Maxwell- Boltzmann Distribution

(Post Graduate Level)

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Maxwell-Boltzmann Distribution Law

Maxwell-Boltzmann statistics is classical statistics, which is given for the classical particles.

Following are the basic postulates of MB statistics:

- The associated particles are distinguishable.
- Each energy state can contain any number of particles.
- Total number of particles in the entire system is constant.
- Total energy of all the particles in the entire system is constant.
- Particles are spinless. Example: gas molecules at high temperature and low pressure.

<u>Classical Particles</u>: Classical particles are identical but far enough to be distinguishable. The wave functions of the classical particles do not overlap on each other.

Distinguishable: Two particles are said to be distinguishable if their separation is large in compare to their De-Broglie wavelength. For distinguishable particles you would know if two particles changes their places.

E=Total energy of the entire system = Constant. N=Total number of identical distinguishable particles=Constant V= Total volume =Constant



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We now focus on the number of particles siting in given energy levels \mathcal{E}_1 , \mathcal{E}_2 , \mathcal{E}_3 \mathcal{E}_n which are available within the system. The energy levels are fixed for the system.

The number of particles in each energy levels are variable and given by $n_1, n_2, n_3, \dots, n_r$.

The number of ways to attained a given microscopic state is given by

$$v = \frac{N!}{n_1! n_2! \dots n_r!}$$

We need to know the distribution of the particles in different energy levels (as stated above) that maximize the value of ω .

The combination result in most probable microstate and in this most probable state the system is considered as the equilibrium state.

Now,

$$\log \omega = \ln \frac{n!}{\prod_{i=1}^{i=r} n_i!} \tag{2}$$

For maximum value of ω instead of dealing with ω deal with logarithmic of ω .

$$\log \omega = \log N! - \sum_{i=1}^{i=r} \ln n_i! \qquad (3)$$

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-----(1)

Using Stirling's approximation

$$\log x! \approx x \log x - x \tag{4}$$

Equation (3) can be expressed using above approximation as

$$\log \omega = N \log N - \sum_{i=1}^{i=r} \left[n_i \ln n_i - n_i \right]$$

Taking the derivative of the above equation,

$$\delta \log \omega = -\sum_{i=1}^{n-1} \delta n_i \ln n_i + n_i \times \frac{1}{n_i} - \delta n_i = 0$$

$$\sum_{i=1}^{n-1} \delta n_i \ln n_i = 0$$

$$\sum n_i = N = \text{Constant}$$

$$\sum \delta n_i = 0$$

(The sum of all the changes in the system is zero)

Total energy,

$$E = \sum \varepsilon_i n_i = \text{Constant}$$

On differentiating the above equation

$$\sum_{i=1}^{n-1} \varepsilon_i \delta n_i = 0$$

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-(5)

----(6)

-----(7)

To maximize the function in (5) subjected to constrain (6) and (7) let us use Lagrange's method of undetermined multipliers equation (6) multiplied by α and equation (7) is multiplied by β and the adding equation (5), (6) and (7) we get,

$$\sum \left[\ln n_i + \alpha + \beta \varepsilon_i \right] \delta n_i = 0$$
(8)
$$\sum \left[\ln n_i + \alpha + \beta \varepsilon_i \right] = 0$$

$$\ln n_i = -\alpha - \beta \varepsilon_i$$

$$n_i = e^{-\alpha} \cdot e^{-\beta \varepsilon_i}$$
(9)
= The number of particle in *i*th level
$$\sum_{i=1}^{t=r} n_i = e^{-\alpha} \sum_{i=1}^{i=r} e^{-\beta \varepsilon_i} = N$$

$$e^{-\alpha} = \frac{N}{\sum_{i=1}^{r} e^{-\beta \varepsilon_i}}$$
(10)
$$e^{-\alpha} = \frac{N}{P}$$

.....(11)

$$n_i = \frac{N}{n} e^{-\beta \epsilon}$$

where,

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The above expression helps us to determine the number of particles in most probable micro-states. The expression is known as Maxwell- Boltzmann statistics expression.

The probability of a particle to occupy the energy state ε_i is given by Maxwell-Boltzmann function

$$f(\varepsilon_i) = \frac{n_i}{g_i} = \frac{1}{e^{\alpha + \beta \varepsilon_i}}$$
(13)
$$f_{MB}(\varepsilon) = A e^{-\frac{\varepsilon}{k_{\beta}T}}$$
(14)

-----(12)

Where,

A=Constant

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

 $n_i = \frac{N}{n} e^{\frac{-\varepsilon_i}{k_{\beta}T}}$

A depends on the number of particles in the system and plays the same role like normalization constant.



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