

THERMODYNAMICS

Therm - heat

dynamics = motion

Thermodynamics means "Heat in motion"

It is that branch of physics which deals with the transformation of heat = energy into mechanical energy and vice versa or

② that branch of physics which deals with the various phenomenon of energy, related properties of matter especially with the laws of transformation of heat with the other forms of energy and vice versa is called thermodynamics

Thermodynamics explain the bulk properties of matter such as pressure, specific heat etc, in microscopic way i.e. It makes no reference to detailed atomic or molecular or other microscopic constituents of matter.

Uses

→ It is widely used in the design of heat engine, steam turbines, refrigerators, physical chemistry and chemical physics

To get a deeper insight and understanding into the laws of thermodynamics, molecular concepts of matter can be incorporated into the study of thermodynamics by means of statistical

Important: mechanics

→ TEMPERATURE:

The average kinetic energy of the molecules of the system is called temperature.

→ MACROSCOPIC AND MICROSCOPIC DESCRIPTION

→ A liter of gas contains about 3×10^{23} molecules which will treat as a point mass, colliding elastically with one another and with the walls of container.

Knowing the initial position and velocity of every point mass (particle) we can deduce their values at any future time by applying Newton's laws. With that information we could calculate the net impulsive force ^{exerted} on an element of area of the container. We call this the microscopic description of the system.

Since the number of particles is large enough we treat the system using average values of the microscopic quantities. This approach is called statistical mechanics.

→ If we describe the system considering its interactions with its surroundings (environment) in terms of small number of overall readily measurable properties, we call this macroscopic description of the system.

⇒ ZEROth LAW OF THERMODYNAMICS:

Statement:

If systems 'A' & 'B' are reached in thermal equilibrium with a third system 'C', then system 'A' & 'B' are in thermal equilibrium with each other.

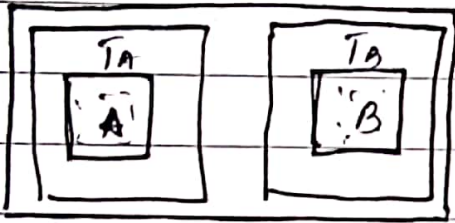


fig (a)

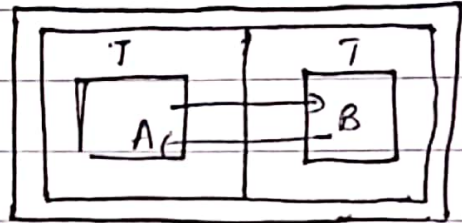


fig (b)

Consider a system 'A' & 'B' isolated from one another and from the environment by surrounding the system with adiabatic ^{walls} or heat insulating walls as shown in figure 'a'. Under this condition changes in the properties of one system may have no effect on the other system - when the two systems are placed in thermal contact through a conducting or diathermic wall, the exchange of energy causes the macroscopic properties of the two systems to change as shown in the fig (b). After some time the macroscopic properties approach constant values and systems are said to be in thermal equilibrium with each other.

In order to test thermal equilibrium separated systems without bringing them into thermal contact we use a third system C. By placing C in thermal contact first with system A and then with system B, we can discover whether systems A and B are in thermal equilibrium without bringing them into direct contact.

This process leads to the postulate called the zeroth law of thermodynamics.

Zeroth law in effect defines the concept of temperature which is fundamental to the first and second laws of thermodynamics. The law that establishes the concept of temperature should precede the first and second laws of thermodynamics in labelling this is why called zeroth law.

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 proportional to the number of molecules per unit volume (N/V) or density of molecules.

It is due to the fact that there will be more collisions when density of molecules is larger which gives small mean free path.

② Mean free path by size of molecules.

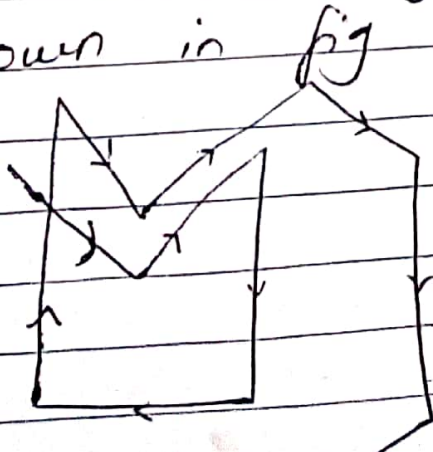
The mean free path travelled by molecules is inversely proportional to size of molecules such as diameter.

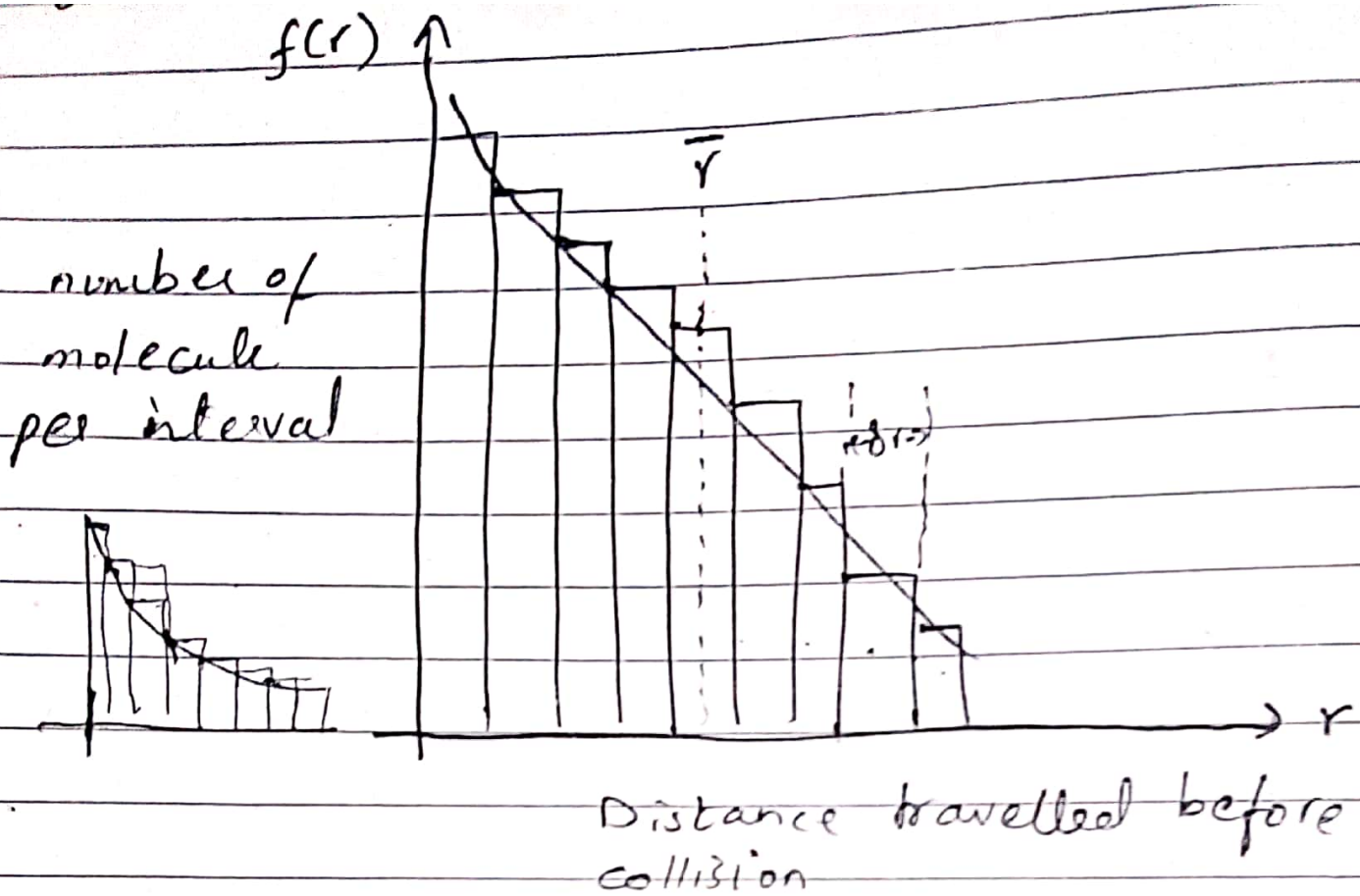
The mean free path is infinite when molecules are point particles because they never collide. The mean free path is small when size of molecules is large.

③ Mean free path by crosssection of molecules.

It should be inversely proportional to the square of molecular diameter because crosssection of a molecule determines its effective target area.

Single out a molecule in a gas then follow its motion. We shall see that the molecule follows a zigzag path due to collisions with neighbouring molecules as shown in fig.





The average distance is defined

$$\bar{r} = \frac{\sum r_i n_i(r_i)}{\sum n_i(r_i)}$$

$$\bar{r} = \frac{\sum r_i n_i(r_i)}{N} \quad \text{--- (1)}$$

(we can also define relative frequency or probability of any value r_i in any interval of width δr as

$$f(r_i) = \frac{n_i(r_i)}{\sum n_j(r_j)}$$

important:

MICROSCOPIC CALCULATION / DERIVATION OF FORMULA OF MEAN FREE PATH:

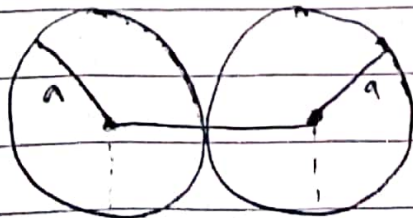
In this section we will try to interpret the mean free path (a macroscopic quantity) from the microscopic properties of the molecules.

~~Ques~~

→ If the molecules are treated as hard point masses they will not collide at all. and hence the mean free path would be infinite.

However molecules are not point masses and hence collision occurs. If the molecules are so abundant that they occupy completely all the space available to them, leaving no room for translational motion, the mean free path will be zero.

Thus we see that free path depends upon the size of molecules & the number of molecules per unit volume (N/V).



$$d = 2a \quad \text{diag (a)}$$

$$a = \frac{d}{2}$$

Important:

Date: 16-5-17

The effective cross-sectional area of the molecule or its collision cross-section d is the area of the circular disc of radius ' $r = d = 2a$ ' centered at the center of moving molecule as shown in fig (c) that is

$$G = \pi r^2$$
$$= \pi d^2$$

$$G = \pi (2a)^2$$

$$G = 4\pi a^2$$

In time t the moving molecule covers a distance $\bar{v}t$ and sweeps a cylinder of length $\bar{v}t$ and base area

$$G = 4\pi a^2 = \pi (2a)^2 = \pi d^2$$

During this time t the moving molecule will make collision with other molecules whose centers lie within the volume of cylinder

$$= \text{cross-section area} \times \text{length}$$

$$= \sigma \times (\bar{v}t)$$

$$= \sigma \bar{v}t$$

2) If n denotes the number of molecules per unit volume of the gas, the number of molecules whose centers lie within the cylinder is $n\sigma\bar{v}t$ which is the measure of

total collisions made by the moving molecule in time t with other molecules (assumed stationary and more geometrical points)

The number of collisions per second is called frequency or collision frequency is obviously

$$f = \frac{n \sigma \bar{v} t}{t} \quad \left. \begin{array}{l} \text{no. of collisions} \\ \text{time} \end{array} \right\} \text{no. of molecules}$$

$$\left. \begin{array}{l} f = n \sigma \bar{v} \\ f = n \sigma \langle v \rangle \end{array} \right\} \textcircled{1}$$

and mean free path is given by
 $\lambda = \frac{\text{total distance covered during collision}}{\text{total number of collisions}}$

or

$$\lambda = \frac{\bar{v} t}{n \sigma \bar{v} t} = \frac{1}{n \sigma}$$

$$\lambda = \frac{1}{n \pi d^2} \quad \textcircled{2}$$

from eq $\textcircled{1}$ we get

$$n = \frac{1}{\lambda}$$

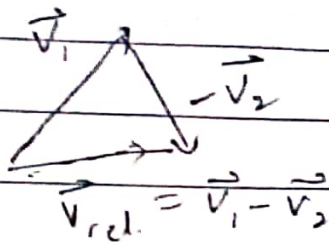
so $\textcircled{2}$ will be

$$\lambda = \frac{1}{\cancel{n \sigma \bar{v}} \pi d^2} = \frac{1}{\frac{1}{\lambda} \sigma \bar{v} \pi d^2} = \frac{\lambda \bar{v}}{\sigma \pi d^2}$$

$$= \frac{\lambda d^2 \bar{v}}{\sigma \pi d^2}$$

$$\lambda = \frac{\bar{v}}{c}$$

Important



The magnitude of relative velocity can be expressed as the square root of the scalar product of the velocity with itself

$$\vec{v}_{rel} \cdot \vec{v}_{rel} = |\vec{v}_{rel}| |\vec{v}_{rel}| \cos 0^\circ$$

$$= |\vec{v}_{rel}| |\vec{v}_{rel}| \quad (1)$$

$$= |\vec{v}_{rel}|^2$$

$$\sqrt{\vec{v}_{rel} \cdot \vec{v}_{rel}} = v_{rel}$$

This expression can be expanded as follows

$$v_{rel} = \sqrt{(\vec{v}_1 - \vec{v}_2) \cdot (\vec{v}_1 - \vec{v}_2)}$$

$$v_{rel} = \sqrt{\vec{v}_1 \cdot \vec{v}_1 - 2\vec{v}_1 \cdot \vec{v}_2 + \vec{v}_2 \cdot \vec{v}_2}$$

taking the average of the terms leads to

$$\langle v_{rel} \rangle = \sqrt{\langle \vec{v}_1 \cdot \vec{v}_1 \rangle - 2\langle \vec{v}_1 \cdot \vec{v}_2 \rangle + \langle \vec{v}_2 \cdot \vec{v}_2 \rangle}$$

where $\langle \vec{v}_1 \cdot \vec{v}_2 \rangle = 0$

so

$$\langle v_{rel} \rangle = \sqrt{\langle \vec{v}_1 \cdot \vec{v}_1 \rangle + \langle \vec{v}_2 \cdot \vec{v}_2 \rangle}$$

$$= \sqrt{\langle v_1^2 \rangle + \langle v_2^2 \rangle}$$

Important:

Since the same average velocity
 $\langle v_1^2 \rangle = \langle v_2^2 \rangle$ or $\langle v_1^2 \rangle = \langle v_2^2 \rangle$ would be associated
 with each molecule - this becomes

~~$$\langle v_{rel} \rangle = \sqrt{\langle v_1^2 \rangle + \langle v_2^2 \rangle}$$~~

$$\langle v_{rel} \rangle = \sqrt{\langle v_1^2 \rangle + \langle v_1^2 \rangle}$$

$$= \sqrt{2 \langle v_1^2 \rangle}$$

$$\langle v_{rel} \rangle = \sqrt{2} \langle v_1 \rangle \text{ or } \sqrt{2} \langle v \rangle$$

The average mean free path when
 actual speed distribution of the
 molecule is taken into account is
 given by

$$\lambda = \frac{\langle v \rangle t}{n \pi d^2 (\langle v_{rel} \rangle t)}$$

$$= \frac{\langle v \rangle}{n \pi d^2 \sqrt{2} \langle v \rangle}$$

$$\lambda = \frac{1}{\sqrt{2} n \pi d^2}$$

Result.

it follows that when we take into account
 the motion of target molecule, collision frequency
 increases and mean free path decreases.

At a given temperature the mean free path
 varies inversely as the gas ~~press~~ pressure.

Since the number of molecules per unit volume
 varies directly as the pressure

important: