11/01/25 MPHYCC-8 Statistical Mechanics

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The Most Probable Distribution:

The distribution having highest probability P is the most probable distribution. Since

$$P = \frac{\lfloor N}{\lfloor n_1 \lfloor n_2 \cdots \lfloor n_k} (g_1)^{n_1} (g_2)^{n_2} \cdots (g_k)^{n_k} \quad \text{--- (iii)}$$

Taking natural logarithm of eqn (iii) we will have;

$$\log_e P = \log_e \lfloor N - \sum_{i=1}^{N} \log_e \lfloor n_i + \sum_{i=1}^{k} n_i \log_e g_i$$

Using Stirling's approximation the above expression may be written as;

Since $\boxed{\log_e \lfloor n = n \log_e n - n}$

We will have

$$\log_e P = N \log_e N - \cancel{N} - \sum_i n_i \log_e n_i + \sum_i n_i + \sum_i n_i \log_e g_i$$

Since $\sum n_i = N$. Therefore

$$\log_e P = N \log_e N - \sum_i n_i \log_e n_i + \sum_i n_i \log_e g_i \quad \text{--- (iv)}$$

For the most probable distribution small changes δn_i in any of the n_i's do not affect the value of P or $\log_e P$, i.e.,

$$\frac{\delta(\log_e P_{max})}{\delta n_i} = 0$$

or $\delta(\log_e P_{max}) = 0$

Using eqn (iv) this yields

$$\delta(\log_e P_{max}) = -\sum_i n_i \delta(\log_e n_i) - \sum_i \delta n_i (\log_e n_i) + \sum_i \delta n_i (\log_e g_i) = 0 \quad \text{--- (v)}$$

Since $\delta(N \log_e N) = 0$, as N is constant. Next,

$$\delta(\log_e n_i) = \frac{1}{n_i}\delta n_i$$

and so $\sum_i n_i \delta(\log_e n_i) = \sum_i \delta n_i$

But $\sum_i \delta n_i = 0$, --- (vi)

since the total number of balls $N = \sum_i n_i$ is constant.

$$\therefore \sum n_i \delta(\log_e n_i) = 0.$$

Making this substitution in eqn (v); we get

$$-\sum_i \delta n_i (\log_e n_i) + \sum_i \delta n_i (\log_e g_i) = 0 \quad \text{--- (vii)}$$

Using the method of Lagrange's undetermined multipliers; we can multiply eqn (vi) by a quantity α which does not depend upon any of the n_i's; and we get;

$$\sum_i \alpha\, \delta n_i = 0.$$

Adding it to eqn (vii); we get

$$-\sum_i \delta n_i (\log_e n_i) + \sum_i \delta n_i (\log_e g_i) + \sum_i \alpha\, \delta n_i = 0$$

or, $\sum_i (-\log_e n_i + \log_e g_i + \alpha)\delta n_i = 0.$

As δn_i's are independent variables, therefore; we have

$$-\log_e n_i + \log_e g_i + \alpha = 0$$

or, $n_i = g_i e^{\alpha}$ --- (viii)

Since α doesn't depend upon i, we have;

$$\sum_i n_i = e^{\alpha} \sum_i g_i.$$

But $\sum_i g_i$ is the sum of the a priori probabilities of all the cells and must be equal to 1, as taken above.

$$\therefore \sum_i n_i = e^{\alpha}$$

But $\sum_i n_i = N$ (total number of balls)

$$\therefore e^{\alpha} = N.$$

Hence from eqn. (viii);

$$\boxed{n_i = N g_i}$$

Thus, for most probable distribution, the number of balls in any cell is proportional both to the total number of balls N and to the a priori probability g_i which is equal to the relative size of the cell.

Since $g_i = \frac{a_i}{A}$, Therefore

$$\boxed{n_i = \left(\frac{N}{A}\right) a_i}$$

Thus for most probable distribution, the number of balls in any cell is equal to the product of the average density of balls N/A and the area of the cell.