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Statistical mechanics is a mathematical tool which describes the macroscopic properties of a system consisting of a large number of particles (atoms or molecules or colloidal particles) with the microscopic parameters. It employs statistical methods and probability theory to relate the microscopic parameters with the macroscopic properties of the systems. It does not propose or utilize any natural laws. Statistical mechanics is highly based on probability theory and hence it does not focus on every individual (microscopic) particle of a (macroscopic) system rather on the average behavior of the large number ($\sim 10^{23}$) of the identical particles which the system consists of.

Statistical mechanics was developed in the late 19th century, primarily by the physicist Ludwig Boltzmann who developed the most fundamental relation in statistical mechanics which relates the entropy of a system with the total number of microstates of the system. Other physicists like Maxwell and Gibbs also contributed hugely to the development of the field.

Statistical Mechanics grew out of classical thermodynamics which describes macroscopic properties like pressure, temperature, heat capacity etc. in terms of the microscopic parameters which fluctuate around average values, determined by the probability distributions. This implies that thermodynamics is essentially a product of the get-together of the “statistics” and “mechanics” of the particles constituting a macroscopic system. These systems can be in equilibrium or away from it but we shall concentrate on the equilibrium state of the systems.

Microstates and Macrostates:

In statistical mechanics we consider a physical system consisting of N identical particles confined in a volume V. In general, the number of particles in the system

N would be extremely large (~ 10^{23}). Statistical methods are applied to the systems in the so-called thermodynamic limit which basically says

$$N \to \infty \text{ and } V \to \infty$$

such that N/V (particle density) remains fixed at pre-assumed value. In the thermodynamic limit, the extensive properties like mass, entropy, internal energy etc. of the system become directly proportional to the size of the system (N or V) and the intensive properties like pressure, temperature, chemical potential etc. become independent of the size of the system.

Now, we can define the terms "macrostate" and "microstate" of a system. Specification of the quantities like number of particles N, volume V, energy E, temperature T, chemical potential μ etc. defines a **macrostate** of a system.

A complete specification of the microscopic details i.e. the position and momentum of every particle of a classical system or the value of the wavefunction at every point in space for a quantum system is said to define the **microstate** of a system.

Maxwell-Boltzmann Statistics:

Maxwell-Boltzmann (M-B) statistics, also known as classical statistics, describes the average distribution of noninteracting identical but distinguishable particles over different energy states in thermal equilibrium. In short, we can say M-B statistics is applicable for classical systems in which particle density needs to be low enough so that inter-particle distance becomes large enough to ensure the negligible quantum effects. ***The basic postulates of Maxwell-Boltzmann statistics are following:***

(i) The particles of the system have to be identical but distinguishable.

(ii) Inter-particle distance has to be large enough to have negligible interaction. So, neither the Heisenberg uncertainty principle nor Pauli's exclusion principle will be applicable to the particles.

(iii) There will be no multiplicity of the energy states that means the states will be non-degenerate states. And there will be no restriction on the number of particles occupying a state.

(iv) The total number of particles (N) of the system will be conserved. If N_i be the number of particles in i-th state then

$$\sum_i N_i = N = constant$$

Or, $$\sum_i \delta N_i = 0 \qquad \text{…………} (1)$$

(v) Total energy (U) of the system will also be conserved. If E_i be the energy of a particle in i-th state then

$$U = \sum_i E_i$$

Or, $$\delta U = \sum_i \delta E_i = 0 \qquad \text{…………} (2)$$

Equations (1) and (2) are the two conditions which are obeyed by the system. Now, we will count the total number of possible microstates in the macroscopic system and using the above two conditions we will derive the distribution function.

Counting of the Total Number of Microstates: Thermodynamic Probability

Let's consider a system of particles which satisfies the above criteria. If N_1, N_2, N_3,........, N_n be the number of particles with energies E_1, E_2, E_3,......., E_n respectively. For the sake of generality, let g_i be the degeneracy of the state with energy E_i. Now, we have to basically find out the total number of ways of distributing the particles among the different states and that will be nothing but the total number of possible microstates of the macrosystem. We will calculate this number in two parts W1 and W2 and the total number of microstates W will be given by

$$W = W_1 W_2 \qquad \ldots\ldots\ldots\ldots (3)$$

where, W_1 is the number of ways of choosing $N_1, N_2, N_3, \ldots\ldots, N_n$ out of N particles and W_2 is the number of ways $N_1, N_2, N_3, \ldots\ldots, N_n$ can be distributed among $g_1, g_2, g_3, \ldots\ldots, g_n$ states.

Calculation of W_1:

The number of ways of choosing N_1 particles out of N particles is given by ${}^{N}C_{N1}$, the number of ways of choosing N_2 particles out of $(N - N_1)$ particles is given by ${}^{(N-N1)}C_{N2}$ and so on. Similarly, the number of ways of choosing N_n particles out of $(N - N_1 - N_2 - \ldots\ldots - N_{n-1})$ *particles is given by* ${}^{(N-N1-N2-\ldots Nn-1)}C_{Nn}$. So, the number of ways of choosing $N_1, N_2, N_3, \ldots\ldots, N_n$ out of N particles is give by

$$W_1 = {}^{N}C_{N_1} \times {}^{(N-N_1)}C_{N_2} \times {}^{(N-N_1-N_2)}C_{N_3} \times \cdots\cdots \times {}^{(N-N_1-N_2-\cdots-N_{n-1})}C_{N_n}$$

$$= \frac{N!}{N_1!\,(N-N_1)!} \times \frac{(N-N_1)!}{N_2!\,(N-N_1-N_2)!} \times \frac{(N-N_1-N_2)!}{N_3!\,(N-N_1-N_2-N_3)!} \times \cdots\cdots \times \frac{(N-N_1-N_2-\cdots-N_{n-1})!}{N_n!\,(N-N_1-N_2-\cdots-N_n)!}$$

$$= \frac{N!}{N_1!\,N_2!\,N_3!\cdots\cdots N_n!}$$

$$= \frac{N!}{\prod_{i=1}^{n} N_i!} \qquad \cdots\cdots\cdots (4)$$

Calculation of W_2:

Since every state has the same a priori probability of being occupied and the particles are distinguishable, the number of ways of distributing N_i particles among g_i states is given by $g_i^{N_i}$. This is due to the fact that any of the g_i states can be occupied by each of the N_i particles. So, the number of ways $N_1, N_2, N_3, \ldots\ldots, N_n$ can be distributed among $g_1, g_2, g_3, \ldots\ldots, g_n$ states is given by

$$W_2 = g_1^{N1} \times g_2^{N2} \times g_3^{N3} \times \ldots\ldots\ldots \times g_n^{Nn}$$

Or, $$W_2 = \prod_{i=1}^{n} g_i^{Ni} \qquad \ldots\ldots\ldots\ldots (5)$$

Now, the total number of possible microstates of the macroscopic system is given by

$$W = W_1 W_2$$

Or, $$W = \frac{N!}{\prod_{i=1}^{n} N_i} \times \prod_{i=1}^{n} g_i^{Ni} \qquad \ldots\ldots\ldots\ldots (6).$$

This total number of possible microstates of the system is also called the thermodynamic probability of the system.

We will now use the Boltzmann theorem which relates the macroscopic property of a system, called entropy (S), to the microscopic property i.e. the total number of microstates (W) of the system. Mathematically,

$$S = K_B \, lnW \qquad \ldots\ldots\ldots\ldots (7)$$

where, K_B is the Boltzmann constant. We assert that the equilibrium state corresponds to the most probable state i.e. the macrostate for which the total number of microstates is maximum.

So in the equilibrium condition, entropy S becomes maximum that implies

$$\delta S = 0$$

Or, $$\delta \, lnW = 0 \qquad \ldots\ldots\ldots (8)$$

Let us now calculate lnW using the equation (6).

$$\ln W = \ln\left(\frac{N!}{\prod_{i=1}^{n} N_i!} \times \prod_{i=1}^{n} g_i^{N_i}\right)$$

$$= \ln(N!) + \sum_{i=1}^{n} \ln(g_i^{N_i}) - \sum_{i=1}^{n} \ln(N_i!)$$

$$= N\ln N - N + \sum_{i=1}^{n} N_i \ln g_i - \sum_{i=1}^{n} N_i \ln N_i - \sum_{i=1}^{n} N_i$$

$$= N\ln N + \sum_{i=1}^{n} N_i \ln g_i - \sum_{i=1}^{n} N_i \ln N_i \qquad \text{.......(9)}$$

$$\delta \ln W = 0 + \sum_{i=1}^{n} \delta N_i . \ln g_i - \sum_{i=1}^{n} \delta N_i . \ln N_i - \sum_{i=1}^{n} \delta N_i$$

$$= \sum_{i=1}^{n} (\ln g_i - \ln N_i)\, \delta N_i \qquad [\text{Using eqn.(1)}]$$

Now, using eqn. (8), we get

$$\sum_{i=1}^{n} (\ln g_i - \ln N_i)\, \delta N_i = 0 \qquad \text{.......(10)}$$

Using Lagrange's method of undetermined multipliers i.e. by multiplying equations (1) and (2) with -$\boldsymbol{\alpha}$ and -$\boldsymbol{\beta}$ respectively, we get

$$\sum_{i=1}^{n} (ln\, g_i - ln\, N_i - \alpha - \beta E_i)\, \delta N_i = 0 \qquad \text{.........(11)}$$

As $\delta N_i's$ are independent, the term in the parenthesis must be zero for every i value. So, we can write

$$ln\, g_i - ln\, N_i - \alpha - \beta E_i = 0$$

Or, $ln\, N_i = ln\, g_i - \alpha - \beta E_i$

Or, $ln\, N_i = ln\, (g_i\, e^{-\alpha - \beta E_i})$

Or, $N_i = g_i\, e^{-\alpha - \beta E_i}$ ……… (12)

Equation (12) gives us the number of particles N_i in terms of the number of states g_i with energy E_i.

Now, we will define a term called distribution function. It is the ratio of the number of particles N_i to the number of states g_i. Mathematically, it is given by

$$f(E_i) = \frac{N_i}{g_i} = e^{-\alpha - \beta E_i} \quad \text{……... (13)}$$

This gives the average number of particles per state of the system. Equation (13) is the Maxwell-Boltzmann (M-B) distribution function.

Now, the Lagrange undetermined multipliers $\boldsymbol{\alpha}$ and $\boldsymbol{\beta}$ are to be determined. Refer to any text book for the determination of $\boldsymbol{\alpha}$ and $\boldsymbol{\beta}$. Their values are given by

$$e^{-\alpha} = \frac{N}{Z} \text{ and } \beta = \frac{1}{K_B T}$$

where, $Z = \sum_{i=1}^{n} g_i\, e^{-E/K_B T}$ is known as the partition function and it plays a very important role in statistical theory. Now the M-B distribution function *f(E$_i$)* takes the following form

$$f(E_i) = \frac{N_i}{g_i} = \frac{N}{Z} e^{-E_i/K_B T} \quad \text{……… (14).}$$

Maxwell-Boltzmann statistics is applicable to a system of dilute gas. It can be used to derive Maxwell's distribution for an ideal gas of classical particles.

References:

(i) Statistical Mechanics by R. K. Pathria and Paul D. Beale

(ii) Thermal Physics (Heat & Thermodynamics) by A. B. Gupta and H. P. Roy

(iii) Introduction to Statistical Physics by Kerson Huang