Statistical Mechanics

For ELTA Sem-2 cc-3

What is Statistical Mechanics

- There are two Types of Properties of matter particles.
- 1. Individual property like position, momentum, kinetic and potential energy.
- 2. Group property like pressure, volume temperature, entropy etc.
- The study to attain group property from individual property is known as Statistical Mechanics

The scope of our study

- There are three types of particle having different individual behavior namely MB,FD and BE particles.
- We are given a system of N molecules with total energy E
- The system has s different allowed energy levels $E_{1,}$ $E_{2,}$ …E_i …E_s .
- Each energy level E_i is composed of g_i number of different momentum states
- We are to find out the energy distribution of particles that is number of particle n_i in the i-th energy level E_i for all the three types of particle.

All Energy in a system is not attainable

- According to Quantum Mechanics a particle in a bound system can have only discreet momentum values.
- As momentum is a vector quantity and kinetic energy a scalar quantity, a number of momentum values can correspond to a single energy. If g_i number of different momentum states corresponds to a single energy E_i then this energy state is said to be g_i fold degenerate.

Particle in three dimensional Box

Consider a particle enclosed in a three dimensional cubical box of size L ($V=L^3$)We have the wave function ψ_i and the energy eigen values ϵ_i has the following relation with the Hamiltonian operator H as

$$H\Psi_i = \varepsilon_i \Psi_i \quad \text{and} \quad H = \hat{p}^2 / 2m = -(\frac{h^2}{8\pi^2 m})\nabla^2$$

$$\Psi_i = A.\sin(\frac{n_1 \pi x_1}{L})\sin(\frac{n_2 \pi x_2}{L})\sin(\frac{n_3 \pi x_3}{L})$$

And the energy levels are $\epsilon_n = \epsilon_{n1} + \epsilon_{n2} + \epsilon_{n3}$

where $n^2 = n_1^2 + n_2^2 + n_3^2$

where n, n_1, n_2 and n_3 are integers

Particle in three dimensional Box

In the n_1, n_2, n_3 space each lattice point, whose co-ordinates are all positive integers correspond to a quantum state (eigen state). Therefore, for large n we can write all the number of momentum states $\Omega(\epsilon_n)$ having energy less than equal to ϵ_n is given by the number of lattice points lying within the sphere having radius n, but as n_1, n_2, n_3 are +eve integers we have to consider only 1/8 of the whole sphere. So for large n we can write

Particle in three dimensional Box

$\Omega(\epsilon_n) = (1/8).(4/3)\pi n^3 \;\; = (1/6).(8mL^2 \epsilon_n)^{3/2}$

$= (4/3)\,\pi(L^3/h^3).(2m\,\epsilon_n)^{3/2}$

Hence $d\,\Omega(\epsilon_n)/d\,\epsilon_n = 8\,\pi(V/h^3)m^{3/2}\,\epsilon_n^{\,½}$

So the number of momentum states corresponding to energy level E to E+dE is given by

$$dn = g(E)dE = 8\,\pi(V/h^3)m^{3/2}\;E^{1/2}\;dE$$

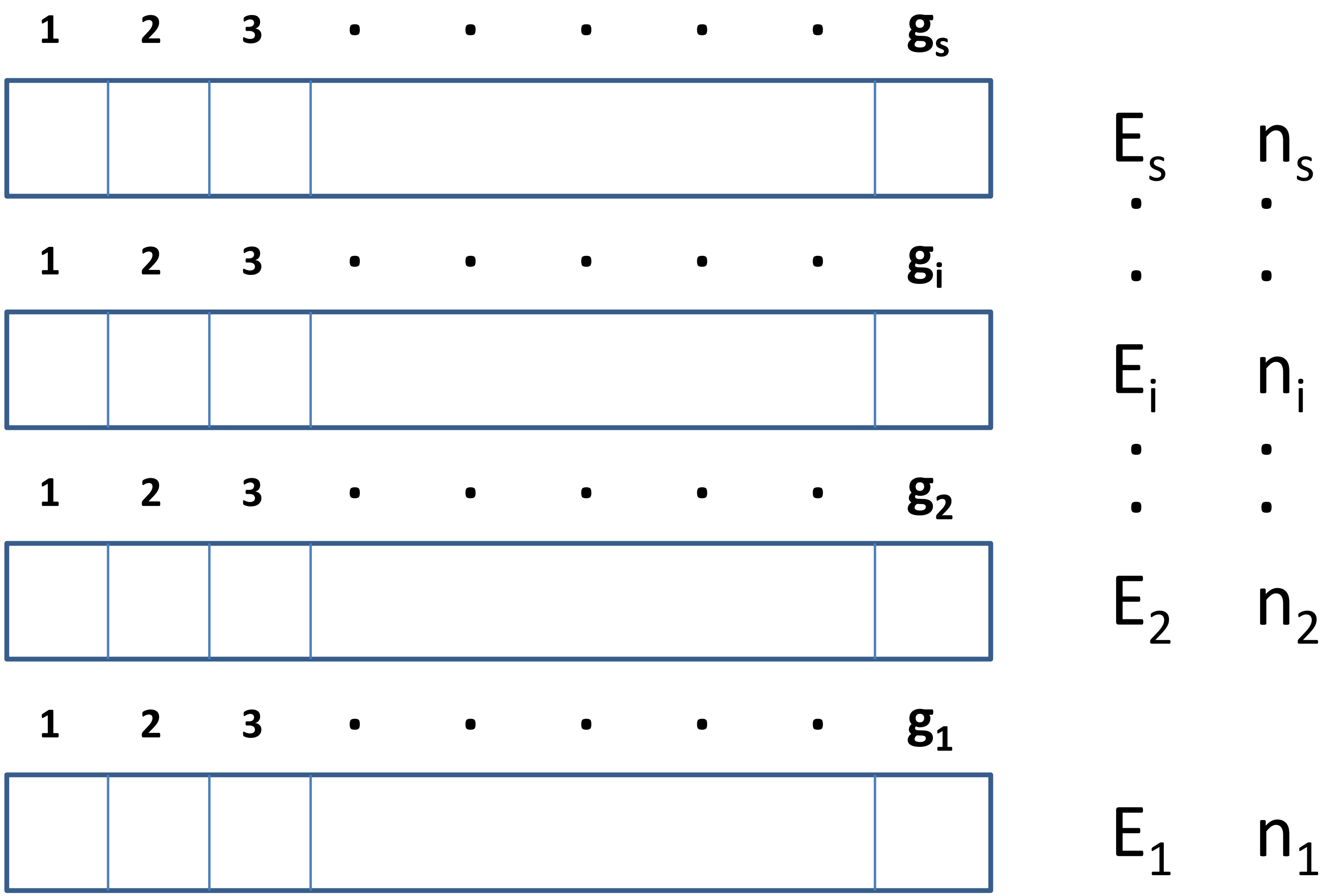
where g(E) is known as the density of states

Three different types of particle

- Particles following Maxwell Boltzman Statistics are classical particle like gas molecules. These particles are 1). Distinguishable 2). Any number of particles can occupy a particular momentum state.
- The particles having half integral spin follows Fermi Dirac Statistics. They are quantum particle like electron, positron, neutron, proton, neutrino, quark etc. They are 1). Indistinguishable 2). Only one particle can occupy one momentum state.
- The particles having zero or integral spin follow Bose Einstein Statistics. They are quantum particle like photon, phonon, gluon, Higgs Boson etc. They are 1). Indistinguishable 2). Any number of particles can occupy a particular momentum state.

The Energy levels and particle Distribution

The i th Energy Level is g_i fold degenerate And contain n_i particles



The Basic question

- There are N particles with total energy E.
- There are s energy levels. Each energy level is made of a number of momentum states. The number of momentum state is called the degeneracy of that level. The i-th energy level being g_i fold degenerate.
- Question what would be the number of particle n_i in i-th energy level so that

$$\sum_{i=1}^{s} n_i = N \quad \text{and} \quad \sum_{i=1}^{s} E_i n_i = E$$

In brief we want to find out the dependence of n in terms of energy and degeneracy in all energy levels. ie,. n_i =f(E_i , g_i) where f() is called the distribution function

The Answer to this Basic question

- There are numerous way we can distribute N particles in s energy states.
- Each particular distribution can be achieved in many ways.
- Nature prefers that particular distribution which can be done in the maximum number of ways.
- So our job is to find out the number of ways in which a particular distribution can be achieved. Then to find, mathematically, the condition for which the number of ways would be maximum.
- That is our target distribution.

Maxwell Boltzmaan Distribution

- Here, all particle are distinguishable so the number of ways in which N particles be distributed in s energy levels are Ω_1 ways where Ω_1 =N!/n_1! n_2! n_3!... n_s!
- And as there is no restriction on the number of particles in a particular momentum state each energy level can be filled in

$$g_i^{\,n_i} \quad \text{ways}$$

and the total number of ways this can be done is given as

Maxwell Boltzmaan Distribution

$$\Omega_2 = \prod_{i=1}^{s} g_i^{n_i}$$

And the total nuber of ways in which the distribution can be achieved is

$$\Omega = \Omega_1 \Omega_2 = \frac{N!}{\prod_{i=1}^{s} n_i} \prod_{i=1}^{s} g_i^{n_i}$$

Maxwell Boltzmaan Distribution

- Taking the logarithm of the total number of ways we get the statistical entropy of the system. Differentiation it w.r.t n_i and setting the result to zero we get the condition of its maximum value.
- This equation along with the two other conditions that total number of particle is N and total energy is E we arrive at the distribution function of Maxwell Boltzmaan equation as

$$\frac{n_i}{g_i} = Ae^{-\frac{E_i}{kT}}$$

Fermi Dirac Distribution

- In Fermi Dirac (FD) distribution particles are indistinguishable hence there is only one way in which N particles can be distributed in s energy states following a particular distribution
- There are g_i momentum states and one state can utmost occupy one particle.
- So one energy state can be occupied by

  $(g_i\ !)/(n_i\ !(g_i\ - n_i\ )!)$ ways.

Fermi Dirac Distribution

So the Total number of ways in a particular distribution can be achieved is given by

$$\Omega = \prod_{i=1}^{s} \frac{g_i!}{n_i!(g_i - n_i)!}$$

Fermi Dirac Distribution

- Taking the logarithm of the total number of ways we get the statistical entropy of the system. Differentiation it w.r.t n_i and setting the result to zero we get the condition of its maximum value.
- This equation along with the two other conditions that total number of particle is N and total energy is E we arrive at the distribution function of Fermi Dirac Distribution equation as

$$\frac{n_i}{g_i} = \frac{1}{e^{\frac{(E_i - E_F)}{kT}} + 1}$$

Bose Einstein Distribution

- In Bose Einstein (BE) distribution, particles are indistinguishable. Hence there is only one way in which N particles can be distributed in s energy states following a particular distribution
- There are g_i momentum states and one state can contain any number of particle.
- So one energy state can be occupied by

  $(g_i + n_i -1)!/(n_i !(g_i -1)!)$ ways.

Bose Einstein Distribution

- So the Total number of ways in a particular distribution can be achieved is given by

$$\Omega = \prod_{i=1}^{s} \frac{(g_i + n_i - 1)!}{n_i!(g_i - 1)!}$$

Bose Einstein Distribution

- Taking the logarithm of the total number of ways we get the statistical entropy of the system. Differentiation it w.r.t n_i and setting the result to zero we get the condition of its maximum value.
- This equation along with the two other conditions that total number of particle is N and total energy is E we arrive at the distribution function of Fermi Dirac Distribution equation as

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