Condition for most probable distribution

The most probable distribution of the particles among various energy states is that for which the probability of occurrence is maximum, i.e. for which Ω_{MB} (eqn (9)) is maximum. Therefore we set,

$$\delta(\log \Omega_{MB}) = 0 \qquad \text{—— (10)}$$

Since Ω_{MB} is very large and inconvenient to handle, we are taking its log here.

According to eqn (1), the total no. of particles of the system are conserved,

$$N = n_1 + n_2 + n_3 + \cdots = \sum n_i = \text{Constant}$$

Therefore in differential form, we can write the above equation as –

$$\sum_i \delta_i n_i = 0 \qquad \text{—— (11)}$$

Similarly from eqn (2), total energy of the system is conserved,

$$E = n_1 E_1 + n_2 E_2 + n_3 E_3 + \cdots = \sum_i n_i E_i = \text{Const.}$$

taking differential of above equation –

$$\sum_i E_i \delta n_i = 0 \qquad \text{—— (12)}$$

Now to find most probable distribution, we have to solve eqn (10), Therefore find the $\log \Omega_{MB}$, by taking log of eqn (9) —

$$\log \Omega_{MB} = \log \left[\frac{N!}{\prod_i n_i!} \left(\prod_i g_i^{n_i} \right) \right]$$

or $\log \Omega_{MB} = \log N! + \sum_i n_i \log g_i - \sum \log n_i!$

Now using stirling approximation -

$\log n! = n \log n - n$ in above eqn -

$$\log \Omega_{MB} = N \log N - N + \sum_i n_i \log g_i - \sum_i (n_i \log n_i - n_i)$$

$$\log \Omega_{MB} = N \log N - \underline{N} + \sum_i n_i \log g_i - \sum n_i \log n_i + \underline{N}$$

$(\because \sum_i n_i = N)$

$$= N \log N + \sum_i n_i \log g_i - \sum_i n_i \log n_i$$

Taking the differential of above eqn -

$$\delta(\log \Omega_{MB}) = \delta(N \log N) + \delta(\sum_i n_i \log g_i) - \delta(\sum_i n_i \log n_i)$$

As N is constant, the above eqn becomes

$$\delta(\log \Omega_{MB}) = \delta(\sum_i n_i \log g_i) - \delta(\sum_i n_i \log n_i)$$

g_i is no. of states of a system, which is also a constant, therefore -

$$\delta(\log \Omega_{MB}) = \sum_i (\delta n_i \log g_i - \delta n_i \log n_i - n_i (\frac{1}{n_i}) \delta n_i)$$

$$= \sum_i (\delta n_i \log g_i - \delta n_i \log n_i - \delta n_i)$$

$$= \sum_i \log \frac{g_i}{n_i} \delta n_i - \delta n_i$$

$$= - \sum_i (\log \frac{n_i}{g_i} + 1) \delta n_i$$

using eqⁿ (10), we equate –

$$\delta(\log \Omega_{MB}) = 0$$

Hence

$$-\sum_i \left(\log \frac{n_i}{g_i} + 1\right) \delta n_i = 0 \quad \text{—— (13)}$$

Now using eqⁿ (11), (12) & (13), & Lagrange's method of undetermined multipliers, where we multiply two unknown constant α and β in eqⁿ (11) & (12) respectively and add into eqⁿ (13) —

$$\sum_i \delta n_i \left[\log \frac{n_i}{g_i} + 1\right] + \alpha \delta n_i + \beta \varepsilon_i \delta n_i = 0$$

or $$\sum_i \left(\left(\log \frac{n_i}{g_i} + 1\right) + \alpha + \beta \varepsilon_i\right) \delta n_i = 0$$

As δn_i can't be zero, hence –

$$\sum_i \left[\left(\log \frac{n_i}{g_i} + 1\right) + \alpha + \beta \varepsilon_i\right] = 0$$

The above result will hold for each i,

$$\log \frac{n_i}{g_i} + \alpha + \beta \varepsilon_i = 0 \quad \left(\text{Here } 1+\alpha = \alpha \text{ new constant}\right)$$

$$\log \frac{n_i}{g_i} = -(\alpha + \beta \varepsilon_i)$$

or $$\frac{n_i}{g_i} = \mathrm{Exp}\left[-(\alpha + \beta \varepsilon_i)\right]$$

or $$n_i = g_i \,\mathrm{Exp}\left[-(\alpha + \beta \varepsilon_i)\right]$$

or $$\boxed{n_i = \frac{g_i}{\mathrm{Exp}(\alpha + \beta \varepsilon_i)}} \qquad (14)$$

The above expression is known as Maxwell-Boltzmann distribution law.

The value of unknown multiplier is—

$$\beta = \frac{1}{kT}$$

Hence $n_i = g_i \, \mathrm{Exp}(-\alpha - \varepsilon_i/kT)$

As $$N = \sum_i n_i$$

$$= \sum_i g_i \, \mathrm{Exp}(-\alpha)\, \mathrm{Exp}(-\varepsilon_i/kT)$$

$$= \mathrm{Exp}(-\alpha) \sum_i g_i \, \mathrm{Exp}(-\varepsilon_i/kT)$$

or $$\mathrm{Exp}(-\alpha) = \frac{N}{\sum_i (g_i \, \mathrm{Exp}(-\varepsilon_i/kT))}$$

Therefore, we can write eq^n (14) as also—

$$n_i = g_i \frac{N}{\sum_i (g_i \, \mathrm{Exp}(-\varepsilon_i/kT))} \mathrm{Exp}(-\beta \varepsilon_i)$$

Here $\sum_i g_i \, \mathrm{Exp}(-\varepsilon_i/kT) = Z$, partition function

$$\Rightarrow \quad n_i = \frac{N}{Z} g_i \, \mathrm{Exp}(-\beta \varepsilon_i)$$

From above formula, we can find, how the distinguishable particles are distributed among the various energy states at a particular temperature.