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MPHYCE-8

Statistical Mechanics

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[#] The Probability of a Distribution:

Consider a large box divided into k cells of areas $a_1, a_2, a_3, \dots, a_k$. Throw N identical (but distinguishable) balls into the box in a completely random manner, so that no part of the box is favoured. Note down the number of balls falling in each cell, and then repeat the experiment a large number of times. It is observed that a particular distribution of balls among the cells occurs more often than any other. This is known as the 'most probable distribution'. Hence, the most probable distribution is one in which the number of balls in each cell is proportional to the size of the cell (a large cell is more likely to be hit than a small cell).

[*] Probabilities of the Various Possible Distributions:

The probability P that the balls be distributed in a certain way among the cells depends upon two factors:

(i) The a priori probability G_i of the distribution, which is based upon the properties of each cell, and

(ii) the Thermodynamic probability W of the distribution, which is the number of different sequences in which the balls may be distributed among the cells without changing the number in each cell.

The a priori probability g_i that a ball falls into the i^{th} cell is the ratio of the area a_i of the cell and the total area A of the entire box. Thus;

$$g_i = \frac{a_i}{A}$$

where $A = a_1 + a_2 + \dots + a_k$.

The sum of the a priori probabilities of all the cells must be 1, since the ball falls somewhere into the box. Thus;

$$\sum_i g_i = g_1 + g_2 + \dots + g_k = 1.$$

From Multiplication Theorem. The probability that two balls fall in the i^{th} cell is $g_i \times g_i = g_i^2$. Therefore, the a priori probability that n_i balls fall in the i^{th} cell is $(g_i)^{n_i}$. Thus the a priori probability G_i of any particular distribution of N balls among the k cells such that n_1 balls fall in the first cell, n_2 balls fall in the second cell

$$G_i = (g_1)^{n_1} (g_2)^{n_2} \dots (g_k)^{n_k}, \dots (2)$$

subject to the condition

$$\sum_i n_i = n_1 + n_2 + \dots + n_k = N$$

If the cells are of equal size; they all have the same a priori probability g , and $G = g^N$.

Next, all the distributions of balls among the cells are not equally probable, then the concept of thermodynamic probability comes. Say n_1 balls in the first cell, n_2 balls in the second cell, ... and so on. There can be a number of ways in which this configuration can be obtained, and this number is the thermodynamic probability Ω for this configuration.

The number of ways in which any n_1 balls out of N balls can fall in the first cell is

$$\Omega_{n_1} = \frac{N!}{n_1! (N-n_1)!}$$

The number of ways in which n_2 balls out of remaining $(N-n_1)$ balls can fall in the second cell is

$$\Omega_{n_2} = \frac{(N-n_1)!}{n_2! (N-n_1-n_2)!}$$

and so on; n_k balls out of remaining $(N-n_1-n_2-\dots-n_{k-1})$ balls can fall in the k th cell in a number of ways

The total number of ways, Ω , in which n_1 balls can fall in cell 1, n_2 in cell 2, ..., and n_k balls in cell k , is

$$\Omega = \frac{N!}{n_1! (N-n_1)!} \times \frac{(N-n_1)!}{n_2! (N-n_1-n_2)!} \times \frac{(N-n_1-n_2)!}{n_3! (N-n_1-n_2-n_3)!} \times \dots \times \frac{(N-n_1-n_2-\dots-n_{k-1})!}{n_k! (N-n_1-n_2-\dots-n_k)!}$$

$$= \frac{N!}{n_1! n_2! n_3! \dots n_k!} \quad \text{--- (ii)}$$

since $n_1 + n_2 + \dots + n_k = N$ and $\Omega = 1$. The total probability P of the distribution is the product of the a priori probability G and the thermodynamic probability Ω given by eqn (i) and (ii)

$$P = \frac{N!}{n_1! n_2! \dots n_k!} (g_1)^{n_1} (g_2)^{n_2} \dots (g_k)^{n_k}$$

where $g_i = \frac{a_i}{A}$, ... (This is the probability of the distribution; n_1 balls in cell of area a_1 , n_2 balls in cell of area a_2 , and so on.)