-5-17 STATISTICAL MECHANICS

In analytical mechanics, we applies laws of motion to individual bodies whose motion can easily observed. for example if we observe the position & velocity of a body at a given time we can predict its position & velocity after some time. Thus the laws of motion enable us to determin the path of body in space.

When we have to be with a system containing billions of small bodies moving at random, such as a gas containing a large number of molecules, the methods of analytical mechanics become impossible.

Our first difficulty is that we cannot observe individual molecule. we can observe only the average properties such as temperature, pressure, volume etc of the gas. Even if we succeed in observing individual molecule the collection of enormous data (i-e a record of position & velocities of millions of molecules) & the ~~observation~~ application of laws of motion to each molecule will make the method of analytical mechanics an impossible task. Hence we adopt an entirely different approach for studying the behaviour of a thermodynamics system composed of large number of

Important: individuals such as gases. Instead of

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measuring the individual velocities of molecules we measure their average velocity. In otherwords we ~~desire~~ try to study the average properties of molecules & not their individual effects. The properties such as temper, pressure, volume, entropy etc indicates the behaviour of molecule as a whole & not the behaviour of a single molecule. Thus the term "temp of gas" indicates some property which is produced by the combined action of all the molecules of the gas. The term "temperature of molecule" has no sense. This type of mechanics which deals with the average effects of large number of individuals is called statistical mechanics. It may be regarded as the collection of laws of mechanics which can be applicable ~~to be~~ / applied to thermal equilibrium

As number of molecules in a gas is very large their motion ~~be~~ is controlled by chance or by the laws of probability and so the gas tends to acquire that states which is more probable. The gas also tend to acquire that ~~that~~ state for which its entropy attains maximum value it is obvious that their must be some relation b/w entropy & probability

Important:

This important relation was first discovered by Boltzman. The probability of an event can be measured very approximately by the relation

$$\text{Probability} = \frac{\text{number of favourable events}}{\text{Total number of possible events}}$$

In thermodynamics we use only dS i.e the change in entropy. The Bolzman relation can also be written as

$$S = K \log W$$

This relation can be used to find the distribution of molecules, energy, molecular velocities in a perfect gas.

While dealing with kinetic theory the average translational K.E of molecules of gas was determined. However the knowledge of average values doesn't tell us how the speeds of individual molecules are distributed above the average value. In some cases the average value might provide sufficient information about the properties of gas such as its temperature. In other cases more information about the distribution of speed may be required.

While designing a commercial passenger aircraft, we must be interested in average

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weight of passengers & their luggage. so as to estimate the lift required for the plane. On the other hand while ordering the suite for ~~a~~ a clothing store, we must be interested in the information about distribution of sizes rather an average size of customers, However in case of commercial passenger aircraft, the number of overweight or underweight passenger is of little importance

In statistical mechanics we are are interested in the distribution of molecular speed & their energies for determining the macroscopic properties of collections of molecules. Maxwell, Gibbs & Boltzmann developed classical formulation ~~found-ation~~ in the 19th century. In the 20th century Einstein, Planck, Fermi & others applied most of their classical formulations to system governed by the laws of Quantum mechanics

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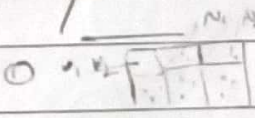
DISTRIBUTION OF MOLECULES IN A PERFECT GAS:

⇒ Let N denote the number of molecule in volume V of a perfect gas. We shall prove that when the gas is in thermodynamic equilibrium its molecules are uniformally distributed throughout the volume of gas and the density of the molecules has the constant value $\left(\frac{N}{V}\right)$ in any part of the gas.

The ration N/V is clearly the average value of the density of molecule for the whole gas



Suppose the volume V is divided into large number of cells having volume $v_1, v_2, v_3 \ldots\ldots$ etc which contain $N_1, N_2, \ldots N_3 \ldots\ldots$ etc molecules respectively. Let the volume of each cell be made very small but large enough to accomodate a large number of molecules which are nearly point masses. Thus $N_1, N_2, \ldots$ etc can be regarded as large numbers.

It is obvious that $N_1 + N_2 + N_3 + \ldots\ldots = N$

or $\Sigma N_i = N$ where $i = 1, 2, 3, \ldots$ etc

as N is a constant we must have $\delta N = 0$ so differentials of above eq shows $\Sigma \delta N_i = 0$

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(a) If all the N molecules are different their possible no. of arrangement is equal to the permutations of N different objects, each permutation containing all the objects or ~~N~~ fictorial $N!$

When N_1 molecules of the cell having volume V_1 are made identical, let the number of different permutations be now 'x' ~~be~~ If the N_1 molecules be again different we can make $N_1!$ different permutations out of each of the x permutations thus

$$(x)(N_1!) = N!$$

$$x = \frac{N!}{N_1!}$$

which shows that by making N_1 molecules of cell 1 exactly similar the number of different permutations $N!$ is reduced to $\frac{N!}{N_1!}$

b) (It follows that if all the gas molecules are identical) in the cell containing N_1, N_2, N_3 ----- etc molecules, the number of different permutations or (microscopic state) will be reduced form

$$N! \text{ to } \frac{N!}{(N_1!)(N_2!)(N_3!)\text{---}}$$

Important: As the molecules of ideal gas are supposed to be identical. The number of microscopic states is given by

$$x = \frac{N!}{(N_1!)(N_2!)(N_3!)\ldots}$$

STATISTICAL DISTRIBUTIONS & MEANS VALUES:

→ Suppose a highway engineer wants to collect information about the distribution of speed of vahicals on a certain section of the road for the purpose of improving the road.

A simple determination of average speed of vehicals cannot provide useful data for the purpose.

The best way to have useful data is to sort out the speeds into groups or intervals of 5mph each. eg speeds between zero & five km/hrs, between 5 & 10mph ....

We then count the number of vehicals possesing the speeds in the sorted interval.

finally we construct a plot between

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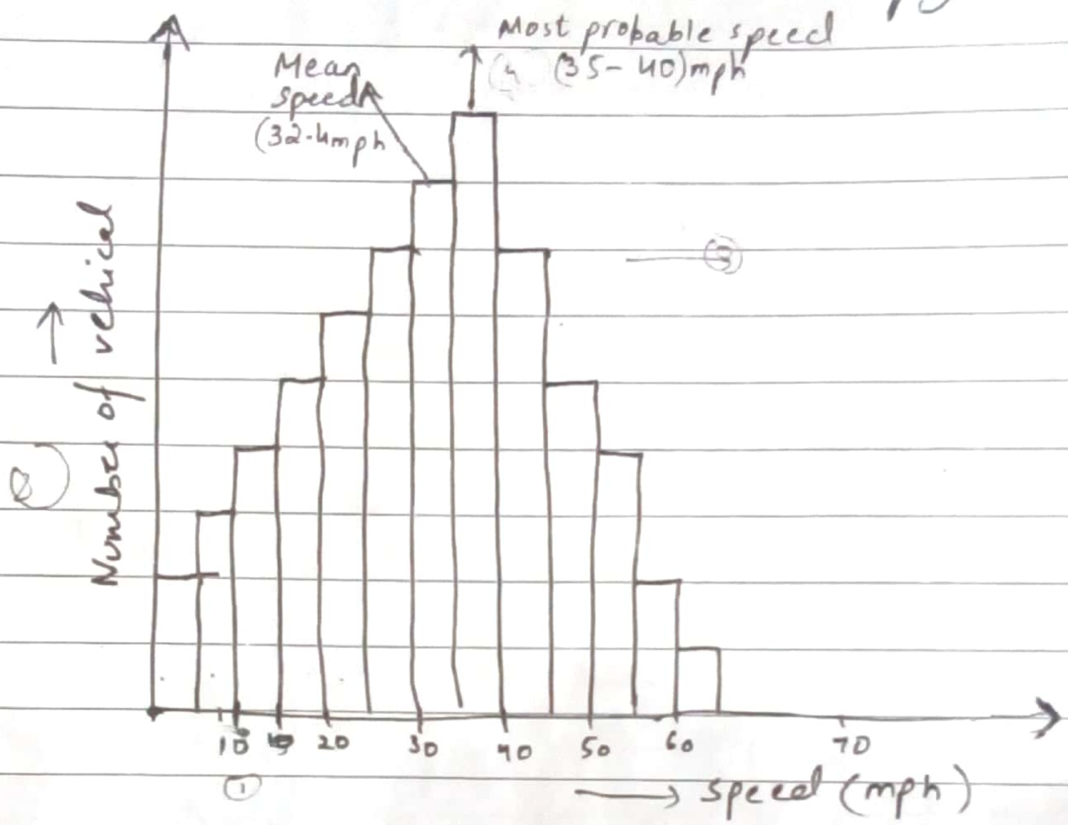
and the number of vehical possessing speed in the sorted intervals along the vertical as shown in the figure



Statichical distribution of speeds of vehicals

As shown in fig.
Such a statistical distribution of speed is called histrogram.

In the histogram, each rectangle has a width equal to size of speed interval i-e 5mph & its height equal to the vehicals possessing speed in that interval or simply the number of observations or relative frequency of values in that intervals.

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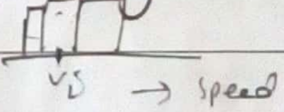
The sum of heighest of all rectangles gives the total number of vehicals in overall survey.

The average or mean value of speed $\bar{v}$ can be computed from the statistical distribution of figure as shown before.

→ let us label the speed interval as $i = 1, 2, 3, 4 \ldots r$ values

let v_i be the representative value of the speed in each interval, probably at the center of each interval.



→ let us assume that each speed interval has the same width δV (for simplicity) defined as $\delta V = V_2 - V_1 = V_3 - V_2 = \ldots\ldots$ and the height

$n_i(v_i)$ representing the number of vehicals (or observations). for the interval corresponding to the representing speed v_i obviously.

* Total number of observations (or total number of vehicals) is given by

$$N = n_1(v_1) + n_2(v_2) + n_3(v_3) + \ldots$$

$$N = \sum_{i=1}^{n} n_i(v_i) \quad \text{———} \quad (I)$$

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The average or mean speed ~~speed~~ is defined as

$$\bar{v} = \frac{n_1(v_1) \times v_1 + n_2(v_2) \times v_2 + n_3(v_3) \times v_3 + \cdots}{n_1(v_1) + n_2(v_2) + n_3(v_3) + \cdots}$$

$$= \frac{\sum_{i=1}^{r} v_i\, n_i(v_i)}{\sum_{i=1}^{r} n_i(v_i)} \quad \text{——— (2)}$$

$$\sum_{i=1}^{r} n_i(v_i) = n$$

This eq (2) is identical with that use for calculating the center of mass of a system of particles

$$R_{cm} = \frac{m_1 r_1 + m_2 r_2 + m_3 r_3 + \cdots}{m_1 + m_2 + m_3 + \cdots}$$

$$= \frac{\sum m_i r_i}{\sum m_i} \quad \text{——— (3)}$$

$v = r\omega$

$I = .$

$$= \frac{\sum m_i v_i}{M}$$

Thus the center of mass of particles in a system can be regarded as a sort of average location for the particle in the system. We can also define relative frequency or probability of any value v_i of any interval of width δ

$$f(v_i) = \frac{n_i(v_i)}{\sum_{i=1}^{r} n_i(v_i)}$$

~~no. of favourable event / total no. of possible events~~

$$= \frac{n_i(v_i)}{N} \quad \text{——— (4)}$$

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combining eq. ② & ④

$$\bar{v} = \sum_{i=1}^{r} v_i f(v_i) \quad \text{——— ⑤}$$

for example if number of observations

(Cars) vehicals having speed in speed intervals (0-5) is 23 & total number of cars is ~~12,005~~ 1205. We have

$$n_i(v_i) = n_i(5) = 23$$

$$\sum_{i=1}^{r} n_i(v_i) = 1205$$

$$f(v_i) = \frac{n_i(v_i)}{\sum_{i=1}^{r} n_i(v_i)} = \frac{23}{1205} = 0.019 = 1.9\%$$

Problem: find the mean value of the speed for the distribution given in the following data taking value of speed at the middle of each speed interval

No of Intervals	Speed Intervals (km/h)	Number of cars in different speed intervals
1	0 - 5	23
2	5 - 10	41
3	10 - 15	54
4	15 - 20	95
5	20 - 25	123
6	25 - 30	142
7	30 - 35	177
8	35 - 40	186
9	40 - 45	170

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10	45 - 50	122
11	50 - 55	50
12	55 - 60	15
13	60 - 65	7
		$\sum n_i(v_i) = 1205$

Average speed:

$$\bar{v} = \frac{\sum_{i=1}^{r} v_i\, n_i(v_i)}{\sum_{i=1}^{r} n_i(v_i)}$$

$$\bar{v} = \frac{n_1(v_1) \times v_1 + n_2(v_2) \times v_2 + n_3(v_3) \times v_3 + \cdots n_{13}(v_{13})\, v_{13}}{n_1(v_1) + n_2(v_2) + n_3(v_3) + \cdots n_{13}(v_{13})}$$

$v_1 = \frac{0+5}{2} = 2.5$ $\qquad v_9$

$v_2 = \frac{5+10}{2} = 7.5$ $\qquad v_{10}$

$v_3 = \frac{10+15}{2} = 12.5$ $\qquad v_{11}$

v_4 $\qquad v_{12}$

v_5 $\qquad v_{13}$

v_6

v_7

Important: v_8

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$$\bar{v} = \frac{(23)(2.5) + (41)(7.5) + \ldots}{1205}$$

$\bar{v} = 32.2$ mph

MEAN FREE PATH:

The molecule of ideal gas travelling through gas collides with other molecules in its path and makes random motion.

"The average distance travelled by molecules between collision is called mean free path and denoted by 'λ'"

The mean free path depend upon the following

① Mean free path and density:-

→ The mean free path travelled by molecules is inversely propotional to the number of molecules per unit volume (N/V) or density of molecules.
It is due to the fact that their will be more collosions when density of molecules is larger which gives smaller mean free path