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 dτ =$(\mathbf{dx\ dy\ dz})\ (\boldsymbol{dp_x dp_y dp_z})$

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

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

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

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

Eq. 2 can be rewriting in the form

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

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)

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

Using Stirling's approximation formula

$\log n! = n \log n - n$ --------(8)

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

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

$= \sum n_s \log\ gs$ ------(9)

$\log(\pi\, n_s)! = \log n_1! + \log n_2! + . \ldots . + \log ns!$

$= n_1 \log n_1 - n_1 + n_2 \log n_2 - n_2 + \cdots .. + ns \log ns - ns$

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

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

Maxwell Boltzmann's Distribution Law

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

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

$\log W = n \log n + \sum n_s \log\ gs - \sum n_s \log ns$----(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

$\delta(\log W) = \sum \log gs\ \delta ns - \sum(1 + \log ns)\ \delta\ ns$ ----(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=$(\boldsymbol{ni}+\boldsymbol{gi}-\boldsymbol{1})!$

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

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

Thermodynamic probability

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

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

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

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

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

For most probable distribution W=W max

$\boldsymbol{\delta(log\, Wmax) = 0}$ and gives

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

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

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

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

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

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

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

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

The probability of system is

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

Taking log of eq. 3

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

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 $\delta(logWm_{ax}) = 0$

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

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 δni are independent of each other , one obtain

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

On simplification

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

Equation 12 is F.D. Distribution law