Quantum statistical mechanics

Lecture Five

1- Bose-Einstein Statistics

Quantum statistical mechanics

is statistical mechanics applied to quantum mechanical systems. In quantum statistics, *Bose–Einstein statistics (or B–E statistics)* describe one of two possible ways in which a collection of non-interacting, indistinguishable particles may occupy a set of available discrete energy states at thermodynamic equilibrium.

The theory of this behavior was developed (1924–1925) by Satyendra Nath Bose, who recognized that a collection of identical and indistinguishable particles can be distributed. The idea was later adopted and extended by Albert Einstein in collaboration with Bose. The Bose–Einstein statistics apply only to those particles not limited to single occupancy of the same state—that is, particles that do not obey the Pauli Exclusion Principle restrictions. Such particles have integer values of spin and are named bosons, after the statistics that correctly describe their behavior.

There must also be no significant interaction between the particles.

Bose–Einstein statistics apply when quantum effects are important and the particles are "indistinguishable".

According to quantum statistical mechanics, particles with half an odd integer spin such as electron and positron follow the

Fermi statistics, and particles with an even integer spin such as photon and phonon follow the Bose-Einstein statistics.

Classical statistical mechanics and quantum statistical mechanics are both based on the statistical probability description of Nature. The M.B.D. law is a result of classical theory; it is valid for molecules of a gas under ordinary conditions.

What is the essential properties of B.E.S.

The Bose-Einstein statistics leads to;

1- The system is completely indistinguishable (there is no limit on the number of particle per quantum state.

2- All particles has a symmetric wave function (i.e. ψ is remain unchanged) under interchange of any two particles.

3- The system have zero or integer angular momentum i.e.

$s = 0, \hbar, 2\hbar, 3\hbar$---------

4- The system not obey Pauli exclusion principle.

5- The particles of the system (i.e. Photon, Phonon, α −particles) is known as a bosons and there is no restriction on the number of such system which may occupy a given energy state.

Phase Space

   In the quantum statistical it is imposed to use Six-dimensional phase space.

$$H = dxdydzdp_xdp_ydP_z$$

According to classical mechanics, the position and momentum of a particle can be specified to any discrete degree of precision.

In quantum mechanics there is a limit both to the experimental precision with which the position and momentum of a particle can be simultaneously determined. This leads to so called Heisenberg Uncertainty Principle.

The H.U. principle states that the point representing the position and momentum of the particle lies some where with in an element of phase space of volume h^3 $i.e. \Delta x. \Delta p \geq h$

$h = 6.6237 \times 10^{-34} J.sec \rightarrow$ Planck's constant

$h^3 \rightarrow$ has dimension of a volume in phase space

$h^3 \rightarrow (J.sec)^3 = (N.m.sec)^3 = m^3(N.sec)^3$

$h^3 = (length)^3 \times (momentum)^3$ Newton second law.

If an element of volume $h^3 \rightarrow$ as a compartment to distinguish it from a cell of volume H. The subdivision of phase space into cell of volume H and liner subdivision into a compartments of volume $h^3 \Longrightarrow i.e. H \gg h^3$

The number of compartment per cell

$n = \frac{H}{h^3} \Longrightarrow$ Number of compartment per cell.

Thermodynamic probability

As before, let $N_i \rightarrow$ represent the number of phase point in the ith cell. In any statistics, the properties of the system determined by the macrostate of the system i.e. number N_i . The thermodynamic probability W of a macrostate is defined as the number of microstate correspond to it.

 Now let return to the same example as in Maxwell-Boltzmann statistics, thus 4 phase point and two cells i and j so, $N_i = 3$ and $N_j = 1$ (abcd)

$\underline{N_i=3}$ $\underline{N_j=1}$

| ... | • | According to Maxwell-Boltzmann stat.

   Cell i   cell j

According to M.B.S. there are 4 microstate corresponding to this macrostate , so that W= 4

Cell i | ☐ | ☐ | ☐ | ☐ | $N_i =3$ W=4

Cell j | a | b | c | d | $N_j =1$
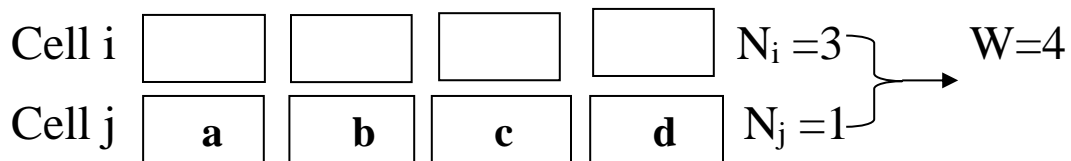
Let these cell subdivision to smaller compartments.

Here we consider only particles to which the Pauli exclusion principle does not apply, and for which there may be any number of phase point in a compartment.

The theory was developed by Einstein and Boltzmann and is called Bose-Einstein statistics.

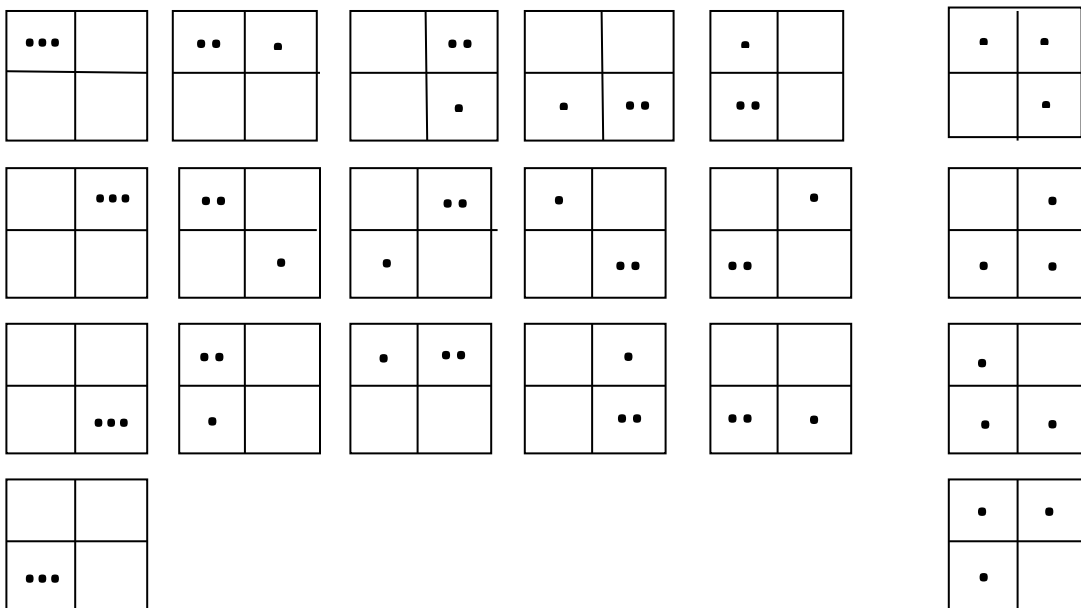Let the cell i and j divided into four compartment each.

According to B.E.S. let us assume there are four compartment per cell, with out making any use of the identities of the particles. Let us assume
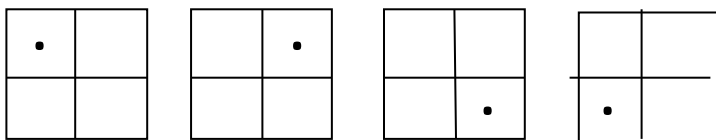
N_i= 3 in the cell i

N_j= 1 in the cell j

Cell i, W_i=20

Cell j, W_j=4

All these distribution not obeys the Pauli exclusion principle.

The thermodynamic probability to each cell equal to the number of possible ways of arranging the phase points with in that cell. This can not done in the M.B.S. 20 different ways of arranging

the three phase points in cell i and 4 ways of arranging the one phase point in cell j.

If $W_i \longrightarrow$ represents the probability of cell i

$W_j \longrightarrow$ represents the probability of cell j

The thermodynamic probability of the macrostate equals the total number of arrangement which is

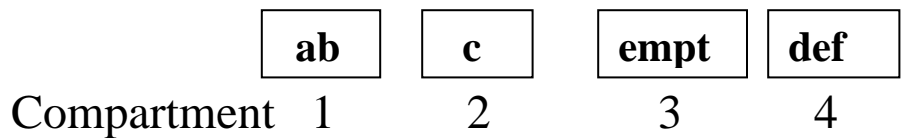$W = W_i W_j = 20 \times 4 = 80$

In M.B.S. $\longrightarrow$ W= 4

In general for n number of cells

$W = \prod W_i$ ---(1)

For deriving the thermodynamic probability in terms of $N_{i'}$ s according to B.E.S.

Suppose the compartment in the ith cell are 1,2,3------n cells and the phase points are lettered a,b,c-------N_i.

In some arrangement of the phase point in cell i.

ab	c	empt	def

Compartment   1   2   3   4

If the numbers and letters are arranged in all possible sequences each sequence will represented a microstate. There are $\underline{n}$ ways in which the sequence can being.
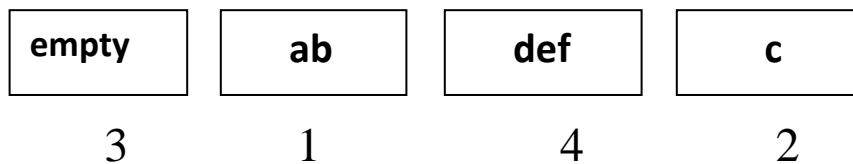
One of each of the n-compartments and in each of these the remaining $(n + N_i - 1)$.

So the number of different sequences that being with number is

$$n(n + N_i - 1)! \text{ -------------------------------------}(2)$$

Each sequence represent $\longrightarrow$ a microstate

Many sequences represents $\longrightarrow$ the same microstate

For different sequences the microstate does not change.

empty	ab	def	c
3	1	4	2

There are <u>n</u> blocks in the sequence one for each compartment so that number of different blocks is $n!$ Equation (2) can be divided on $n! \, N_i!$.

Hence the number of microstate for the ith cell is;

$$W_i = \frac{n(N_i+n-1)!}{n!N_i!} \text{ -------------------------------}(3)$$

$$n! = n(n-1)! \quad \text{then equation (3) becomes}$$

$$W_i = \frac{n(N_i+n-1)!}{n(n-1)!N_i}$$

$$W_i = \frac{(N_i+n-1)!}{(n-1)!N_i} \text{ -----------------------------}(4)$$

Where N_i represent the number of indistinguishable

particles. And n represents the number of compartments.

The total number of microstate or the thermodynamic probability;

$$W = \prod W_i = \prod \frac{(N_i+n-1)!}{(n-1)!N_i!}$$

Example 1:

Let, $n = 5$ for cell i and cell j and let $N_i = 3, \ N_j = 2$

$$W_i = \frac{(N_i+n-1)!}{(n-1)!N_i} = \frac{(3+5-1)!}{(5-1)!3!} = \frac{7!}{4!3!}$$

$$= \frac{1\times2\times3\times4\times5\times6\times7}{1\times2\times3\times4\times1\times2\times3} = 35$$

$$W_j = \frac{(2+5-1)!}{(5-1)!2!} = \frac{6!}{4!2!}$$

$$W_j = \frac{1\times2\times3\times4\times5\times6}{1\times2\times3\times4\times1\times2} = 15$$

$$W_{tot} = W_iW_j = 35 \times 15 = 525$$

Bose-Einstein Distribution Law

Bose-Einstein statistics describes the statistical behavior of bosons.

Bosons

Bosons are particle which have integer spin and which therefore are not constrained by the Pauli exclusion principle . The energy distribution of bosons is described by Bose-Einstein statistics. The wave function which describes a collection of bosons must be symmetric with respect to the exchange of identical particles. At low temperature, bosons can behave very differently than fermions because an unlimited number of them can collect into the same energy state.

Driving Bose-Einstein Distribution Law

For driving the Bose-Einstein distribution law, starting from the statistical relation of entropy.

$$S = k \ln W$$

To maximize the thermodynamic probability W with respect to the number of particles N_i having each ε_i.

It is necessary to taking logarithm on both side of equation 4

$$W = \frac{(N_i+n-1)!}{(n-1)!N_i}$$

$$\ln W = \sum \ln \frac{(N_i+n-1)!}{(n-1)!N_i!}$$

$$= \sum[\ln(N_i + n - 1)! - \ln(n - 1)! - \ln N_i!] \text{---}(5)$$

Using the Striling approximation

$$\ln x_i = x \ln x - x$$

$$\ln W = \sum \{(N_i + n - 1) \ln(N_i + n - 1) - (N_i + n - 1)$$
$$- [(n - 1) \ln(n - 1) - (n - 1)] - \{N_i \ln N_i - N_i\}$$
$$= \sum (N_i + n - 1) \ln(N_i + n - 1) - n - N_i + 1 -$$
$$(n - 1) \ln(n - 1) + n - 1 - N_i \ln N_i + N_i$$
$$= \sum [(N_i + n - 1) \ln(N_i + n - 1) -$$
$$(n - 1) \ln(n - 1) - N_i \ln N_i]----(6)$$

If we neglect 1 in comparison with n and N_i, then;

$$\ln W = \sum [(n + N_i) \ln(n + N_i) - n \ln n - N_i \ln N_i]-----(7)$$

Using the statistical condition

$$N = \sum N_i \qquad \text{Constant number of particles}$$
$$U = \sum \varepsilon_i N_i \qquad \text{Constant total internal energy}$$

For maximum thermodynamic probability

$$\partial N = \sum \partial N_i = 0$$
$$\partial U = \sum \varepsilon_i \partial N_i = 0$$
$$\frac{\partial \ln W}{\partial N_i} = 0 \qquad\qquad \text{---------------------------------(8)}$$

This condition means that the variation in $\ln W$ is zero for a small variation in N_i.

From the equilibrium distribution

1- $\quad \partial \ln W = 0 = \dfrac{\partial \ln W}{\partial N_i} \partial N_i$

Now taking the derivative of equation (7) we get;

$$\frac{\partial \ln W}{\partial N_i} \partial N_i = \sum \left[\ln \frac{N_i + n}{N_i} \partial N_i - N_i \frac{1}{N_i} \partial N_i \right] = 0$$

Then

$$\sum \ln \frac{N_i + n}{N_i} \partial N_i = 0 \text{ --------------------------(9)}$$

2- $\partial U = 0 = \frac{\partial U}{\partial N_i} \partial N_i$ Constant internal energy condition

Or $\sum \varepsilon_i \partial N_i = 0$ ------------------------------------(10)

3- $\partial N = 0 = \frac{\partial N}{\partial N_i} \partial N_i$ Particle conservation condition

Or $\sum \partial N_i = 0$ ------------------------------------(11)

We thus have three conditions to satisfy in order to establish the maximum thermodynamic probability.

If we were not bound by the constant energy and number of particles restriction, then the number of particles in each energy state N_i could be considered as independent variable. In this case we apply equation (9);

$$\ln \frac{N_i + n}{N_i} = 0 \Longrightarrow \text{ as the maximizing conditions}$$

Now multiplying equation (10) by a constant $(-\beta)$ and equation (11) by $(-\alpha)$ we obtain;

$$\sum -\beta \varepsilon_i \partial N_i = 0 \text{ ------------------------------(12)}$$

$$\sum -\alpha \partial N_i = 0 \text{ ------------------------------(13)}$$

Adding equations 9, 12 and 13 together we get;

$$\sum \left[\ln \frac{N_i + n}{N_i} \partial N_i - \beta \varepsilon_i \partial N_i - \alpha \partial N_i \right] = 0$$

$$\Sigma \left[\ln \frac{N_i + n}{N_i} - \beta \varepsilon_i - \alpha \right] \partial N_i = 0 \quad \text{-----------------(14)}$$

If the number of the particles treated as independent particles, in this case equation (14) becomes;

$$\ln \frac{N_i + n}{N_i} - \beta \varepsilon_i - \alpha = 0$$

Or $\quad \ln \dfrac{N_i + n}{N_i} = \beta \varepsilon_i + \alpha$

$$1 + \frac{n}{N_i} = e^{\beta \varepsilon_i + \alpha}$$

$$\frac{n}{N_i} = e^{\beta \varepsilon_i + \alpha} - 1$$

$$\frac{N_i}{n} = \frac{1}{e^{\beta \varepsilon_i + \alpha} - 1} = \frac{1}{e^{\alpha} e^{\beta \varepsilon_i} - 1}$$

$$\frac{N_i}{n} = \frac{1}{A e^{\beta \varepsilon_i} - 1} \qquad \text{Where } A = e^{\alpha}$$

$$N_i = \frac{n}{A e^{\beta \varepsilon_i} - 1} \quad \text{------------------------------(15)}$$

Equation (15) is the Bose-Einstein distribution law.

The M.B. distribution law is given by

$$N_i = \alpha e^{-\beta \varepsilon_i}$$

$$N_i = \frac{1}{A e^{\beta \varepsilon_i}}$$

Determination of the constant α

The evaluation of α for both Bose-Einstein and Fermi-Dirac is no simple and depends on the physical system (gas, liquid or solid).

1- To evaluate α

Let us consider a system in which the number of phase point in a cell N_i is very smaller than the number of compartment (n) i.e.
$N_i \ll n$

In this case $\quad \dfrac{N_i}{n} \ll 1$ and $\quad e^{\beta \varepsilon_i} \gg 1$

Then the Bose-Einstein function becomes,

$$\frac{N_i}{n} = \frac{1}{Ae^{\beta \varepsilon_i} - 1}$$

$$\frac{N_i}{n} = \frac{1}{Ae^{\beta \varepsilon_i}} \quad \text{Or}$$

$$\frac{N_i}{n} = \frac{1}{Ae^{\varepsilon_i / kT}} \qquad \text{where} \quad \beta = \frac{1}{kT}$$

From Maxwell-Boltzmann statistics $\quad \alpha = \dfrac{1}{A}$ then

$$N_i = n\alpha e^{-\varepsilon_i / kT} \quad \text{---(1)}$$

For determining α using the conditions

$$N = \sum N_i$$

And the volume phase space

$$H = nh^3$$

$$n = \frac{H}{h^3} = \frac{1}{h^3} dx \, dy \, dz \, dp_x \, dp_y \, dp_z$$

Or $\quad n = \dfrac{m^3}{h^3} dx \, dy \, dz \, dv_x \, dv_y \, dv_z \quad \text{----------------(2)}$

Substituting equation (2) into (1)

$$d^6 N = \frac{\alpha m^3}{h^3} e^{-\varepsilon_i/kT} dx\,dy\,dz\,dv_x\,dv_y\,dv_z$$

Integrating over all volume

$$d^3 N = \frac{\alpha m^3}{h^3} e^{-\varepsilon_i/kT} \iiint dx\,dy\,dz\,dv_x\,dv_y\,dv_z$$

Where V is the volume $= \iiint dx\,dy\,dz$

$$d^3 N = \frac{\alpha m^3 V}{h^3} e^{-\varepsilon_i/kT} dv_x\,dv_y\,dv_z \text{ -------------------(3)}$$

Let $\varepsilon_i = \frac{1}{2}mv^2$ and substituting in equation 3 we get;

$$d^3 N = \frac{\alpha m^3 V}{h^3} e^{-mv^2/2kT} dv_x\,dv_y\,dv_z \text{ ------------------(4)}$$

Integrating over all velocities v_x, v_y, v_z

Then equation (4) becomes;

$$N = \frac{\alpha m^3 V}{h^3} \iiint e^{-mv^2/2kT} dv_x\,dv_y\,dv_z$$

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

$$N = \frac{\alpha V}{h^3} (2\pi mkT)^{3/2}, \text{ then}$$

$$\alpha = \frac{N h^3}{V(2\pi mkT)^{3/2}} \text{ -------------------------------------(5)}$$

Or $\alpha = \frac{N h^3}{V} (2\pi mkT)^{-3/2}$ -------------------------------(5)

Now substituting the value of α into equation (4)

$$d^3 N = \frac{m^3 V}{h^3} \frac{N h^3}{V} (2\pi mkT)^{-3/2} e^{-mv^2/2kT} dv_x\,dv_y\,dv_z$$

$$= m^3 N (2\pi mkT)^{-3/2} \, e^{-mv^2/2kT} \, dv_x dv_y dv_z$$

$$= m^3 N \frac{1}{(2\pi mkT)^{3/2}} \, e^{-mv^2/2kT} \, dv_x dv_y dv_z$$

$$d^3 N = N \left(\frac{m}{2\pi kT}\right)^{3/2} e^{-mv^2/2kT} \, dv_x dv_y dv_z \text{ --------(6)}$$

Equation (6) represents the Maxwell-Boltzmann velocity distribution function.

The Bose-Einstein (quantum) statistics leads to the same Maxwell-Boltzmann (classical) statistics provides the assumption that $\frac{N_i}{n}$ is very less than unity is true.