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Maxwell's law of velocity distribution:-

We know from kinetic theory that a gas is made up of very large number of molecules which are always in a state of motion. They are frequently colliding with one another and also with the walls of the containing vessel. Hence their speeds and directions of motion are changing. We may therefore conclude that at any time, molecules of all possible speeds are present in the gas. However, the root-mean-square speed of the gas molecules remains unchanged at a given temperature.

Maxwell considered the distribution of speeds among the molecules of the gas. He made the following assumptions:

(1) The gas consists of molecules with all possible speeds between 0 and ∞.

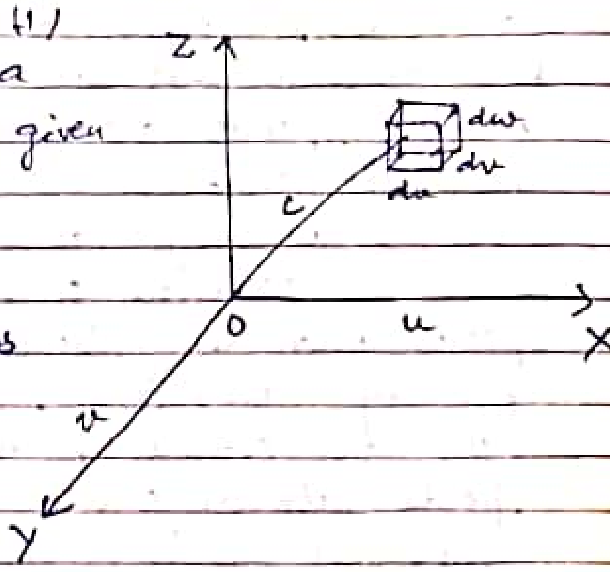
(2) When the gas is in the steady state, its density remains, on the average, uniform througout.

(3) Though the speeds of individual molecules are changing, but definite numbers of molecules have speeds between definite ranges.

Derivation:- Let us consider a gas containing a total number of molecules N. Let u, v, w be the component velocities of a molecule. From probability theory, the number of molecules having component velocities between u and $u+du$ can be denoted by $N f(u)\,du$, $f(u)$ is a function of u to be determined. Similar expressions exist for other directions with the same function f because there is no preferred direction in the gas. Therefore, the number of molecules whose velocity components lie between u and $u+du$, v and $v+dv$, and w and $w+dw$ is

$$dN = N f(u) f(v) f(w)\, du\, dv\, dw \quad \text{--- (1)}$$

Let us draw coordinate axes OX, OY, OZ along which the components u, v, w of a velocity c are respectively measured. A molecule having the velocity components u, v, w will be represented by a point whose coordinates are u, v, w and the molecules dN will be contained in the element of volume $du, dv\, dw$ in fig (1)



These molecules have a resultant velocity c given by

$$c^2 = u^2 + v^2 + w^2,$$

and so we can express dN also as

$$dN = N F(c^2)\, du\, dv\, dw, \qquad \text{—— (ii)}$$

where F is some function of c^2. Thus, from eq^n. (i) & (ii), we have

$$f(u) f(v) f(w)\, du\, dv\, dw = F(c^2)\, du\, dv\, dw.$$

The function $F(c^2)$ is constant at all points at the same radial distance c from the origin. Therefore, $dF(c^2) = 0$ for c = constant.

This, from the last expression, means that

$$d\left[f(u) f(v) f(w)\right] = 0$$

or $f'(u)\, du\, f(v) f(w) + f'(v)\, dv\, f(u) f(w) + f'(w)\, dw\, f(u) f(v) = 0$

Dividing by $f(u) f(v) f(w)$, we get

$$\frac{f'(u)}{f(u)} du + \frac{f'(v)}{f(v)} dv + \frac{f'(w)}{f(w)} = 0 \qquad \text{—— (iii)}$$

Now, for constant value of c, since $u^2+v^2+w^2=c^2$, we have

$$u\,du + v\,dv + w\,dw = 0 \qquad \text{—— (iv)}$$

To solve ~~the~~ eqn. (iii) and (iv), we multiply (iv) by an arbitrary constant β and add the result to (iii). This gives

$$\left\{\frac{f'(u)}{f(u)} + \beta u\right\} du + \left\{\frac{f'(v)}{f(v)} + \beta v\right\} dv + \left\{\frac{f'(w)}{f(w)} + \beta w\right\} dw = 0. \qquad \text{—— (v)}$$

Each term is independent of others, so each must be separately zero. Since du, dv, dw are not zero, we have

$$\frac{f'(u)}{f(u)} + \beta u = 0$$

or

$$\frac{f'(u)}{f(u)} = -\beta u$$

Integrating with respect to u, we obtain

$$\log f(u) = -\frac{1}{2}\beta u^2 + \log a,$$

where $\log a$ ~~is~~ is integration constant. This can be written as

$$f(u) = a e^{-\frac{1}{2}\beta u^2} = a e^{-bu^2},$$

where a and b are constants.

Treating the other ~~terms~~ two terms of eq (v) in the same manner, we shall have,

$$f(u) f(v) f(w) = a^3 e^{-b(u^2+v^2+w^2)}.$$

The eqn. (i) may now be written as

$$dN = N a^3 e^{-b(u^2+v^2+w^2)}\, du\, dv\, dw \qquad \text{—— (vi)}$$

The value of the constant a may be found by expressing the fact that the total number of molecules is N, that is,

$$\int dN = N$$

or $$N a^3 \int_{-\infty}^{+\infty}\int\int e^{-b(u^2+v^2+w^2)}\, du\, dv\, dw = N$$

The value of the integrals is $\left(\frac{\pi}{b}\right)^{3/2}$. Therefore,

$$a^3 (\pi/b)^{3/2} = 1$$

or $$a = \sqrt{b/\pi}$$

The constant b can be determined by using $\frac{1}{2} m\bar{c}^2 = \frac{3}{2} kT$ and calculating $\bar{c}^2$.

It is found that

$$b = \frac{m}{2kT}$$

and so $$a = \sqrt{\frac{m}{2\pi kT}}$$

Making these substitutions in eqn. (vi), the number dN of molecules having velocity components lying between u and $u+du$, v and $v+dv$ and $w+dw$ is

$$dN = N\left(\frac{m}{2\pi kT}\right)^{3/2} e^{-\frac{m(u^2+v^2+w^2)}{2kT}}\, du\, dv\, dw \qquad \text{—(vii)}$$

This is Maxwell's distribution law of velocities.

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