

# *Classical Statistical Mechanics*

## *Maxwell-Boltzmann Statistics*

### *Lecture Four*

# Maxwell-Boltzmann Statistics:

In statistical mechanics, Maxwell–Boltzmann statistics describes the distribution of classical material particles over various energy states in thermal equilibrium. It is applicable when the temperature is high enough or the particle density is low enough to render quantum effects negligible. This is sometimes called the classical case. In statistical thermodynamics, two central quantities are Maxwell-Boltzmann statistics and its partition function.

Maxwell-Boltzmann distribution is an important relationship that finds many applications in physics and chemistry. It is a result of the kinetic theory of gases, which provides a simplified explanation of many fundamental gaseous properties including pressure and diffusion.

Maxwell-Boltzmann statistics describes the statistical distribution of particles over various energy states in thermal equilibrium, which throw a light on microstate, and Maxwell-Boltzmann statistics is valid when the temperature is high enough and density is low enough to omit quantum effects.

The importance of the traditional Maxwell-Boltzmann statistics appears in many important theoretical applications such as calculating the physical properties of an ideal gas.

The Maxwell–Boltzmann distribution applies to ideal gases close to thermodynamic equilibrium, negligible quantum effects, and non-relativistic speeds.

## **The basic postulates associated with the MB statistics are-**

•The particles of the system are *identical* and *distinguishable*.

1-The phase space can be divided into a very large number of cells.

2-There is no restriction on the number of particles which can occupy a single phase cell.

3-The available volume of the phase space cell can be very small and may even approach zero.

4-The total number of particles in the system remains constant.

5-The total energy of the system remains constant.

6- The M.B.S. describes particle speeds in gases.

7- The M.B.S. applies to ideal gas close to thermodynamic equilibrium with negligible quantum effect.

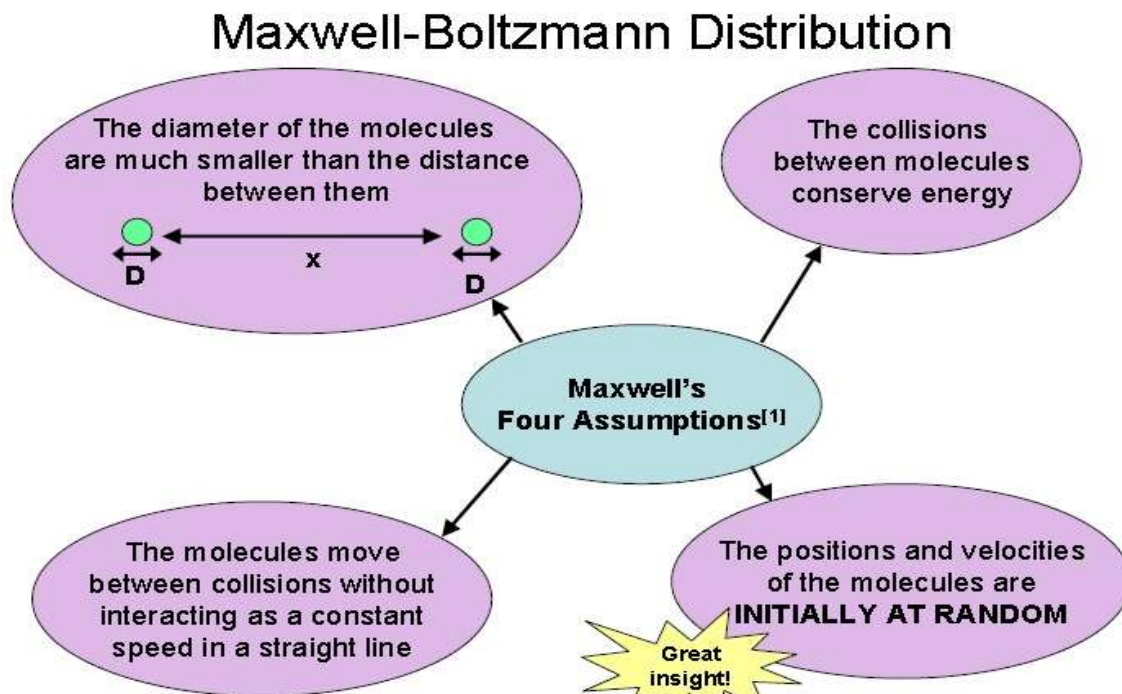
Examples; Molecular and speed distribution.

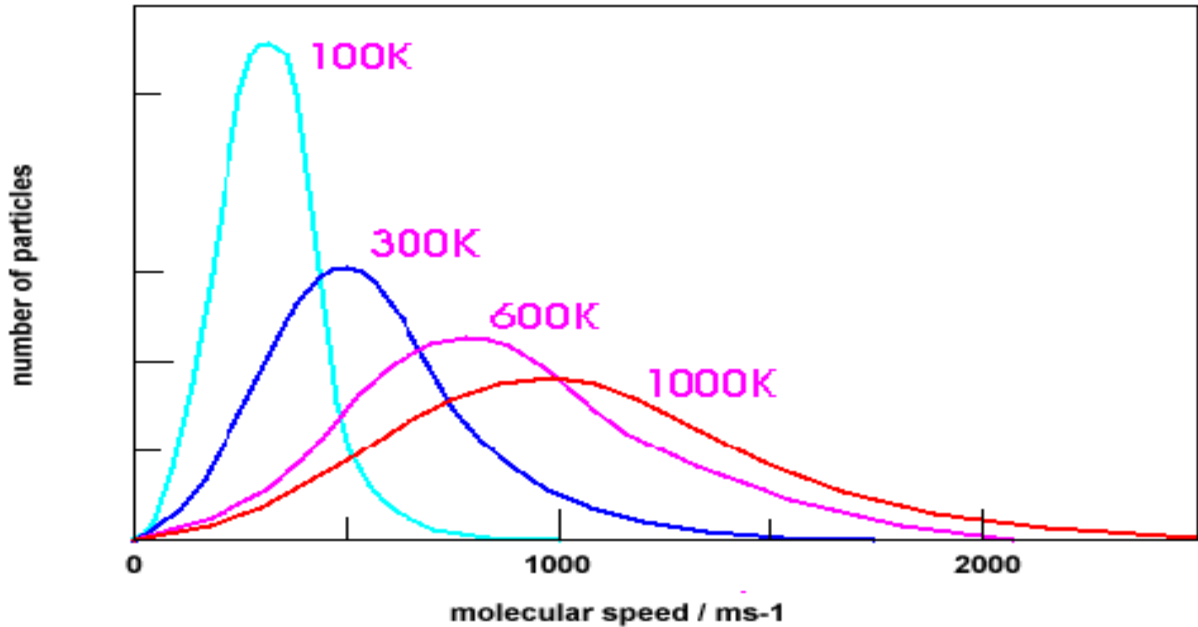
# Maxwell-Boltzmann Distribution Function

Maxwell pictured the gas to consist of billions of molecules moving rapidly at random, colliding with each other and the wall of the container.

If we accept the notion that raising the temperature causes the molecules to move faster and collide with the walls of the container more frequently.

Maxwell made four assumptions.....





The Maxwell-Boltzmann distribution is a mathematical function that speaks about how many particles are in a container have a certain energy.

The number of particles with energy  $\varepsilon_i$  is  $N_i$ . The number of particles possessing another energy  $\varepsilon_j$  is  $N_j$ . In physical speech this statement states that those many particles  $N_i$  with the same energy amount  $\varepsilon_i$ , all occupy a so called (energy level). Physically, each container corresponds to a state in which each particle can be put.

- In the classical case, there are no restriction on how many particles that can put into any one container o state.
- In the quantum state where there are restriction for some particles.

Now consider an isolated system of volume  $v$  containing  $N$  distinguishable particles. The internal energy  $U$  is then fixed the

macrostate will be characterized by (N,V,U). There are n energy levels (like boxes) available. There following restrictions:

$$\sum_{j=1}^n N_j = N \quad (\text{conservation of particles})$$

$$\sum_{j=1}^n N_j E_j = U \quad (\text{conservation of energy})$$

The central problem is then to determine the most probable distribution. The actual distribution of particles amongst the energy level will be maximize the thermodynamic probability of the system.

For finding the Maxwell-Boltzmann distribution law;

Let the thermodynamic probability of the macrostate is;

$$W = \frac{N!}{\sum N_i!} \text{-----} (1)$$

Taking logarithm of the both side of equation 1

$$\ln W = \ln \frac{N!}{\sum N_i!}$$

$$\ln W = \ln N! - \sum \ln N_i! \text{-----}(2)$$

Applying Stirling' s approximation

$$\ln x! = x \ln x - x + 1$$

For large x

$$\ln x! = x \ln x - x \text{ -----(3)}$$

Using this approximation for eqn. (2) then we get

$$\ln W = N \ln N - N - \sum N_i \ln N_i + \sum N_i$$

Where  $\sum N_i = N$

$$\therefore \ln W = N \ln N - \sum N_i \ln N_i \text{ -----(4)}$$

For maximizing thermodynamic probability W

$\partial \ln W = 0$  , then

$$\partial \ln W = - \sum N_i \partial \ln N_i - \sum \ln N_i \partial N_i = 0 \text{ ----(5)}$$

But  $\sum N_i \partial \ln N_i = \sum N_i \frac{\partial N_i}{N_i} = 0$

Since the total number of particles is constant, hence

$$\sum \ln N_i \partial N_i = 0 \text{ ----- (6)}$$

There are two physical constrains on our classical system:

1- The total number of particles must be conserved.

2- The total energy of the system must be conserved.

Constrain 1 implies  
 $\sum N_i = N \rightarrow \text{constant}$

Constrain 2 implies  
 $\sum \epsilon_i N_i = U \rightarrow \text{constant}$

$$\sum \partial N_i = \partial N = 0 \text{ -----(7)}$$

The total number of particles is constant.  
 $\sum \varepsilon_i \partial N_i = \partial U = 0$  ----- (8)

The total internal energy remains constant.

Now, multiplying eqn.(6) by a constant  $(-\ln \alpha)$  and eqn.(8) by a constant  $(\beta)$ . Then eqns. 6 and 8 can be written as;

$$\sum \ln N_i \partial N_i \times (-\ln \alpha) = 0$$

$$\sum (\ln N_i - \ln \alpha) \partial N_i = 0$$
 ----- (9)

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

Adding eqn. (9) and (10) to each other we get;

$$\sum (\ln N_i - \ln \alpha) \partial N_i + \sum \beta \varepsilon_i \partial N_i = 0$$

$$\sum (\ln N_i - \ln \alpha + \beta \varepsilon_i) \partial N_i = 0$$

$$\ln N_i - \ln \alpha + \beta \varepsilon_i = 0$$

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

$$N_i = \alpha e^{-\beta \varepsilon_i}$$
 ----- (11)

Let  $A = \frac{1}{\alpha}$  then eqn. 11 becomes

$$N_i = \frac{1}{A e^{\beta \varepsilon_i}}$$
 ----- (12)



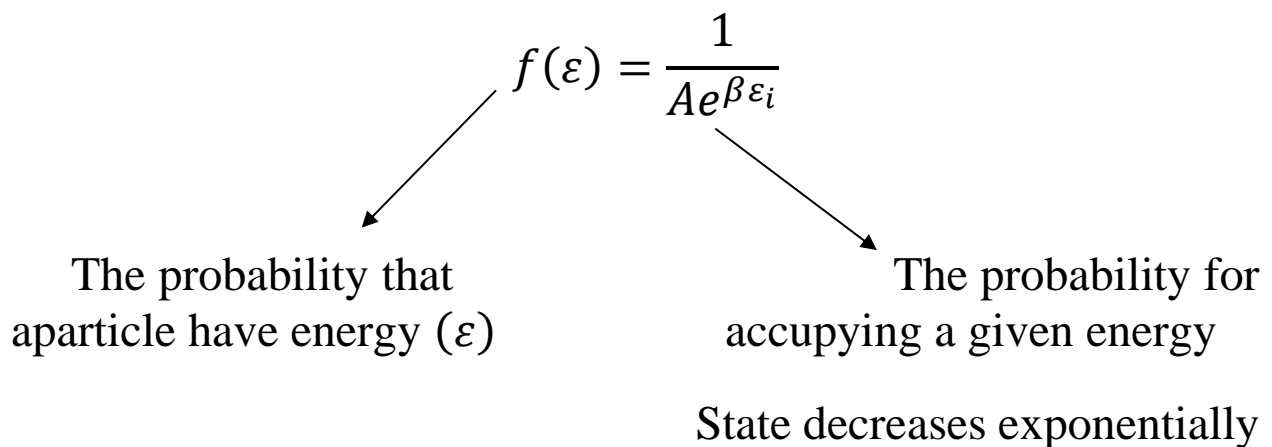
Eqn. (11) or (12) is known as Maxwell-Boltzmann distribution law , or Energy distribution function.

Boltzmann showed that the statistical factor  $e^{\beta \epsilon_i}$  is a characteristic of any classical system in equilibrium (in agreement with maxwell's speed distribution).

## Energy Distribution Function

The distribution function  $f(\epsilon)$  is the probability that a particle is in energy state  $E$ .

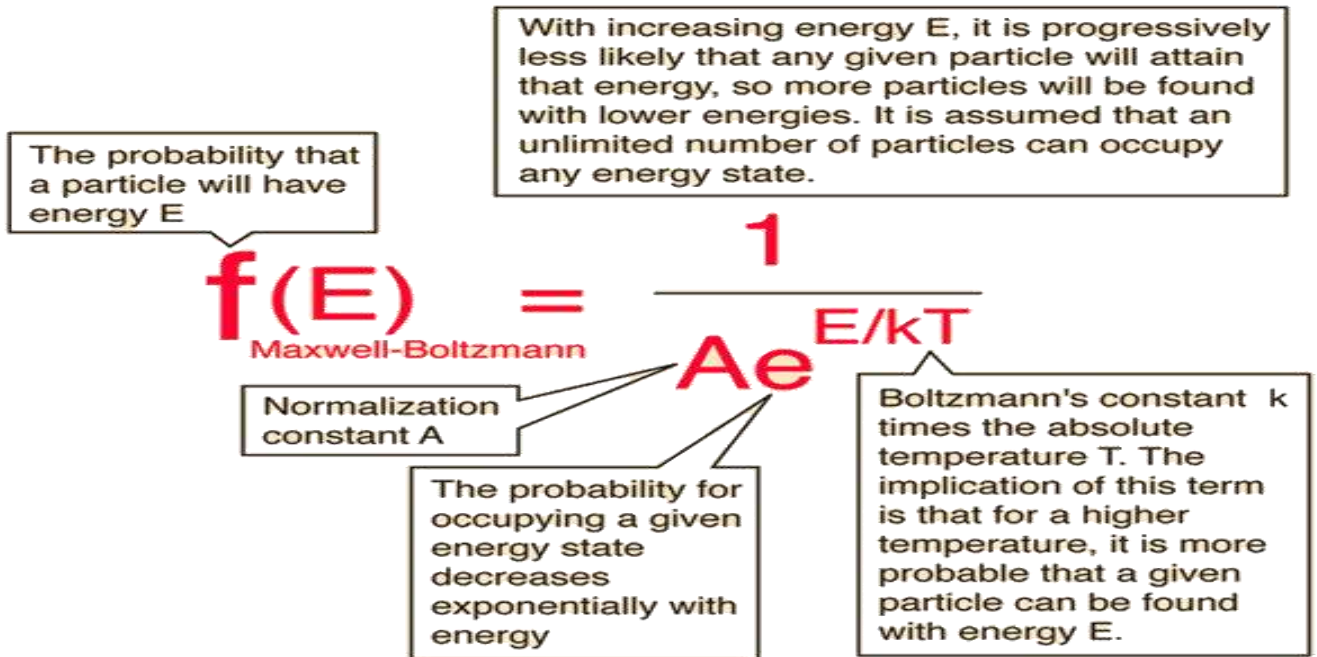
The Maxwell-Boltzmann distribution is the classical distribution function of an amount of energy between identical but distinguishable particles.



$A$  —————> Normalization constant state

An expression for  $\alpha$  can be obtained from the requirement that all the sum of all  $N_i$ 's must be equal to the total number of particles  $N$ .

$$\sum N_i = N = \alpha \sum e^{-\beta \epsilon_i} \text{----- (13)}$$



## Partition Function

In physics, a partition function describes the statistical properties of a system in thermodynamic equilibrium. They are functions of temperature and other parameters, such as the volume enclosing a gas. Most of the aggregate thermodynamic variables of the system, such as the total energy, free energy, entropy, and pressure, can be expressed in terms of the partition function or its derivatives.

The sum over states is called the *Partition function*.





and from equation (4) as derived  
 $\ln W = \ln N! - \sum \ln N_i! = N \ln N - \sum N_i \ln N_i$

From the definition of entropy in statistical mechanics.

$$S = k \ln W \text{ -----(18)}$$

Substituting eqn.(4) in to eqn. (18)

$$S = k \ln W = k[N \ln N - \sum N_i \ln N_i] \text{ --- (19)}$$

Using Maxwell-Boltzmann distribution law in eqn.(19) we get;

$$N_i = \frac{N}{Z} e^{-\beta \epsilon_i}$$

$$S = k \left[ N \ln N - \sum N_i \ln \frac{N}{Z} e^{-\beta \epsilon_i} \right]$$

$$S = k[N \ln N - \sum N_i (\ln N - \ln Z - \beta \epsilon_i)] \text{ --- (20)}$$

But,  $\sum N_i = N$  and  $\sum N_i \epsilon_i = U$

Therefore eqn.(20) becomes;

$$S = k[N \ln N - N \ln N + \sum N_i \ln Z + \beta U]$$

$$S = k[\sum N_i \ln Z + \beta U]$$

$$S = k[N \ln Z + \beta U]$$

Then the statistical definition of entropy is

$$S = Nk \ln Z + k\beta U \text{ -----(21)}$$

## Definition of $\beta$

$$S = Nk \ln Z + k\beta U \text{ -----(21)}$$

Taking the derivation of eqn.(21) with respect to the internal energy;

$$\left(\frac{\partial S}{\partial U}\right)_V = \frac{Nk}{Z} \left(\frac{\partial Z}{\partial U}\right)_V + k\beta + kU \left(\frac{\partial \beta}{\partial U}\right)_V \text{ ----(22)}$$

Let

$$\left(\frac{\partial Z}{\partial U}\right)_V = \left(\frac{\partial Z}{\partial \beta}\right)_V \left(\frac{\partial \beta}{\partial U}\right)_V \text{ -----(23)}$$

Now from the definition of partition function

$$Z = \sum e^{-\beta \epsilon_i} \Rightarrow \left(\frac{\partial Z}{\partial \beta}\right)_V = - \sum \epsilon_i e^{-\beta \epsilon_i} \text{ ----(24)}$$

And  $U = \sum N_i \epsilon_i = \frac{N}{Z} \sum \epsilon_i e^{-\beta \epsilon_i}$

Then  $\sum \epsilon_i e^{-\beta \epsilon_i} = \frac{ZU}{N} \text{ -----(25)}$

Substituting eqn. (25) in to eqn. (24) we get;

$$\left(\frac{\partial Z}{\partial \beta}\right)_V = - \frac{ZU}{N} \text{ -----(26)}$$

And eqn.(23) can be written as

$$\left(\frac{\partial Z}{\partial U}\right)_V = - \frac{ZU}{N} \left(\frac{\partial \beta}{\partial U}\right)_V \text{ -----(27)}$$

Substituting eqn.(27) in to eqn.(22)

$$\left(\frac{\partial S}{\partial U}\right)_V = \frac{Nk}{Z} \left[ -\frac{ZU}{N} \left(\frac{\partial \beta}{\partial U}\right)_V \right] + k\beta + kU \left(\frac{\partial \beta}{\partial U}\right)_V$$

$$\left(\frac{\partial S}{\partial U}\right)_V = -kU \left(\frac{\partial \beta}{\partial U}\right)_V + k\beta + kU \left(\frac{\partial \beta}{\partial U}\right)_V$$

$$\left(\frac{\partial S}{\partial U}\right)_V = k\beta \text{ -----(28)}$$

From the principle of thermodynamics

$$\left(\frac{\partial U}{\partial S}\right)_V = T \quad \text{or} \quad \left(\frac{\partial S}{\partial U}\right)_V = \frac{1}{T}$$

Eqn. (28) becomes

$$\frac{1}{T} = k\beta$$

Then

$$\beta = \frac{1}{kT} \text{ -----(29)}$$

## Internal Energy

The internal energy of the system is defined as;

$$U = \sum \varepsilon_i N_i$$

And the Maxwell-Boltzmann distribution law is given by;

$$N_i = \frac{N}{Z} e^{-\beta \varepsilon_i} = \frac{N}{Z} e^{-\frac{\varepsilon_i}{kT}}$$

The partition function is defined by;

$$Z = \sum e^{-\beta \epsilon_i} = \sum e^{-\frac{\epsilon_i}{kT}}$$

Where  $e^{-\frac{\epsilon_i}{kT}} \longrightarrow$  is called the Boltzmann coefficient.

Now the internal energy can be written as;

$$U = \sum \epsilon_i \frac{N}{Z} e^{-\frac{\epsilon_i}{kT}} = \frac{N}{Z} \sum \epsilon_i e^{-\frac{\epsilon_i}{kT}} \text{-----(30)}$$

Return to the definition of the partition function

$$Z = \sum e^{-\frac{\epsilon_i}{kT}}$$

$$\frac{\partial Z}{\partial T} = \frac{1}{kT^2} \sum \epsilon_i e^{-\frac{\epsilon_i}{kT}}$$

$$\sum \epsilon_i e^{-\frac{\epsilon_i}{kT}} = kT^2 \frac{\partial Z}{\partial T} \text{-----(31)}$$

substituting eqn.(31) in to eqn.(30) we obtains


$$U = \frac{N}{Z} kT^2 \frac{\partial Z}{\partial T}$$

$$U = NkT^2 \frac{\partial \ln Z}{\partial T} \text{-----(32)}$$



# Helmholtz Function

The thermodynamic function of a system that is equal to its internal energy minus the product of its absolute temperature and entropy: a decrease in the function is equal to the maximum amount of work available during a reversible isothermal process.



## Helmholtz Free Energy

The Helmholtz free energy is a thermodynamic potential that measures the “useful” work obtainable from a closed thermodynamic system at a constant temperature and volume.

The Helmholtz energy is defined as:  $A = U - TS$   
where  
 $A$  is the Helmholtz free energy (SI: joules, CGS: ergs),  
 $U$  is the internal energy of the system (SI: joules, CGS: ergs),  
 $T$  is the absolute temperature (Kelvins),  
 $S$  is the entropy (SI: joules per Kelvin, CGS: ergs per kelvin).

The Helmholtz function is defined thermodynamically as;

$$A = U - TS \text{ -----(33)}$$

Using eqn.(21)

$$S = Nk \ln Z + k\beta U \text{ -----(21)}$$

Eqn. (21) can be written in the form

$$S = Nk \ln Z + \frac{U}{T} \text{-----(34)}$$

Substituting eqn.(34) in to eqn.(33) then the Helmholtz function can be written as;

$$A = U - T \left( Nk \ln Z - \frac{U}{T} \right)$$

$$A = U - NkT \ln Z - U$$

Then the Helmholtz function can be written statistically as;

$$A = -NkT \ln Z \text{-----(35)}$$

## Pressure

The TdS equation in thermodynamic is defined by

$$TdS = dU + pdV$$

$$T \frac{dS}{dV} = \frac{dU}{dV} + p$$

Then,

$$p = T \frac{dS}{dV} - \frac{dU}{dV} = - \frac{dU}{dV} + T \frac{dS}{dV}$$

$$p = - \frac{d}{dV} (U - TS) \text{-----(36)}$$

Substituting eqn.(35) in to eqn.(36)

$$p = - \frac{d}{dV} (-NkT \ln Z)$$

$$p = \left( \frac{dA}{dV} \right)_T \text{-----}(37)$$

Or

$$p = NkT \left( \frac{\partial \ln Z}{\partial V} \right)_T \text{-----}(38)$$

Eqns.(37) and (38) is the statistical approaches of the pressure.

### Examples:

A system consisting of 4000 particles distributed over three energy levels:  $\epsilon_1=0$ ,  $\epsilon_2= \epsilon$ ,  $\epsilon_3=2 \epsilon$  where  $\epsilon$  is constant and has units of energy  $\epsilon$ .

- a- Find the most likely number of particles in each state of the distribution, given that the total energy of the system is  $2300 \epsilon$
- b- Calculate the ratio between the two probabilities if we take two particles out of level 2 and one of them is vacant in level 1 and the second in level 3.

Sol.

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

$$N_1 = \alpha e^{-\beta 0} \quad N_2 = \alpha e^{-\beta \epsilon} \quad N_3 = \alpha e^{-\beta 2\epsilon}$$

If  $e^{-\beta \epsilon} = X$  then

$$N_1 = \alpha e^{-\beta 0} = \alpha \quad N_2 = N_1 X \quad N_3 = N_1 X^2$$

Total Number of particles

$$N_1 + N_2 + N_3 = 4000 \quad \text{then} \quad N_1 + N_1X + N_1X^2 = 4000$$

$$(1 + X + X^2) N_1 = 4000 \quad \text{.....a}$$

And the total energy is equal to 2300  $\epsilon$

$$N_1\epsilon_1 + N_2\epsilon_2 + N_3\epsilon_3 = 2300 \epsilon$$

$$N_1 \cdot 0 + N_2\epsilon + N_3 2\epsilon = 2300 \epsilon$$

$$0 + N_2\epsilon + N_3 2\epsilon = 2300 \epsilon$$

$$N_1X \epsilon + N_1X^2 \epsilon = 2300 \epsilon$$

$$\epsilon (N_1X + 2 N_1X^2) = 2300 \epsilon$$

Delet  $\epsilon$  then  $N_1X + 2N_1X^2 = 2300$

$$N_1(X + 2X^2) = 2300 \quad \text{.....b}$$

Delet  $N_1$  from each equ. a and b then

$$57X^2 + 17X - 23 = 0$$

$$X = \cancel{-0.802} \quad \text{or} \quad X = 0.5034 \quad \text{from equ. B}$$

$$N_1 = \frac{2300}{X+2X^2} = \frac{2300}{0.5034+2(0.5034)^2} = 2277$$

$$N_2 = 2277 \times (0.5034) = 1146$$

$$N_3 = N_1X^2 = 2277 \times (0.5034)^2 = 577$$

The thermodynamic probability is

$$W_1 = \frac{4000!}{2277!1146!577!}$$

$$b. W_2 = \frac{4000!}{2278!1144!578!}$$

$$\frac{W_2}{W_1} = \frac{4000!}{2278!1144!578!} \times \frac{2277!1146!577!}{4000!}$$

$$\frac{W_2}{W_1} = 0.9966$$

## Examples:

Suppose a system of  $N$  particles a phase space of  $n$  cells. suppose that all particles have the same energy. Calculate;

- 1- The partition function
- 2-  $N_i$  <sup>th</sup> particle.
- 3- The internal energy.
- 4- Entropy.

## Solution

### 1-The partition function

$$Z = \sum_{i=1}^n e^{-\frac{\epsilon_i}{kT}} = n e^{-\frac{\epsilon}{kT}}$$

### 2- $N_i$ <sup>th</sup> particle.

$$N_i = \frac{N}{Z} e^{-\frac{\epsilon}{kT}} = \frac{N}{n e^{-\frac{\epsilon}{kT}}} e^{-\frac{\epsilon}{kT}} \longrightarrow N_i = \frac{N}{n}$$

### 3- The internal energy.

$$U = NkT^2 \frac{\partial \ln Z}{\partial T}$$

$$\begin{aligned}
&= NkT^2 \frac{\partial \ln\left(ne^{-\frac{\epsilon}{kT}}\right)}{\partial T} \\
&= NkT^2 \frac{\partial\left(\ln n - \frac{\epsilon}{kT}\right)}{\partial T} \\
&= NkT^2 \frac{\partial}{\partial T} \left(-\frac{\epsilon}{kT}\right) \\
U &= NkT^2 \frac{\epsilon}{kT^2} = N\epsilon
\end{aligned}$$

This means that all particles have the same energy

#### 4- Entropy.

$$\begin{aligned}
S &= Nk \ln Z + \frac{U}{T} \\
&= Nk \ln\left(ne^{-\frac{\epsilon}{kT}}\right) + \frac{U}{T} \\
&= Nk \left(\ln n - \frac{\epsilon}{kT}\right) + \frac{U}{T} \\
&= Nk \ln n - Nk \frac{\epsilon}{kT} + \frac{U}{T} = Nk \ln n - \frac{N\epsilon}{T} + \frac{U}{T}
\end{aligned}$$

$$S = Nk \ln n$$

The internal energy and entropy of all particles are constant and independent on the temperature.

