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.

Classical Particles: 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.

\[
E = \text{Total energy of the entire system} = \text{Constant.} \\
N = \text{Total number of identical distinguishable particles} = \text{Constant} \\
V = \text{Total volume} = \text{Constant}
\]
We now focus on the number of particles sitting in given energy levels $\varepsilon_1, \varepsilon_2, \varepsilon_3, \ldots, \varepsilon_n$ 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 $n_1, n_2, n_3, \ldots, n_r$.

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

$$\omega = \frac{N!}{n_1!n_2!\ldots n_r!} \quad \text{----------(1)}$$

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

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

Now,

$$\log \omega = \ln \frac{n!}{\prod_{i=1}^{r} n_i!} \quad \text{----------(2)}$$

For maximum value of $\omega$ instead of dealing with $\omega$ deal with logarithmic of $\omega$.

$$\log \omega = \log N! - \sum_{i=1}^{r} \ln n_i! \quad \text{----------(3)}$$
Using Stirling’s approximation

\[ \log x! \approx x \log x - x \]  

\[ \text{...............}(4) \]

Equation (3) can be expressed using above approximation as

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

Taking the derivative of the above equation,

\[ \delta \log \omega = - \sum_{i=1}^{i=r} \delta n_i \ln n_i + n_i \times \frac{1}{n_i} - \delta n_i = 0 \]

\[ \sum_{i=1}^{i=r} \delta n_i \ln n_i = 0 \]  

\[ \text{----------}(5) \]

\[ \sum n_i = N = \text{Constant} \]

\[ \sum \delta n_i = 0 \]  

\[ \text{----------}(6) \]

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

Total energy,

\[ E = \sum \epsilon_i n_i = \text{Constant} \]

On differentiating the above equation

\[ \sum_{i=1}^{i=r} \epsilon_i \delta n_i = 0 \]  

\[ \text{-----------}(7) \]
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 $\alpha$ and equation (7) is multiplied by $\beta$ and the adding equation (5), (6) and (7) we get,

$$\sum [\ln n_i + \alpha + \beta \varepsilon_i] \delta n_i = 0$$

$\sum [\ln n_i + \alpha + \beta \varepsilon_i] = 0$

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

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

$$\text{The number of particle in } i^{th} \text{ level } \sum_{i=1}^{r} n_i = e^{-\alpha} \sum_{i=1}^{p} e^{-\beta \varepsilon_i} = N$$

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

where,

$$p = \sum_{i=1}^{r} e^{-\beta \varepsilon_i}$$

$$n_i = \frac{N}{p} e^{-\beta \varepsilon_i} \quad \text{...........(11)}$$
\[ \beta = \frac{1}{k_B T} \]  

\[ n_i = \frac{N}{P} e^{-\frac{\varepsilon_i}{k_B T}} \]  

\[ \text{(12)} \]

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 \( \varepsilon_i \) is given by Maxwell-Boltzmann function

\[ f(\varepsilon_i) = \frac{n_i}{g_i} = \frac{1}{e^{\alpha+\beta \varepsilon_i}} \]  

\[ \text{----------------} \]  

\[ f_{MB}(\varepsilon) = A e^{-\frac{\varepsilon}{k_B T}} \]  

\[ \text{----------------} \]

\[ \text{(13)} \]  

\[ \text{(14)} \]

Where,

\[ A = \text{Constant} \]

\[ \text{A depends on the number of particles in the system and plays the same role like normalization constant.} \]

\[ k_B = \text{Boltzmann Constant} \]

\[ = 1.38 \times 10^{-23} \text{ J/K} \]

\[ = 8.617 \times 10^{-3} \text{ eV/K} \]

\[ g_i = \text{Number of quantum states of the} \]

\[ \text{i}^{\text{th}} \text{ energy level} \]