energy depends on its temp. At absolute zero ,energy is zero	Energy at absolute zero is taken to be zero	Energy at absolute zero is not taken to be zero

COMPARISION OF THE THREE STATISTICS:

Maxwell-Boltzmann	Bose-Einstein	Fermi-Dirac
10. $\mathrm{n}_i = \frac{g_i}{e^{(\alpha+\beta\epsilon_i)}}$	$\mathrm{n}_i = \frac{g_i}{[e^{(\alpha+\beta\epsilon_i)} - 1]}$	$\mathrm{n}_i = \frac{g_i}{[e^{(\alpha+\beta\epsilon_i)} + 1]}$

APPLICATIONS OF QUANTUM STATISTICS TO:
1) Photon gas

Introduced by S.N.Bose in 1924
Considering thermal radiation as a photon gas
Obtained Planck's formula
Einstein developed further idea known B-E statistics
Photon gas analyser is double walled hollow sphere with narrow opening at one point is a perfect absorber as its inner surface is coated with lamp black and sharp projection opposite to opening

Photon Gas Analyser

APPLICATIONS OF QUANTUM STATISTICS TO:
1) Photon gas

If thermal radiation enters through narrow opening, absorbed completely inside by successive multiple reflection as designed by Fery
If enclosure maintained at constant temperature T , atoms of walls of encloser emits electromagnetic radiation and at the same time these radiations are absorbed by atoms in walls
Thus atoms of walls will emit and reabsorb photons continuously
When thermodynamic equilibrium is reached,then amount of energy emitted per unit time is equal to amount of energy absorbed by atom per unit time

APPLICATIONS OF QUANTUM STATISTICS TO:
1) Photon gas

Thus interaction of em radiation with matter led to idea of radiation composed of discrete energy particles called *PHOTON*

Each photon has energy $h\upsilon$ and momentum h/λ

Radiation trapped in cavity and in thermal equilibrium walls of cavity are termed as ***black body radiation***

In equilibrium black body radiation can be considered as *Photon gas*

APPLICATIONS OF QUANTUM STATISTICS TO:
2) Electron gas

Metals are good conductors
High conductivity in metals are due to presence of free electrons
Free electrons inside metal moves freely
Continuously collides with fixed atoms and behaves like electron gas
Free electrons belongs to system of fermions
Obeys Pauli's exclusion principle
Obeys Fermi –Dirac statistics
Electrons in metal have energy quantised