Introduction To Statistical Thermodynamics -1

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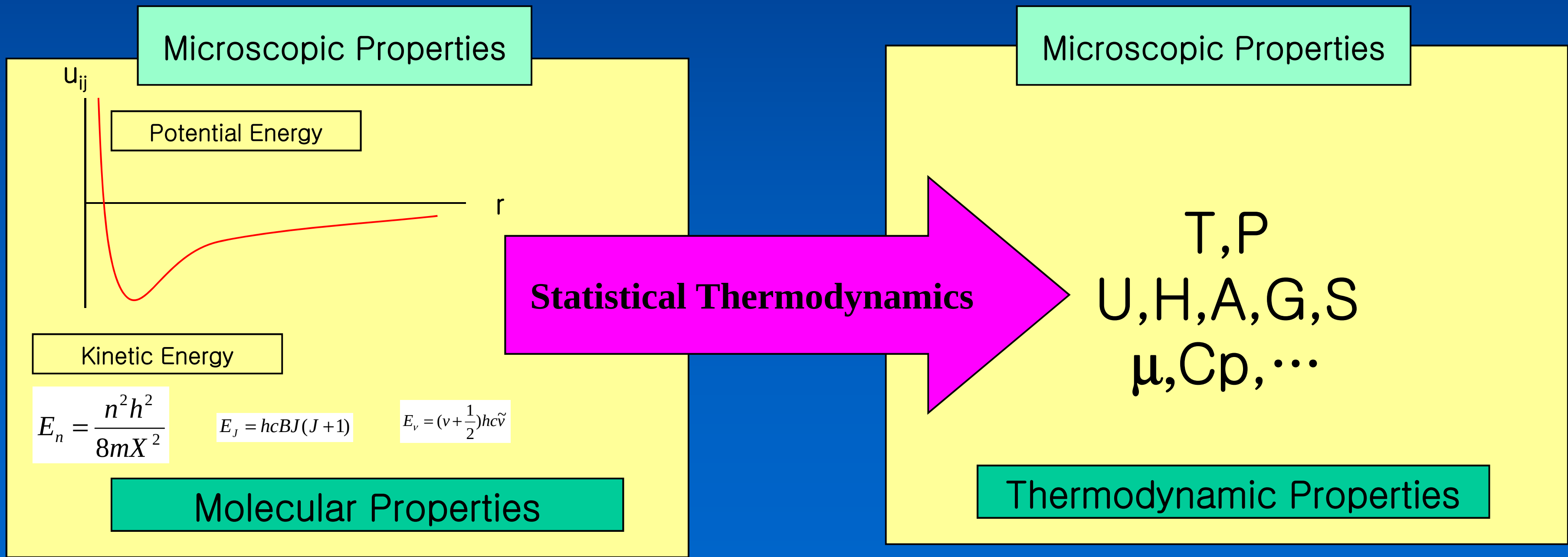
Statistical Thermodynamics ?

- **Link between microscopic properties and bulk properties**



Two Types of Approach for Microscopic View

- **Classical Mechanics**
  - **Based on Newton's Law of Motion**

$$H = \sum_i \frac{p_i}{2m_i} + U(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N)$$

Hamiltonian

- **Quantum Mechanics**
  - **Based on Quantum Theory**

$$-\sum_i \frac{h^2}{8\pi^2 m_i}\nabla_i^2\Psi + U\Psi = E\Psi$$

Schrodinger's Wave Equation

Solutions

- Using classical mechanics, values of position and momentum can be found as a function of time.

- Using quantum mechanics, values of allowed energy levels can be found. (For simple cases)

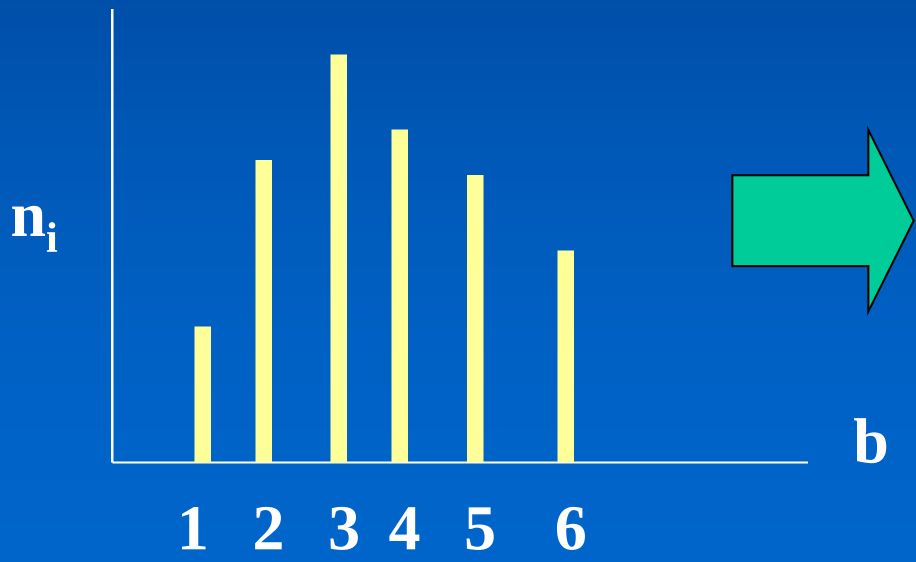
Purpose of statistical thermodynamics

- Assume that energies of individual molecules can be calculated.

- How can we calculate overall properties (energy, pressure,…) of the whole system ?

Statistical Distribution

- n : number of object
- b : a property (can have 1,2,3,4, … discrete values)



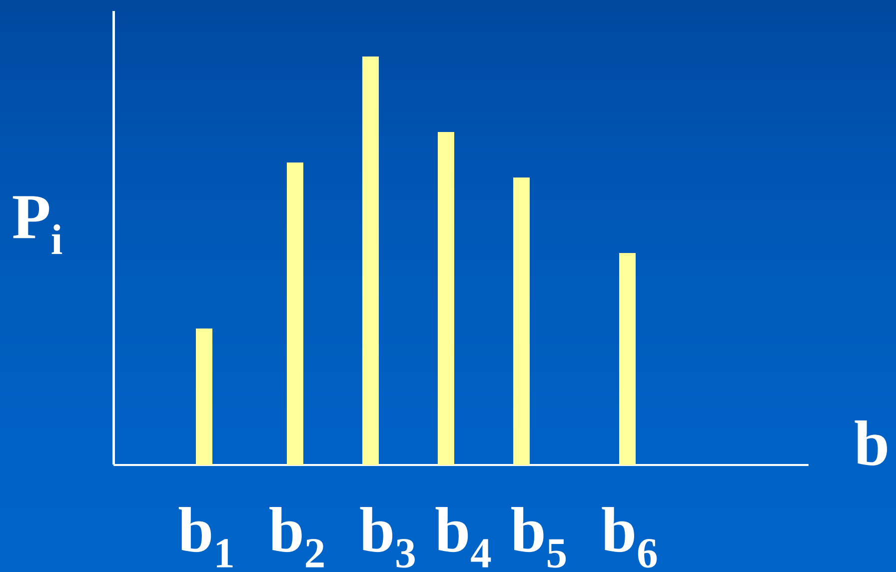
if we know "Distribution" then we can calculate the average value of b

Normalized Distribution Function → Probability Function

b : energies of individual molecule,…
F(b) : internal energy, entropy, …

$$P_i(b_i) = \frac{n_i(b_i)}{n} = \frac{n_i(b_i)}{\sum_i n_i(b_i)}$$

$$\sum_i P_i(b_i) = 1$$



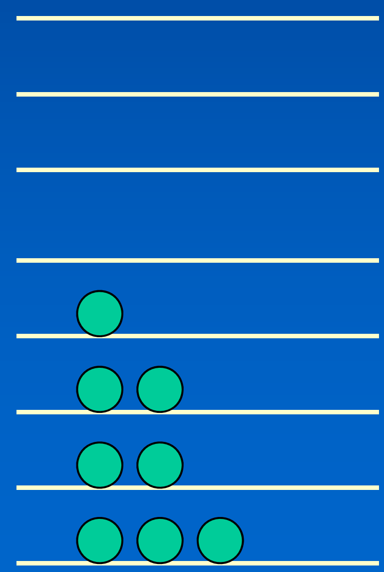
$$< b > = \sum_i b_i P_i$$

$$< F(b) > = \sum_i F(b_i) P_i$$

Finding probability (distribution) function is the main task in statistical thermodynamics

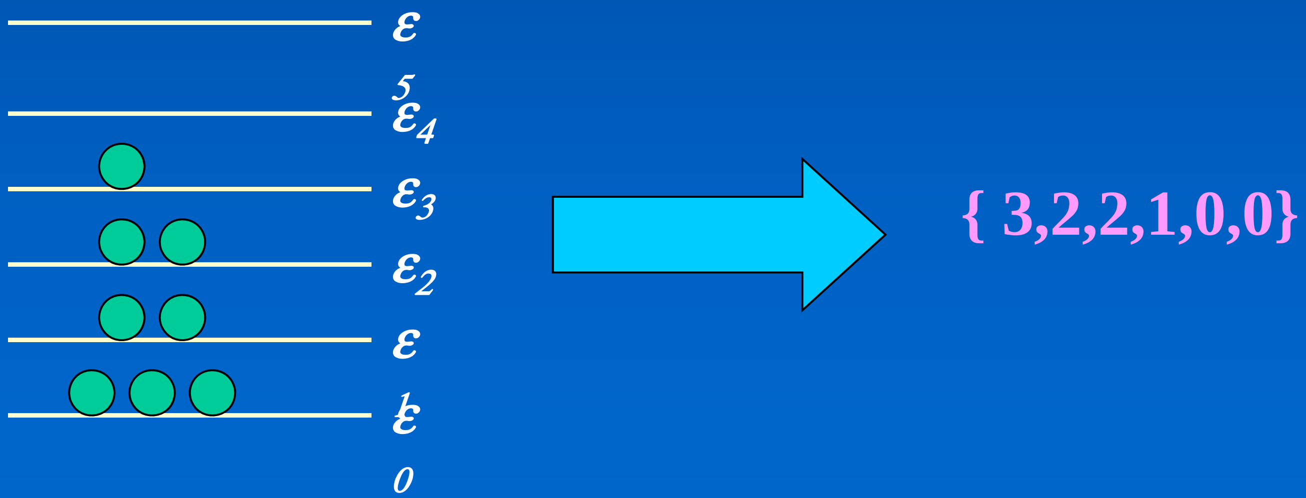
The distribution of molecular states

- Quantum theory says ,
  - Each molecules can have only discrete values of energies
- Evidence
  - Black-body radiation
  - Planck distribution
  - Heat capacities
  - Atomic and molecular spectra
  - Wave-Particle duality



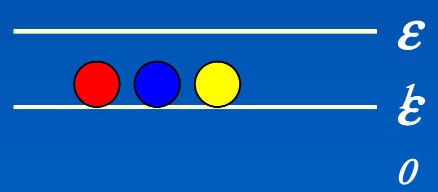
Configurations…

- **Instantaneous configuration**
  - **At any instance, there may be n_o molecules at ε_0, n_1 molecules at ε_1, n_2 molecules at ε_2, … → {n_0 , n_1 , n_2 …} configuration**

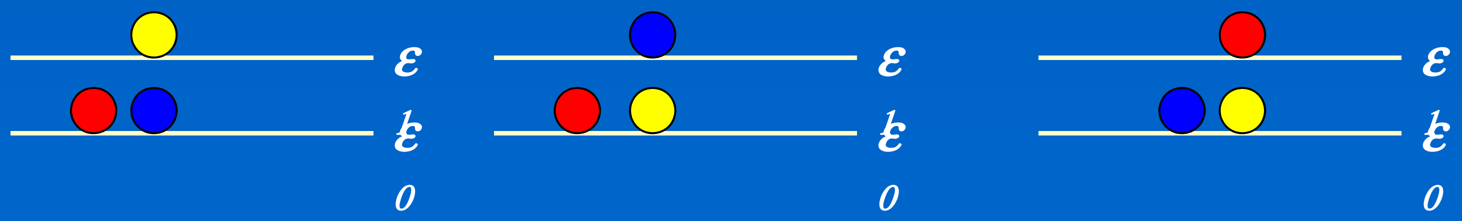


Weight ….

- Each configuration can be achieved in different ways …
- Example1 : {3,0} configuration → 1



- Example2 : {2,1} configuration → 3



Weight …

- **Weight (W) : number of ways that a configuration can be achieved in different ways**
- **General formula for the weight of**

$\{n_0 , n_1 , n_2 \ \ldots\}$ configuration

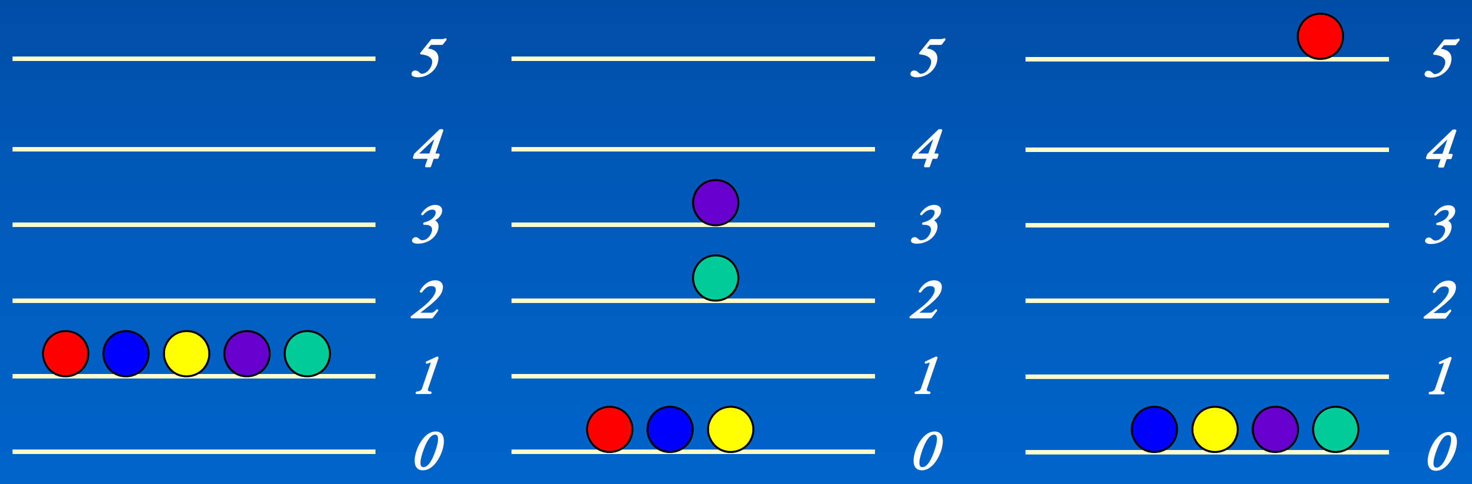
$$W = \frac{N!}{n_1!n_2!n_3!\ldots} = \frac{N!}{\prod_i n_i!}$$

Example1
{1,0,3,5,10,1} of 20 objects
W = 9.31E8

Example 2
{0,1,5,0,8,0,3,2,1} of 20 objects
W = 4.19 E10

Principle of equal a priori probability

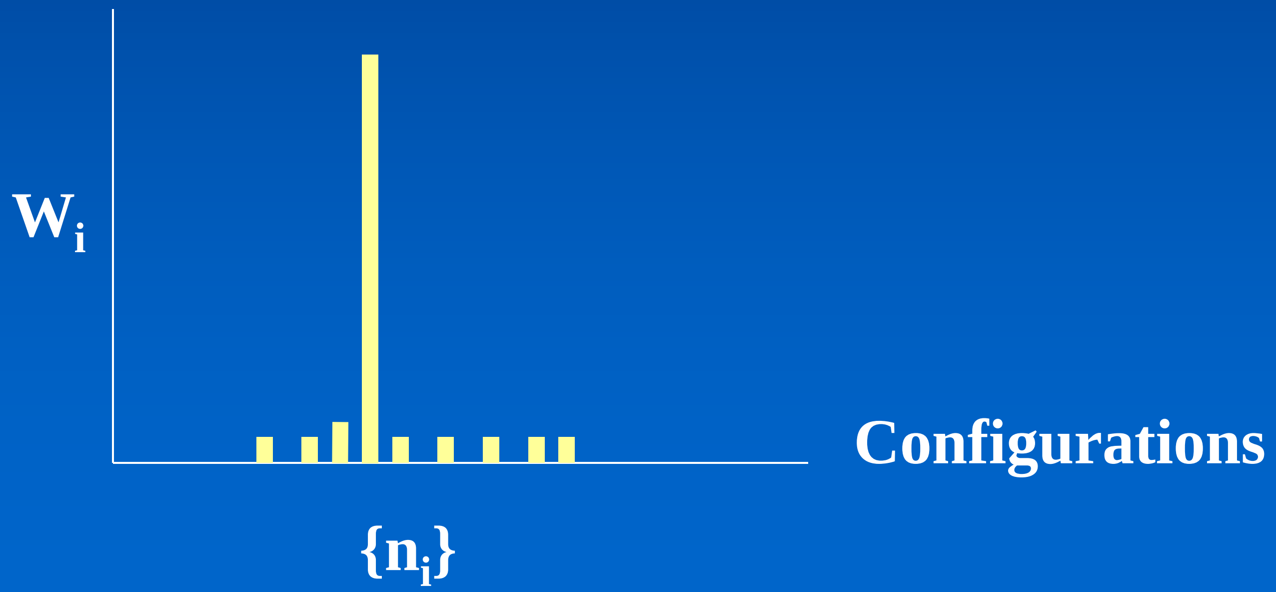
- **All distributions of energy are equally probable**
- **If E = 5 and N = 5 then**



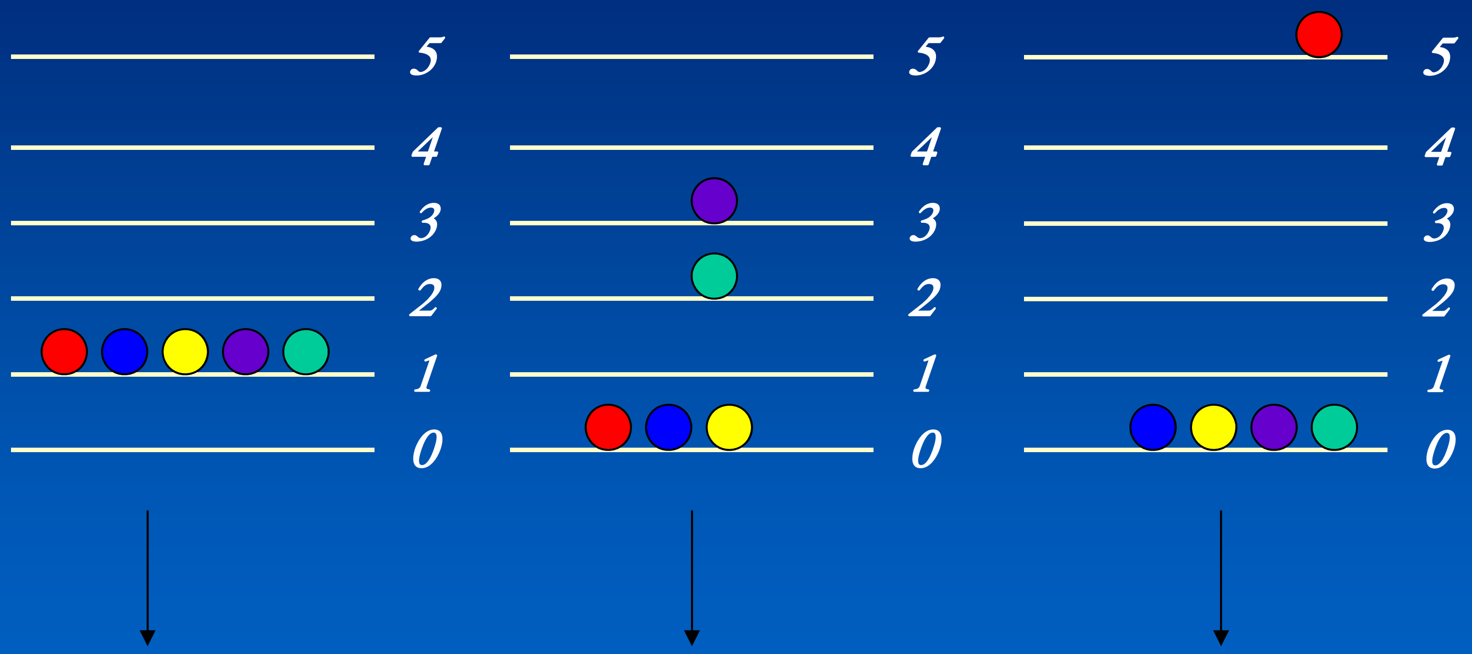
→ All configurations have equal probability, but possible number of way (weight) is different.

The dominating configuration

- For large number of molecules and large number of energy levels, there is a dominating configuration.
- The weight of the dominating configuration is much more larger than the other configurations.



The dominating configuration



W = 1 (5!/5!)

W = 20 (5!/3!)

W = 5 (5!/4!)

→ **Difference in W becomes larger when N is increased !**

Stirling's Approximation

- **A useful formula when dealing with factorials of numbers.**

$$\ln N! = N \ln N - N$$

$$\ln W = \ln \frac{N!}{n_1! n_2! n_3! \ldots} = \ln N! - \sum_i \ln n_i!$$

$$= N \ln N - N - \sum_i n_i \ln n_i + \sum_i n_i$$

$$= N \ln N - \sum_i n_i \ln n_i$$

The Boltzmann Distribution

- Task : Find the dominating configuration for given N and total energy E.
- → Find Max. W which satisfies ;

$$N = \sum_i n_i$$

$$E = \sum_i \varepsilon_i n_i$$

$$\Rightarrow$$

$$\sum_i dn_i = 0$$

$$\sum_i \varepsilon_i dn_i = 0$$

Method of Undetermined Multiplier

- **Maximum weight , W**
  - **→Recall the method to find min, max of a function…**

$$d \ln W = 0$$

$$\left(\frac{\partial \ln W}{dn_i} \right) = 0$$

- **Method of undetermined multiplier :**
  - **Constraints should be multiplied by a constant and added to the main variation equation.**

Method of undetermined multipliers

$$d \ln W = \sum_i \left(\frac{\partial \ln W}{dn_i} \right) dn_i + \alpha \sum_i dn_i - \beta \sum_i \varepsilon_i dn_i$$

$$= \sum_i \left\{ \left(\frac{\partial \ln W}{dn_i} \right) + \alpha - \beta \varepsilon_i \right\} dn_i = 0$$

$$\Downarrow$$

$$\left(\frac{\partial \ln W}{dn_i} \right) + \alpha - \beta \varepsilon_i = 0$$

$$\ln W = N \ln N - \sum n_i \ln n_i$$

$$\left(\frac{\partial \ln W}{\partial n_i}\right) = \frac{\partial N \ln N}{\partial n_i} - \sum_j \frac{\partial (n_j \ln n_j)}{\partial n_i}$$

$$\frac{\partial N \ln N}{\partial n_i} = \left(\frac{\partial N}{\partial n_i}\right) \ln N + N \times \frac{1}{N}\left(\frac{\partial N}{\partial n_i}\right) = \ln N + 1$$

$$\sum_j \frac{\partial (n_j \ln n_j)}{\partial n_i} = \sum_j \left\{\left(\frac{\partial n_j}{\partial n_i}\right) \ln n_j + n_j \times \frac{1}{n_j}\left(\frac{\partial n_j}{\partial n_i}\right)\right\} = \ln n_i + 1$$

$$\frac{\partial \ln W}{\partial n_i} = -(\ln n_i + 1) + (\ln N + 1) = -\ln \frac{n_i}{N}$$

$$-\ln\frac{n_i}{N} + \alpha + \beta\varepsilon_i = 0$$

$$\frac{n_i}{N} = e^{\alpha - \beta\varepsilon_i}$$

$$N = \sum_j n_j = Ne^{\alpha}\sum_j e^{-\beta\varepsilon_j}$$

$$e^{\alpha} = \frac{1}{\sum_j e^{-\beta\varepsilon_j}}$$

$$P_i = \frac{n_i}{N} = \frac{e^{-\beta\varepsilon_i}}{\sum_j e^{-\beta\varepsilon_j}}$$

→

Boltzmann Distribution

(Probability function for energy distribution)

The Molecular Partition Function (분자 분배 함수)

- **Boltzmann Distribution**

$$p_i = \frac{n_i}{N} = \frac{e^{-\beta\varepsilon_i}}{\sum_j e^{-\beta\varepsilon_j}} = \frac{e^{-\beta\varepsilon_i}}{q}$$

- **Molecular Partition Function**

$$q = \sum_j e^{-\beta\varepsilon_j}$$

- **Degeneracies : Same energy value but different states (g_j-fold degenerate)**

$$q = \sum_{\substack{levels \\ j}} g_j e^{-\beta\varepsilon_j}$$

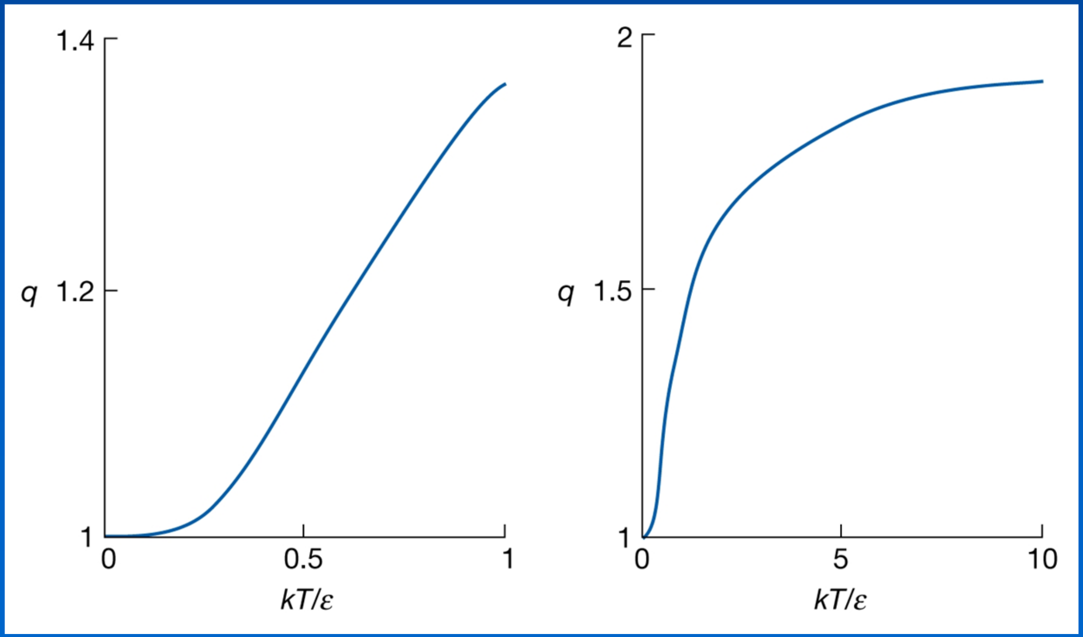
An Interpretation of The Partition Function

- **Assumption :** $\beta = 1/kT$
- **T→ 0 then q → 1**
- **T→ infinity then q → infinity**
- **The molecular partition function gives an indication of the average number of states that are thermally accessible to a molecule at T.**

An example : Two level system

- **Energy level can be 0 or ε**

$$q = 1 + e^{-\beta\varepsilon} = 1 + e^{-\varepsilon/kT}$$



Example

- **Energy levels : ε, 2ε, 3ε , ….**

$$q = 1 + e^{-\beta\varepsilon} + e^{-2\beta\varepsilon} + \ldots = \frac{1}{1 - e^{-\beta\varepsilon}}$$