STATISTICAL PHYSICS

(Part-4)

B.Sc. III (paper-1)

Unit-II

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DISTRIBUTION OF PARTICLES WITH A GIVEN TOTAL ENERGY INTO A DISCRETE SET OF ENERGY STATE

Let N be the total number of particles and E the total energy of a system. There N particles are to be distributed in n energy states of discrete energy values E_1, E_2, E_3, ...$E_{n.}$ If n_1, n_2, n_3,.....n_i are the no. of particles in these energy states in equilibrium, then thermodynamic probability of this macrostat (n_1, n_2, n_3,.....n_i) is given by

$$W = \frac{N}{n1\ n2\ \ldots\ldots\ Ni\ldots\ldots}$$

$$\text{Log } W = \log N - \log n_1 - \log n_2 - \log n_i \qquad \ldots (1)$$

As n_i are in large no. we can use **Stirling's theorem [log x=x log$_e$ x- x]**

$$\text{Log } W = N \log N - N - \{n_1 \log n_1 - n_1\} - \{n_2 \log n_2 - n_2\} \ldots\ldots\ldots \{ni\ log\ ni - ni\}$$

$$= N \log N - N - \sum_i \{\text{ni} \log \text{ni} - \text{ni}\} \qquad \ldots\ldots (2)$$

Now according to constraints

1. Total no. of molecules of the system is constant, i.e. ,

$$N = n_1 + n_2 + n_3 + \ldots.. + n_i + \ldots\ldots.. = \text{constant}$$

$$\delta N = \delta n_1 + \delta n_2 + \delta n_3 + \ldots.. + \delta n_i + \ldots\ldots.. = 0 \qquad .. (3)$$

2. Total energy of the system is constant, i.e. ,

$$E=\varepsilon_1 n_1+ \varepsilon_2 n_2 + \varepsilon_3 n_3 +.....+\varepsilon_i n_i +........=\text{constant}$$

$$E=\varepsilon_1 \delta n_1+ \varepsilon_2 \delta n_2 + \varepsilon_3 \delta n_3 +.....+\varepsilon_i \delta n_i +........=0 \qquad ..... (4)$$

Now diff. eq. (2) w. r. t (n_1, n_2 .... n_i) and remembering that in equilibrium, the thermodynamic probability W is maximum, i.e., W=0 and hence $\delta \log_e W=0$.

Thus, we get

$$\delta \log_e (W) = - \sum_i \{ \log ni\, \delta ni + ni(\log ni) - \delta ni \} = 0$$

$$\sum_i \{ \log ni\, \delta ni + ni \left(\frac{1}{ni}\right) \delta ni - \delta ni \} = 0$$

$$\sum_i \{ \log ni\, \delta ni \} =0$$

$$logn_1 \delta n_1+ logn_2 \delta n_2 + logn_3 \delta n_3 +.....+logn_i \delta n_i +........=0 \qquad ..... (5)$$

Now from eq. (3),we have

$$\delta n_1+ \delta n_2 + \delta n_3 +.....+ \delta n_i +........= 0 \qquad .... (6)$$

This means if any of the cells gains molecules, the orther cells must given up the same no. of molecules.

Now from eq. (4), we have

$$\varepsilon_1 \delta n_1+ \varepsilon_2 \delta n_2 + \varepsilon_3 \delta n_3 +.....+\varepsilon_i \delta n_i +........=0 \qquad ..... (7)$$

Equations(5), (6) and (7) are independent of one other and they must be satisfied at the same time.

Let us multiply eq. (6) by α and eq. (7) by β and sdding the resultant equations and eq. (5), we get

$$(log\,n_1 \delta n_1 + log\,n_2 \delta n_2 + log\,n_3 \delta n_3 + \ldots + log\,n_i \delta n_i + \ldots) + \alpha(\delta n_1 + \delta n_2 + \delta n_3 + \ldots + \delta n_i + \ldots) + \beta(\varepsilon_1 \delta n_1 + \varepsilon_2 \delta n_2 + \varepsilon_3 \delta n_3 + \ldots + \varepsilon_i \delta n_i + \ldots) = 0$$

Collecting the coefficient of $\delta n_{1,}\ \delta n_2$ …. δn_i …….We get

$$(log\,n_1 + \alpha + \beta\,\varepsilon_1)\,\delta n_1 + (log\,n_2 + \alpha + \beta\,\varepsilon_2)\,\delta n_2 + \ldots + (log\,n_i + \alpha + \beta\,\varepsilon_i)\,\delta n_i + \ldots = 0 \qquad \ldots (8)$$

There δn_i's must satisfy the conditions eq.(6) and eq.(7), otherwise they may vary arbitarity. Let us consider δn_3 , δn_4 as independent, then eq.(6) and eq.(7), determine $\delta n_{1,}$ δn_2 in term other δn_i's . as α and β are conditions, let us assign them value such that

$$log\,n_1 + \alpha + \beta\,\varepsilon_1 = 0$$

$$log\,n_2 + \alpha + \beta\,\varepsilon_2 = 0 \qquad \ldots\ldots (9)$$

Then eq. (8) become

$$(log\,n_3 + \alpha + \beta\varepsilon_3)\,\delta n_3 + (log\,n_4 + \alpha + \beta\,\varepsilon_4)\,\delta n_4 + \ldots + (log\,n_i + \alpha + \beta\,\varepsilon_i)\,\delta n_i + \ldots = 0 \qquad \ldots (10)$$

In this eq. all δn_i's are independent of each other, therefore, if eq. (10) is to be satisfied, the coefficient of each must vanish.

Thus $log n_i + \alpha + \beta \varepsilon_i = 0$ for any value of i.

Which given

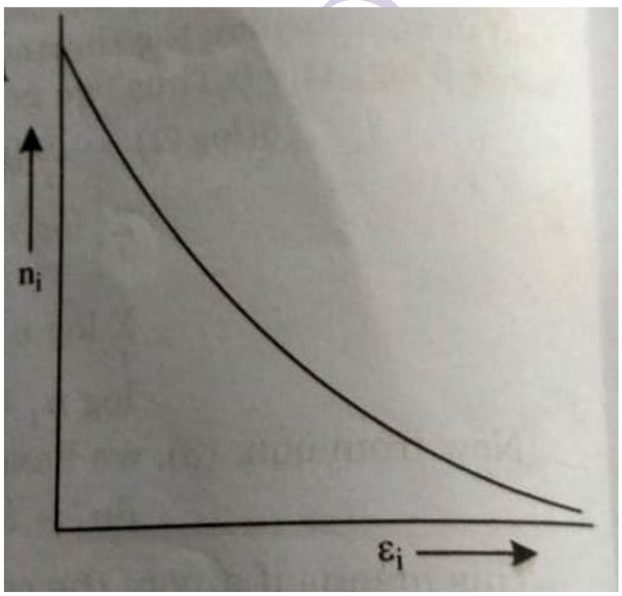
$$n_i = e^{-(\alpha + \beta \varepsilon_i)}$$

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

Let $A = e^{-\alpha}$

Then,

$$n_i = A e^{-\beta \varepsilon_i} \qquad \ldots\ldots (11)$$



This eq.(11) gives the no. of particles n_i in each other energy state ε_i. According to graph the no. of molecules per cell decreases exponentially with ε_i associated with the cell.

Now consider a group of adjacent cells in the phase space. Such group is called zone of cells. Since the cells are of equal size, the size is proportional to the no. of cells in it. If gi is the number of cells in a zone, then clearly the probability of finding a molecule in the zone which only be proportional to gi. This gi is called then a **priori probability** for zone number only depends on the size of the zone.

If we consider a zone of cells all corresponding to about the same time energy ε_i then the no. of particles in this zone will be given by

,
$$n_i = A\, g_i e^{-\beta \varepsilon_i}$$

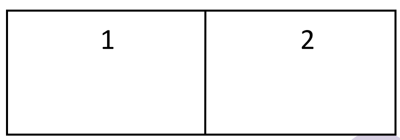
<u>THE POSTULATE OF EQUAL A PRIORI *PROBABILITIES*</u>

Suppose you have measured a set of macroscopic variables for an isolated system. You now know which macrostate it is in, but there may be a huge number of microstates all consistent with that macrostate. What can you say about which one of those it is most likely to be in?

The answer, of course, is that you have no idea. Your measurements do not provide any further information to answer that question. Nonetheless, to calculate any averages or other statistical quantities you must assume something. This leads us to the following assumption:

A system has an equal probability of being in any microstate that is consistent with its current macrostate. **or** An isolated system that satisfies the postulate of equal *a priori* probabilities is said to be in *equilibrium*.

Ex: if we toss a coin, the coin will fall either with its head up or tail up. Similarly, if we have an open box divided into two compartment of equal size in below fig. and a small particle is thrown in such a way that it must fall in either of the two compartment, then the probability of falling the particle in compartment 1 is equal to ½ and it is equal to the probability of falling the particle in the compartment 2. Thus the probabilities for events, which are equally likely, are



Example- A coin is tossed twice. What is the probability of getting two consecutive tails ?

Probability of getting a tail in one toss = 1/2

The coin is tossed twice. So 1/2 * 1/2 = 1/4 is the answer.

Here's the verification of the above answer with the help of sample space.

When a coin is tossed twice, the sample space is {(H,H), (H,T), (T,H), (T,T)}.

Our desired event is (T,T) whose occurrence is only once out of four possible outcomes and hence, our answer is 1/4.

Example : What is the probability of drawing a king and a queen consecutively from a deck of 52 cards, without replacement.
Probability of drawing a king = 4/52 = 1/13

After drawing one card, the number of cards are 51.

Probability of drawing a queen = 4/51.

Now, the probability of drawing a king and queen consecutively is 1/13 * 4/51 = 4/663

Reference books:

Statistical mechanics by **Satya Prakash.**

Relativity and statistical physics by **J.C. Agarwa**l.

Heat thermodynamics and statistical by **Dr. N. Subramaniam Brijlal**.