

# STATISTICAL THERMODYNAMICS

## Part - B

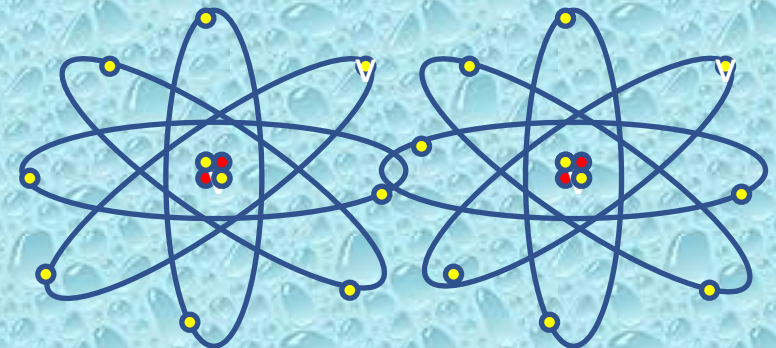
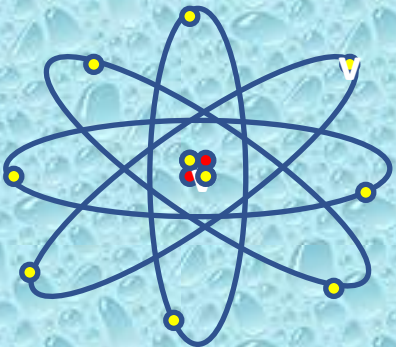
### Lecture – 3: Quantum Statistics

(M.Sc. Sem –II/ Chemistry, Paper -III, Unit – II)

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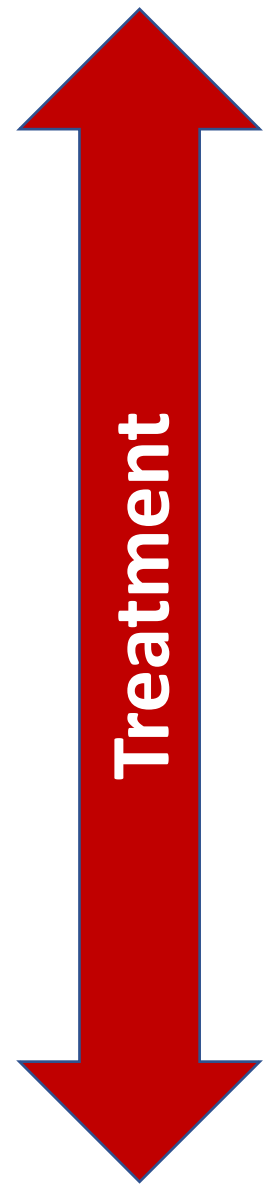
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# Contents:

- **Recapitulation: Maxwell – Boltzmann Distribution Law**
- **Limitations of Maxwell – Boltzmann Statistics**
- **Bose – Einstein Statistics**
- **Fermi – Dirac Statistics**
- **Comparison of the three Statistics**



STATISTICAL THERMODYNAMICS



Bulk / Macroscopic System



**Nature** of microscopic constituents  
& **Occupancy** of the energy level



Different Statistics

# PARTICLE STATISTICS

## CLASSICAL STATISTICS

Internal structure ignored  
**Particles distinguishable**

**MAXWELL –  
BOLTZMANN  
STATISTICS**

## QUANTUM STATISTICS

Internal structure  
considered

**Particles  
indistinguishable**

**BOSE –  
EINSTEIN  
STATISTICS**

**FERMI –DIRAC  
STATISTICS**

←  
No restriction  
on occupancy  
→

↓  
Integral Spin

↓  
Restriction  
on  
occupancy

↓  
Half Integral Spin

# MAXWELL – BOLTZMANN DISTRIBUTION : Classical Statistics

- Bulk/ macroscopic system with the following conditions:
  - Consist of **N distinguishable particles** with **total energy E** at **temperature T**
  - **No interaction** between particles
  - **No restriction** on **Occupancy** of energy levels
  - Total number of particles **N** and energy **E must remain constant**  
 $\sum N_i = N$  and  $\sum N_i \epsilon_i = E$  ;  $\sum \delta N_i = 0$  and  $\sum \epsilon_i \delta N_i = 0$
  - Such particles are called **Boltzmannons** or **Maxwellons** e.g. **System composed of gas**
  - No. of ways of achieving :

$$W = \frac{N!}{N_0! N_1! N_2! \dots}$$

- Maxwell- Boltzmann Distribution Law:

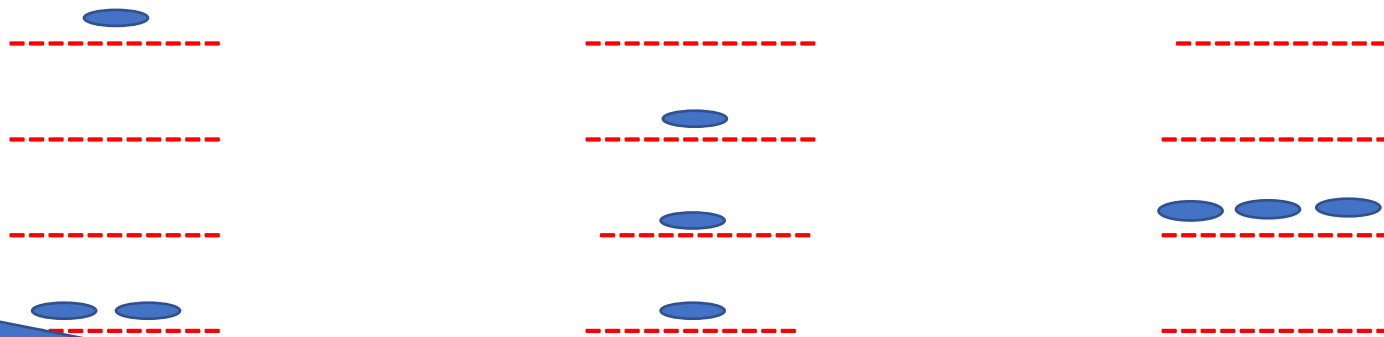
$$N_i = g_i e^{-\alpha} e^{-\epsilon_i/kT}$$

## Limitations of Maxwell – Boltzmann Distribution law

- Maxwell- Boltzmann statistics is based on Classical Mechanics: **Classical Statistics**, so is valid only within classical limit
- **Not valid** at **very low temperature** and **very high particle density**, where quantum effects become significant
- Satisfactorily explains **pressure, temperature**, etc. of gaseous systems
- But can we distinguish between gas molecules? In the light of Quantum theory, this leads to that this law is only an approximation & is valid for **gases at comparatively low density**
- Couldn't explain some experimental results like black body radiation distribution, specific heat at low temperature, etc.
- In case of **photon gas**, according to M-B distribution there is continuous no. of photons per unit range of frequency as it increases which is contradicted by Planck's law
- **The molar heat capacity of a metal** is  $3R$  but according to M-B Statistics free electron contributes  $3R/2$

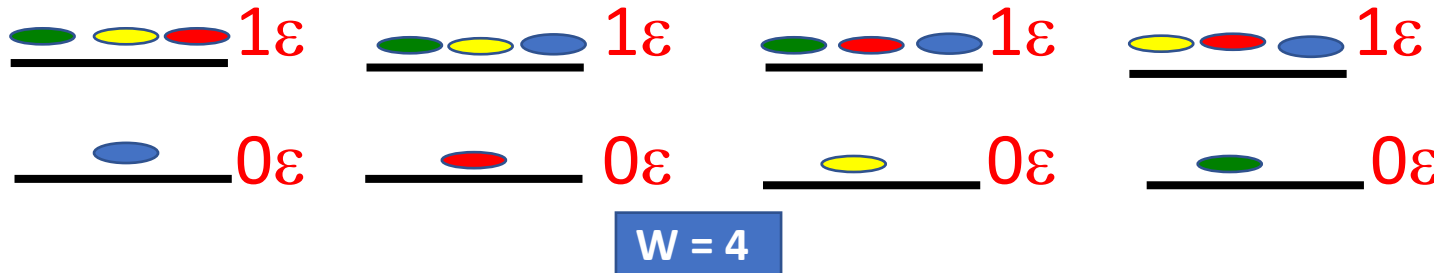
# BOSE - EINSTEIN STATISTICS : DERIVATION

- Suppose we have a bulk/ macroscopic system with the following conditions:
  - Consist of **N indistinguishable particles** with **total energy E** at **temperature T**
  - Total number of particles and energy must remain conserved
  - **No restriction** on **Occupancy** of energy states
  - **Internal structure** taken into consideration
  - Particle have zero or integral spin eg. Photon, mesons,  $^4\text{He}$ ,  $^2\text{H}$ , .....
  - The wave function is symmetric
  - Such particles are called **Bosons**

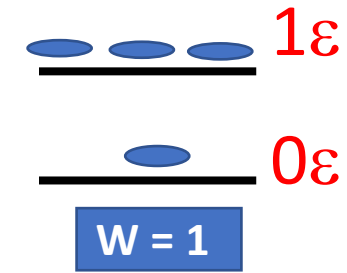


- Consider four particles distributed in two energy levels in such a way that there are
- 3** particles in  $1\varepsilon$  and **1** particle in  $0\varepsilon$  then no. of microstates according to

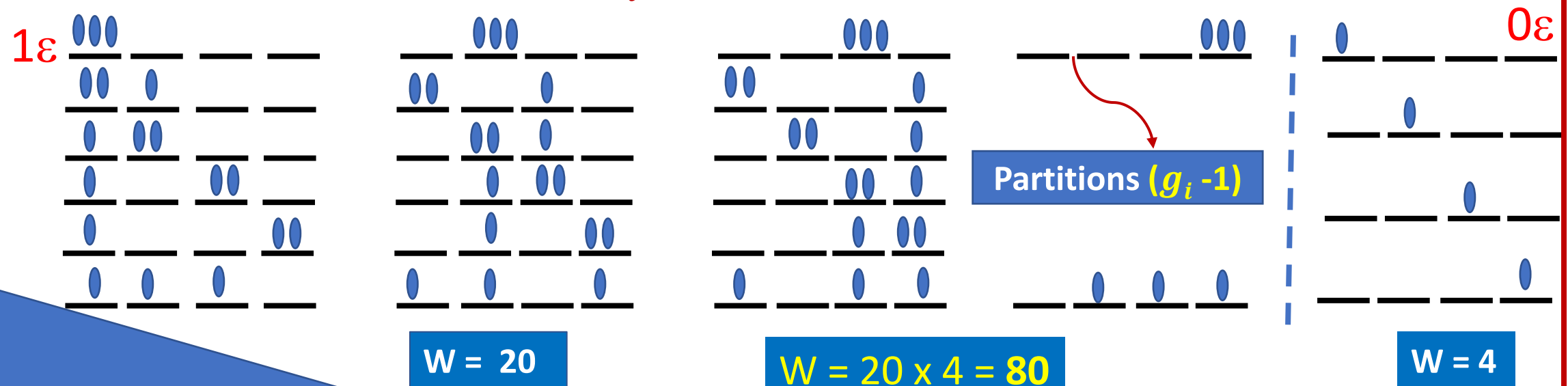
### Maxwell- Boltzmann Statistics



### Bose –Einstein Statistics



- Now if each energy levels have  $g_i = 4$  energy states, then no. of microstates will be





# Derivation of Bose – Einstein Distribution

- Most Probable Distribution ???
  - The one with maximum no. of microstates or gives Maximum Thermodynamic Probability
  - $W_{\max} : \delta W(N) = 0$  or  $\delta \ln W(N) = 0$
- Consider the distribution of  $N$  identical and indistinguishable particles among various energy levels -  $\epsilon_0, \epsilon_1, \epsilon_2, \dots$  having  $g_0, g_1, g_2, \dots$  energy states with Total energy  $E$  at temperature  $T$
- Total number of particles  $N$  and Total energy  $E$  remains constant

$$\sum N_i = N \text{ and } \sum N_i \epsilon_i = E$$

$$\sum \delta N_i = 0 \text{ and } \sum \epsilon_i \delta N_i = 0$$

- $N_0$  particles are present in  $\epsilon_0$  energy level with  $g_0$  energy states,  $N_1$  in  $\epsilon_1$  energy level with  $g_1$  energy states,  $N_2$  in  $\epsilon_2$  energy level with  $g_2$  energy states,  $N_i$  in  $\epsilon_i$  energy level with  $g_i$  energy states, ..... with no restriction

# Derivation of Bose – Einstein Distribution

- Suppose there are  $N_i$  particles are present in  $\epsilon_i$  energy level
- The energy level  $\epsilon_i$  is considered to be degenerate, in which there are  $g_i$  energy states
- $(g_i - 1)$  partitions are required to place the  $N_i$  particles in  $g_i$  energy states
- **No restriction** on no. of particles occupying each energy state
- Permutations of  $N_i$  particles and  $(g_i - 1)$  partitions simultaneously is given by  
 $(N_i + g_i - 1)!$
- Particles are **identical and indistinguishable**
- Permutations of  $N_i$  particles amongst themselves and  $(g_i - 1)$  partitions amongst themselves has to be included
- Actual no. in which  $N_i$  particles may be allocated in  $g_i$  states will be given by

$$\frac{(N_i + g_i - 1)!}{N_i! (g_i - 1)!}$$

## Example

The **Thermodynamic Probability** will be given by:

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

$$\bullet W = \frac{(N_i + g_i - 1)!}{N_i! (g_i - 1)!} = \frac{(3 + 4 - 1)!}{3! (4 - 1)!} = \frac{6!}{3! (3)!} = \frac{\cancel{6} \times \cancel{5} \times 4 \times \cancel{3} \times \cancel{2} \times \cancel{1}}{\cancel{3} \times \cancel{2} \times \cancel{1} (\cancel{3} \times \cancel{2} \times \cancel{1})} = 20$$

$$\bullet W = \frac{(N_i + g_i - 1)!}{N_i! (g_i - 1)!} = \frac{(1 + 4 - 1)!}{1! (4 - 1)!} = \frac{4!}{1! (3)!} = \frac{4 \times \cancel{3} \times \cancel{2} \times \cancel{1}}{1 (\cancel{3} \times \cancel{2} \times \cancel{1})} = 4$$

$$\bullet W = \prod \frac{(N_i + g_i - 1)!}{N_i! (g_i - 1)!} = 20 \times 4 = 80$$

# Derivation of Bose – Einstein Statistics

- The Thermodynamic Probability is given by:

$$W = \prod \frac{(N_i + g_i - 1)!}{N_i! (g_i - 1)!} \dots\dots\dots (1)$$

- Taking **logarithm**, we get

$$\ln W = \Sigma \{ \ln(N_i + g_i - 1)! - [\ln(N_i!) + \ln(g_i - 1)!] \} \dots\dots\dots (2)$$

- Neglecting **Unity** as compared to  $g_i$

$$\ln W = \Sigma \{ \ln(N_i + g_i)! - [\ln(N_i!) + \ln(g_i)!] \} \dots\dots\dots (3)$$

- Applying **STIRLING'S Approximation**:  $\ln(N_i!) = N_i \ln N_i - N_i$ , we get

$$\begin{aligned} \ln W &= \Sigma \{ [(N_i + g_i) \ln(g_i + N_i) - (N_i + g_i)] - [N_i \ln N_i - N_i + g_i \ln g_i - g_i] \} \\ &= \Sigma \{ (N_i + g_i) \ln(g_i + N_i) - \cancel{N_i} - \cancel{g_i} - N_i \ln N_i + \cancel{N_i} - g_i \ln g_i + \cancel{g_i} \} \\ &= \Sigma \{ N_i \ln(g_i + N_i) + g_i \ln(g_i + N_i) - N_i \ln N_i - g_i \ln g_i \} \end{aligned}$$

$$\ln W = \Sigma \left\{ N_i \ln \left( \frac{g_i + N_i}{N_i} \right) + g_i \ln \left( \frac{g_i + N_i}{g_i} \right) \right\}$$

$$\ln W = \Sigma \left\{ N_i \ln \left( 1 + \frac{g_i}{N_i} \right) + g_i \ln \left( 1 + \frac{N_i}{g_i} \right) \right\} \dots\dots\dots (4)$$

$$\ln \mathbf{W} = \Sigma \left\{ N_i \ln \left( 1 + \frac{g_i}{N_i} \right) + g_i \ln \left( 1 + \frac{N_i}{g_i} \right) \right\} \dots\dots\dots (4) \quad \text{[where } \delta \ln x_i = \frac{1}{x_i} \delta x_i \text{]}$$

- On differentiating, we get

$$\begin{aligned} \delta \ln \mathbf{W} &= \Sigma \left\{ \ln \left( 1 + \frac{g_i}{N_i} \right) \delta N_i + N_i \delta \ln \left( 1 + \frac{g_i}{N_i} \right) + \ln \left( 1 + \frac{N_i}{g_i} \right) \delta g_i + g_i \delta \ln \left( 1 + \frac{N_i}{g_i} \right) \right\} \\ &= \Sigma \left\{ \ln \left( 1 + \frac{g_i}{N_i} \right) \delta N_i + N_i \frac{N_i}{g_i + N_i} \delta \left( \frac{g_i + N_i}{N_i} \right) + \ln \left( 1 + \frac{N_i}{g_i} \right) \delta g_i + g_i \frac{g_i}{g_i + N_i} \delta \left( \frac{g_i + N_i}{g_i} \right) \right\} \\ &= \Sigma \left\{ \ln \left( 1 + \frac{g_i}{N_i} \right) \delta N_i + \cancel{N_i} \frac{\cancel{N_i}}{g_i + N_i} \left( -\frac{g_i}{N_i^2} \right) \delta N_i + \cancel{g_i} \frac{1}{\cancel{g_i}} \frac{g_i}{g_i + N_i} \delta N_i \right\} \text{ [where } \delta g_i = 0 \text{]} \\ &= \Sigma \left\{ \ln \left( 1 + \frac{g_i}{N_i} \right) \delta N_i \right\} \dots\dots\dots (5) \end{aligned}$$

- Most Probable Distribution of particles

- The one for which  $\mathbf{W}$  is maximum ( $\mathbf{W}_{\max}$ )
- Condition for maxima:  $\delta \mathbf{W} = \delta \ln \mathbf{W} = 0$  \dots\dots\dots (6)

- Putting the condition of **eqn. 6**

$$\delta \ln \mathbf{W} = \Sigma \left\{ \ln \left( 1 + \frac{g_i}{N_i} \right) \delta N_i \right\} = 0 \quad \dots\dots\dots (7)$$

- Distribution must satisfy the condition:  $N$  &  $E$  must remain constant,
  - $\delta N$  &  $\delta E$  must be equal to zero

$$\delta N = \sum \delta N_i = 0 \quad \dots\dots\dots (8)$$

$$\delta E = \sum \epsilon_i \delta N_i = 0 \quad \dots\dots\dots (9)$$

- Using **Lagrange's Method of Undetermined Multipliers**
  - multiplying **eqn. 8** by  $(\alpha)$  and **eqn. 9** by  $(\beta)$

$$\alpha \delta N = \sum \alpha \delta N_i = 0 \quad \dots\dots\dots (10)$$

$$\beta \delta E = \sum \beta \epsilon_i \delta N_i = 0 \quad \dots\dots\dots (11)$$

$$\sum \ln \left( 1 + \frac{g_i}{N_i} \right) \delta N_i = 0 \quad \dots\dots\dots (7)$$

- adding **eqn.10 & 11** and subtracting **eqn. 7**, we get

$$\sum [\alpha + \beta \epsilon_i - \ln \left( 1 + \frac{g_i}{N_i} \right)] \delta N_i = 0 \quad \dots\dots\dots (12)$$

- $\delta N_0, \delta N_1, \delta N_2, \delta N_3, \dots, \delta N_i$  are independent of each other, so each term in summation must be zero  
 $\delta N_i \neq 0$

$$\alpha + \beta \epsilon_i - \ln \left( 1 + \frac{g_i}{N_i} \right) = 0 \quad \dots\dots\dots (13)$$

$$\ln \left( 1 + \frac{g_i}{N_i} \right) = (\alpha + \beta \epsilon_i) \quad \dots\dots\dots (14)$$

- Removing logarithm from **eqn. 14**

$$\ln \left( 1 + \frac{g_i}{N_i} \right) = (\alpha + \beta \epsilon_i) \dots\dots\dots (14)$$

$$\left( 1 + \frac{g_i}{N_i} \right) = e^{(\alpha + \beta \epsilon_i)} \dots\dots\dots (15)$$

$$\frac{g_i}{N_i} = e^{(\alpha + \beta \epsilon_i)} - 1 \quad \text{where } \beta = 1/kT \quad [k = \text{Boltzmann constant}]$$

$$\frac{N_i}{g_i} = \frac{1}{e^{(\alpha + \beta \epsilon_i)} - 1} \dots\dots\dots (16)$$

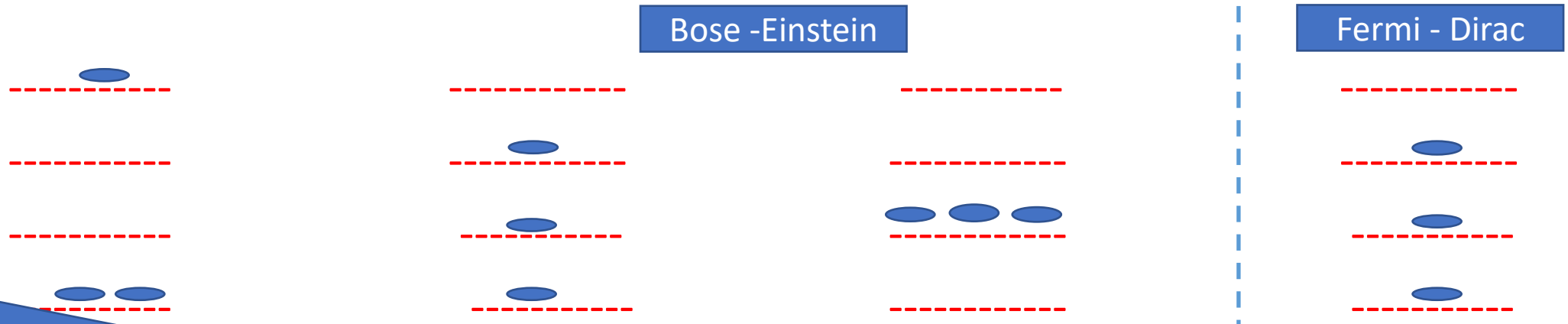
$$N_i = \frac{g_i}{e^{(\alpha + \beta \epsilon_i)} - 1} \dots\dots\dots (17)$$

**This equation gives Bose – Einstein Distribution**

- Application:** Putting  $e^\alpha = 1$  we can derive Planck's Radiation Law

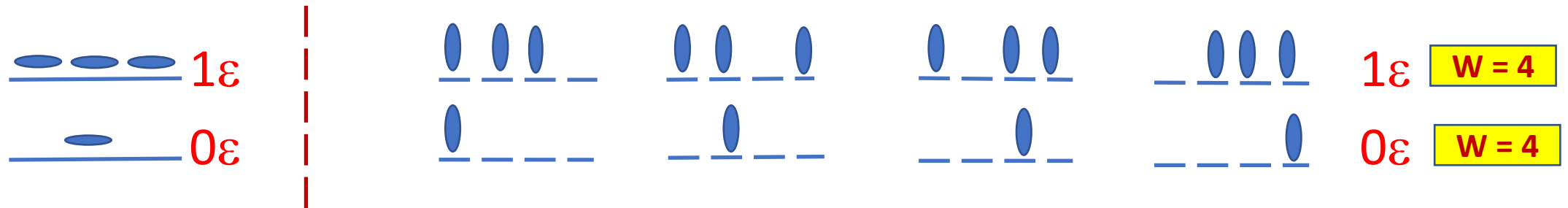
# FERMI - DIRAC STATISTICS - DERIVATION

- Suppose we have a bulk/ macroscopic system with the following conditions:
  - Consist of **N indistinguishable particles** with **total energy E** at **temperature T**
  - Total number of particles and energy must remain conserved
  - **Restriction on Occupancy** of energy states i.e., **Not more than one particle**
  - **Internal structure** taken into consideration
  - Particle have half integral spin e.g. Electron, proton, .....
  - The wave function is antisymmetric
  - Such particles are called **Fermions**





- Consider **4** particles distributed in **2** energy levels in such a way that there are **3** particles in  $1\varepsilon$  and **1** particle in  $0\varepsilon$
- Now if each energy level has **4** energy states, and with restriction that **only 1** particle occupy each energy state, then no. of microstates will be:



- Fermi-Dirac Statistics:  $W = 4 \times 4 = 16$  (Pauli's Exclusion Principle)
- Bose – Einstein Statistics:  $W = 20 \times 4 = 80$  (No restriction)

# Derivation of Fermi – Dirac Distribution

- Most Probable Distribution ???
  - The one with maximum no. of microstates - gives Maximum Thermodynamic Probability ( $W_{\max}$ )
  - $\delta W(N) = 0$  or  $\delta \ln W(N) = 0$
- Consider the distribution of  $N$  identical and indistinguishable particles among various energy levels -  $\epsilon_0, \epsilon_1, \epsilon_2, \dots$  having  $g_0, g_1, g_2, \dots$  energy states with Total energy  $E$  at temperature  $T$ , with not more than one particle in each energy state (Pauli's Exclusion Principle)
- Total number of particles  $N$  and Total energy  $E$  remains constant

$$\sum N_i = N \text{ and } \sum N_i \epsilon_i = E$$

$$\sum \delta N_i = 0 \text{ and } \sum \epsilon_i \delta N_i = 0$$

- $N_0$  particles are present in  $\epsilon_0$  energy level with  $g_0$  energy states,  $N_1$  in  $\epsilon_1$  energy level with  $g_1$  energy states,  $N_2$  in  $\epsilon_2$  energy level with  $g_2$  energy states, ....  $N_i$  in  $\epsilon_i$  energy level with  $g_i$  energy states with only one particle per energy state

## Derivation of Fermi – Dirac Statistics

- Suppose there are  $N_i$  particles present in  $\epsilon_i$  energy level
- The energy level  $\epsilon_i$  is considered to be degenerate, in which there are  $g_i$  energy states where  $g_i \gg N_i$
- $N_i$  particles has to be arranged in  $\epsilon_i$  energy level with  $g_i$  energy states
- **Restriction** on no. of particles i.e., only 1 particle occupy per energy state
- Permutations for  $g_i$  energy state will be  $g_i!$
- Particles are **identical and indistinguishable**
- Permutations of  $N_i$  particles amongst themselves and  $(g_i - N_i)$  vacant energy state amongst themselves has to be included
- Actual no. in which  $N_i$  particles may be allocated in  $\epsilon_i$  energy level will be given by

$$\frac{g_i!}{N_i! (g_i - N_i)!}$$

## Example

The **Thermodynamic Probability** will be given by:

$$W = \prod \frac{g_i!}{N_i! (g_i - N_i)!}$$

$$\bullet W = \frac{g_i!}{N_i! (g_i - N_i)!} = \frac{4!}{3!(4-3)!} = \frac{4!}{3!(1)!} = \frac{4 \times \cancel{3} \times \cancel{2} \times \cancel{1}}{\cancel{3} \times \cancel{2} \times \cancel{1} (1)} = 4$$

$$\bullet W = \frac{g_i!}{N_i! (g_i - N_i)!} = \frac{4!}{1!(4-1)!} = \frac{4!}{1!(3)!} = \frac{4 \times \cancel{3} \times \cancel{2} \times \cancel{1}}{1(\cancel{3} \times \cancel{2} \times \cancel{1})} = 4$$

$$\bullet W = \prod \frac{g_i!}{N_i! (g_i - N_i)!} = 4 \times 4 = 16$$

- The Thermodynamic Probability will be given by :

$$W = \prod \frac{g_i!}{N_i! (g_i - N_i)!} \dots\dots\dots (1)$$

- Taking logarithm, we get

$$\ln W = \sum \{ \ln g_i! - [\ln(N_i!) + \ln (g_i - N_i)!] \} \dots\dots\dots (2)$$

- Applying **STIRLING'S Approximation:**  $\ln(N_i!) = N_i \ln N_i - N_i$ , we get

$$\begin{aligned} \ln W &= \sum \{ [g_i \ln g_i - g_i] - [N_i \ln N_i - N_i + (g_i - N_i) \ln (g_i - N_i) - (g_i - N_i)] \} \\ &= \sum \{ g_i \ln g_i - \cancel{g_i} - N_i \ln N_i + \cancel{N_i} - (g_i - N_i) \ln (g_i - N_i) + \cancel{g_i} - \cancel{N_i} \} \\ &= \sum \{ g_i \ln g_i - N_i \ln N_i - g_i \ln (g_i - N_i) + N_i \ln (g_i - N_i) \} \end{aligned}$$

$$\ln W = \sum \{ g_i \ln \left( \frac{g_i}{g_i - N_i} \right) + N_i \ln \left( \frac{g_i - N_i}{N_i} \right) \}$$

$$\ln W = \sum \{ N_i \ln \left( \frac{g_i}{N_i} - 1 \right) - g_i \ln \left( \frac{g_i - N_i}{g_i} \right) \}$$

$$\ln W = \sum \{ N_i \ln \left( \frac{g_i}{N_i} - 1 \right) - g_i \ln \left( 1 - \frac{N_i}{g_i} \right) \} \dots\dots\dots (3)$$

$$\ln \mathbf{W} = \Sigma \{ \mathbf{N}_i \ln \left( \frac{g_i}{N_i} - 1 \right) - g_i \ln \left( 1 - \frac{N_i}{g_i} \right) \} \dots \dots \dots (3) \quad \text{[where } \delta \ln x_i = \frac{1}{x_i} \delta x_i \text{]}$$

- On differentiating, we get

$$\begin{aligned} \delta \ln \mathbf{W} &= \Sigma \{ \ln \left( \frac{g_i}{N_i} - 1 \right) \delta N_i + N_i \delta \ln \left( \frac{g_i}{N_i} - 1 \right) - \ln \left( 1 - \frac{N_i}{g_i} \right) \delta g_i - g_i \delta \ln \left( 1 - \frac{N_i}{g_i} \right) \} \\ &= \Sigma \{ \ln \left( \frac{g_i}{N_i} - 1 \right) \delta N_i + N_i \frac{N_i}{g_i - N_i} \delta \left( \frac{g_i - N_i}{N_i} \right) - g_i \frac{g_i}{g_i - N_i} \delta \left( \frac{g_i - N_i}{g_i} \right) \} \quad \text{[where } \delta g_i = 0 \text{]} \\ &= \Sigma \{ \ln \left( \frac{g_i}{N_i} - 1 \right) \delta N_i + \cancel{N_i} \frac{\cancel{N_i}}{g_i - N_i} \left( -\frac{g_i}{\cancel{N_i^2}} \right) \delta N_i - g_i \frac{\cancel{g_i}}{g_i - N_i} \left( -\frac{\cancel{g_i}}{\cancel{g_i^2}} \right) \delta N_i \} \\ &= \Sigma \{ \ln \left( \frac{g_i}{N_i} - 1 \right) \delta N_i - \frac{\cancel{g_i}}{g_i - N_i} \delta N_i + \frac{\cancel{g_i}}{g_i - N_i} \delta N_i \} \\ &= \Sigma \ln \left( \frac{g_i}{N_i} - 1 \right) \delta N_i \dots \dots \dots (4) \end{aligned}$$

- Most Probable Distribution of particles
  - The one for which  $\mathbf{W}$  is maximum ( $\mathbf{W}_{\max}$ )
  - Condition for maxima:  $\delta \mathbf{W} = \delta \ln \mathbf{W} = 0$  (5)

- Putting the condition of **eqn. 5**

$$\delta \ln \mathbf{W} = \Sigma \ln \left( \frac{g_i}{N_i} - 1 \right) \delta N_i = 0 \dots \dots \dots (6)$$

- Distribution must satisfy the condition:  $N$  &  $E$  must remain constant,
  - $\delta N$  &  $\delta E$  must be equal to zero

$$\delta N = \sum \delta N_i = 0 \quad \dots\dots\dots (7)$$

$$\delta E = \sum \epsilon_i \delta N_i = 0 \quad \dots\dots\dots (8)$$

- Using **Lagrange's Method of Undetermined Multipliers**
  - multiplying **eqn. 7** by  $(\alpha)$  and **eqn. 8** by  $(\beta)$

$$\alpha \delta N = \sum \alpha \delta N_i = 0 \quad \dots\dots\dots (9)$$

$$\beta \delta E = \sum \beta \epsilon_i \delta N_i = 0 \quad \dots\dots\dots (10)$$

$$\sum \ln \left( \frac{g_i}{N_i} - 1 \right) \delta N_i = 0 \quad \dots\dots\dots (6)$$

- adding **eqn. 9 & 10** and subtracting **eqn. 6**, we get

$$\sum [\alpha + \beta \epsilon_i - \ln \left( \frac{g_i}{N_i} - 1 \right)] \delta N_i = 0 \quad \dots\dots\dots (11)$$

- $\delta N_0, \delta N_1, \delta N_2, \delta N_3, \dots, \delta N_i$  are independent of each other, so each term in summation must be zero  
 $\delta N_i \neq 0$

$$\alpha + \beta \epsilon_i - \ln \left( \frac{g_i}{N_i} - 1 \right) = 0 \quad \dots\dots\dots (12)$$

$$\ln \left( \frac{g_i}{N_i} - 1 \right) = (\alpha + \beta \epsilon_i) \quad \dots\dots\dots (13)$$

- Removing logarithm from **eqn. 13**

$$\ln \left( \frac{g_i}{N_i} - 1 \right) = (\alpha + \beta \epsilon_i) \dots\dots\dots (13)$$

$$\left( \frac{g_i}{N_i} - 1 \right) = e^{(\alpha + \beta \epsilon_i)} \dots\dots\dots (14)$$

$$\frac{g_i}{N_i} = e^{(\alpha + \beta \epsilon_i)} + 1 \quad \text{where } \beta = 1/kT \quad [k = \text{Boltzmann constant}]$$

$$\frac{N_i}{g_i} = \frac{1}{e^{(\alpha + \beta \epsilon_i)} + 1} \dots\dots\dots (15)$$

$$N_i = \frac{g_i}{e^{(\alpha + \beta \epsilon_i)} + 1} \dots\dots\dots (16)$$

**This equation gives Fermi – Dirac Distribution**

- **Application:** Derive expression for heat capacity  $C_v$  of metals at low temperature



# COMPARISON BETWEEN THE THREE STATISTICS

## Maxwell - Boltzmann

- Classical Statistics
- Internal Structure ignored
- Identical & distinguishable particles
- No restriction on occupancy of energy states
- Phase space not known
- Spin can have any value
- Wavefunction not involved
- At absolute zero, energy taken as zero
- Boltzmannons or Maxwellons
- Eg. Ideal gas molecules

## Bose - Einstein

- Quantum Statistics
- Internal Structure taken into account
- Identical & indistinguishable particles
- No restriction on occupancy of energy states
- Phase space is known  $\sim h^3$
- Zero or Integral Spin
- Wavefunction Symmetric
- At absolute zero, energy is taken to be zero
- Bosons
- Eg. Photons, mesons,  $^4\text{He}$ ,  $^2\text{H}$ , ....
- At high temperature approaches Maxwell-Boltzmann distribution

## Fermi - Dirac

- Quantum Statistics
- Internal Structure taken into account
- Identical & indistinguishable particles
- Not more than one particle in each state –Pauli's Exclusion Principle
- Phase space is known  $\sim h^3$
- Half Integral Spin
- Wavefunction Antisymmetric
- At absolute zero, energy is not zero.
- Fermions
- Eg. Electron, proton,.....
- At high temperature approaches Maxwell-Boltzmann distribution

# COMPARISON BETWEEN THE THREE STATISTICS

## Maxwell - Boltzmann

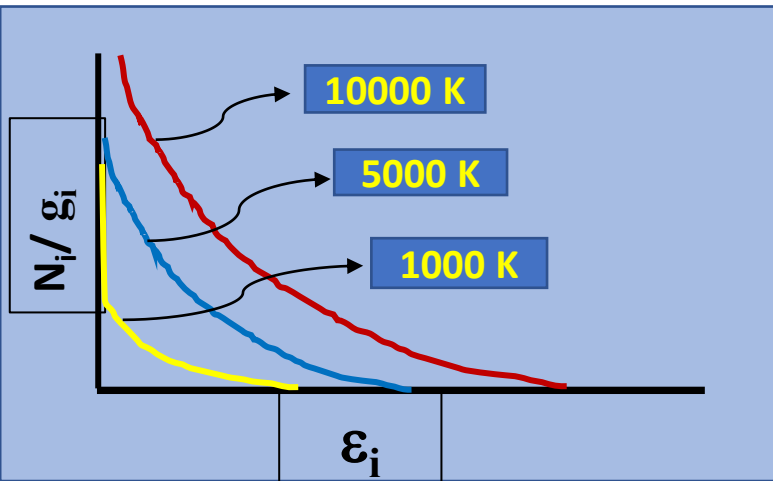
- No. of ways of achieving:

$$W = N! \prod \frac{g_i^{N_i}}{N_i!}$$

- Max. Probability distribution

$$\propto \frac{1}{e^{(\alpha + \beta \epsilon_i)}}$$

- Distribution  $N_i = \frac{g_i}{e^{(\alpha + \beta \epsilon_i)}}$



## Bose - Einstein

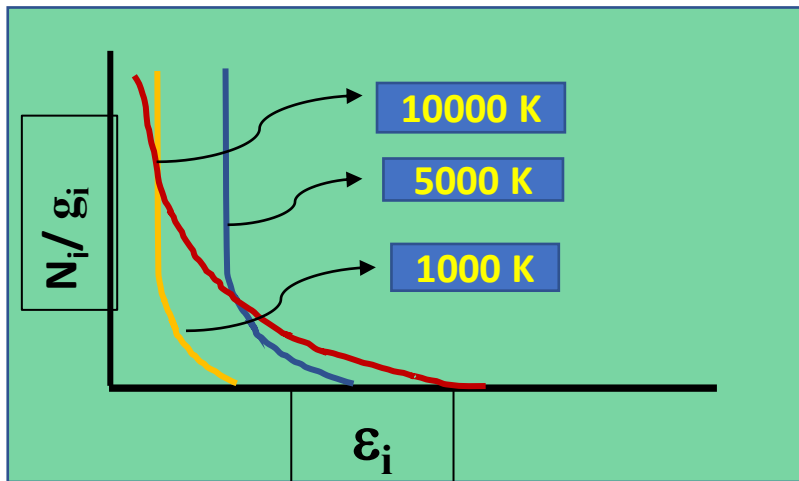
- No. of ways of achieving:

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

- Max. Probability distribution

$$\propto \frac{1}{e^{(\alpha + \beta \epsilon_i)} - 1}$$

- Distribution  $N_i = \frac{g_i}{e^{(\alpha + \beta \epsilon_i)} - 1}$



## Fermi - Dirac

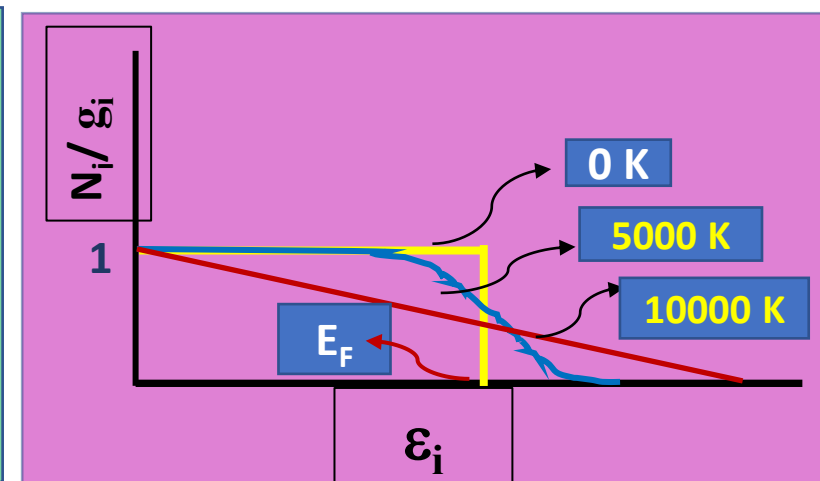
- No. of ways of achieving:

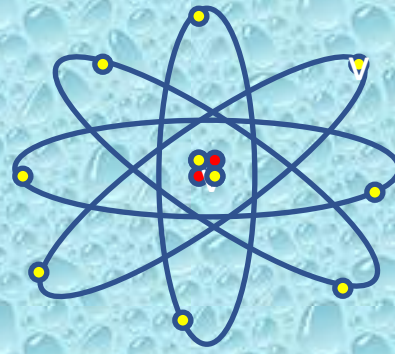
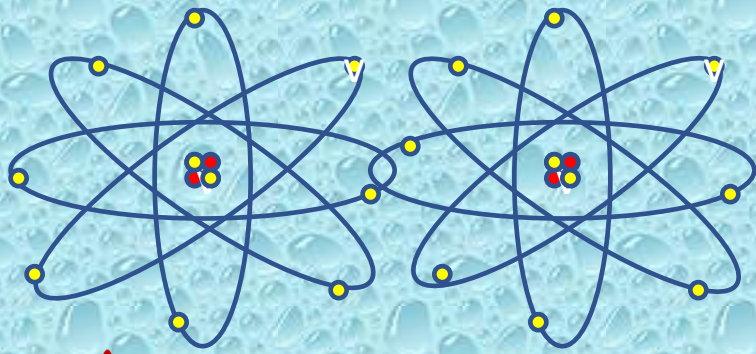
$$W = \prod \frac{g_i!}{N_i! (g_i - N_i)!}$$

- Max. Probability distribution

$$\propto \frac{1}{e^{(\alpha + \beta \epsilon_i)} + 1}$$

- Distribution  $N_i = \frac{g_i}{e^{(\alpha + \beta \epsilon_i)} + 1}$





THANK  
YOU

