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Topic for

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MAXWELL'S DISTRIBUTION LAW FOR THE DISTRIBUTION OF MOLECULAR SPEEDS

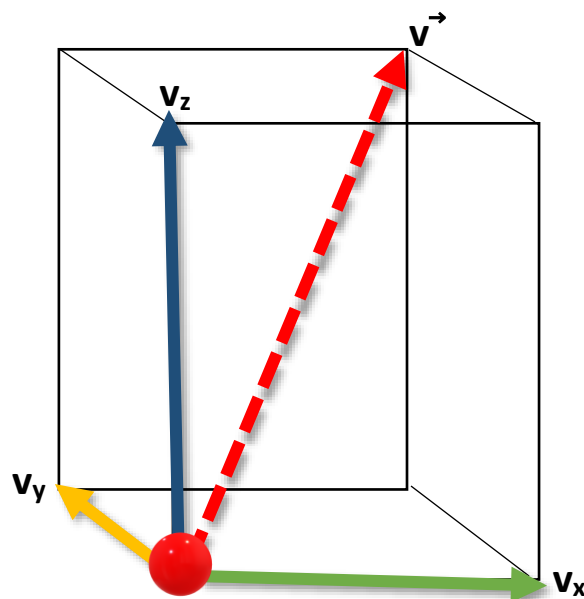
Scottish physicist James Clerk Maxwell developed his kinetic theory of gases in 1859. He determined the distribution of velocities among the molecules of a gas. In 1871 German physicist, Ludwig Boltzmann generalized Maxwell's finding to express the distribution of energies among the molecules.

**Speed vs Velocity**

Speed is the rate of change of distance with time. It has only magnitude. So, it is a scalar quantity.

Velocity is the rate of change of displacement with time. It has both magnitude and direction. So, it is a vector quantity

In Cartesian coordinate system the velocity vector  $\vec{v}$  of a gas molecule can be represented by its components ( $v_x, v_y, v_z$ ) along three directions (x,y,z).



We can write,  $|\mathbf{v}^{\rightarrow}| = (v_x^2 + v_y^2 + v_z^2)^{1/2}$

$$|\mathbf{v}^{\rightarrow}|^2 = (v_x^2 + v_y^2 + v_z^2)$$

### **Assumptions of Kinetic Theory**

- (a) Gas molecules are continuously colliding against one another. Still in the steady state these collisions do not affect the molecular density in any element of volume of the gas.  
The molecules do not gather at any place in larger numbers than at others.
- (b) Between two successive collisions a molecule moves along a straight path with a uniform velocity. This straight path is called free path.
- (c) The dimension of a molecule can be neglected in comparison with the distance travelled by it in between two collisions.
- (d) The time during which a collision lasts is negligible compare to the time taken by a molecule to travel the free path.
- (e) The molecules are perfectly elastic hard spheres. So, they do not exert any appreciable force of attraction or repulsion on one another or on the walls; except during the collisions.

From these assumptions we know that at any instant the molecules in a perfect gas can move along any direction with any velocity ranging from 0 to  $\infty$  (We now know the limiting velocity is  $c$ , the velocity of light). The direction and magnitude of the velocity of a molecule are both distributed at random.

Let the velocity of a molecule be denoted by  $\mathbf{v}$  having components  $p, q, r$  along  $x, y, z$  direction respectively ( $p=v_x, q=v_y, r=v_z$ )

$$v^2 = p^2 + q^2 + r^2. \quad v \text{ may vary from } 0 \text{ to } \infty, \text{ but } p, q, r \text{ can vary from } -\infty \text{ to } +\infty.$$

Though the Gas molecules are continuously colliding against one another, yet there is a steady state in which  $n_p$  the number of molecules with velocity component  $p$  is not affected by collisions. Otherwise, molecules would gather at

place in larger number than at other. We wish to find out  $n_p$  in terms of  $p$  and other known quantities.

### **Average score in Environmental Studies**

Let us try to find out the average score of students in environmental studies.

What we usually do? We just find out the sum of the scores and then divide it by total no of students.

But here the total number of students is very large. So, we can divide them in groups.

Group A: Score 0-10, Group B: Score 11-20, ....., Group J: Score 91-100

Our task is to find out how many students are there in a group. We can say that the number of students  $n_A$  in a group A will be a function of that group.

Now if we choose the groups like below:

Group A: Score 0-5, Group B: Score 6-10, Group C: Score 11-15 .....

Then we can surely say that this time the number of students in group A will be lesser than previously.

Again, if we choose the groups like below:

Group A: Score 0-2, Group B: Score 3-5, Group C: Score 6-8 .....

Then we can surely say that this time the number of students in group A will be much lesser than previously.

So, the number depends on the interval as well. To get the correct average score we should choose the interval as small as possible.

We can conclude this discussion by saying that the number of students whose score lies between  $x$  and  $x+dx$  is  $n_x dx$ .

### **Probability of an event**

$$\text{Probability of an event} = \frac{\text{number of cases in which the event occurs}}{\text{total number of cases}}$$

Let us proceed to deduce Maxwell's velocity distribution law.

The number of molecules per c.c. having the velocity component lying between  $p$  and  $p+dp$  can be denoted by  $n_p dp$ .

$n_p$  must be a function of  $p$ . Say  $n_p = n \cdot f(p)$

$n$  = number of molecules per c.c.;  $f(p)$  is some function of  $p$ .

The number of molecules per c.c. having the velocity component lying between  $p$  and  $p+dp$  is  $n_p = n \cdot f(p) dp$

If we randomly select a molecule then the probability that the molecule has velocity component lying between  $p$  and  $p+dp$  is  $\{n \cdot f(p) dp / n\} = f(p) dp$ .

The velocity component  $p, q, r$  are mutually perpendicular. So, the distribution of one of these components among the molecules does not depend upon the value of other components.  $f(p)$  is independent of  $q$  and  $r$ .

Gas molecules can move along any direction, there is no preferred direction over other. So, we can use the same function 'f' for other directions as well.

Therefore, the probability that the molecule has velocity component lying between  $q$  and  $q+dq$  is  $f(q) dq$ .

The probability that the molecule has velocity component lying between  $r$  and  $r+dr$  is  $f(r) dr$ .

If we randomly select a molecule then the probability that the molecule has velocity components lying between  $p$  and  $p+dp$ ,  $q$  and  $q+dq$ ,  $r$  and  $r+dr$  is

$$f(p) dp \cdot f(q) dq \cdot f(r) dr = f(p) f(q) f(r) dp dq dr$$

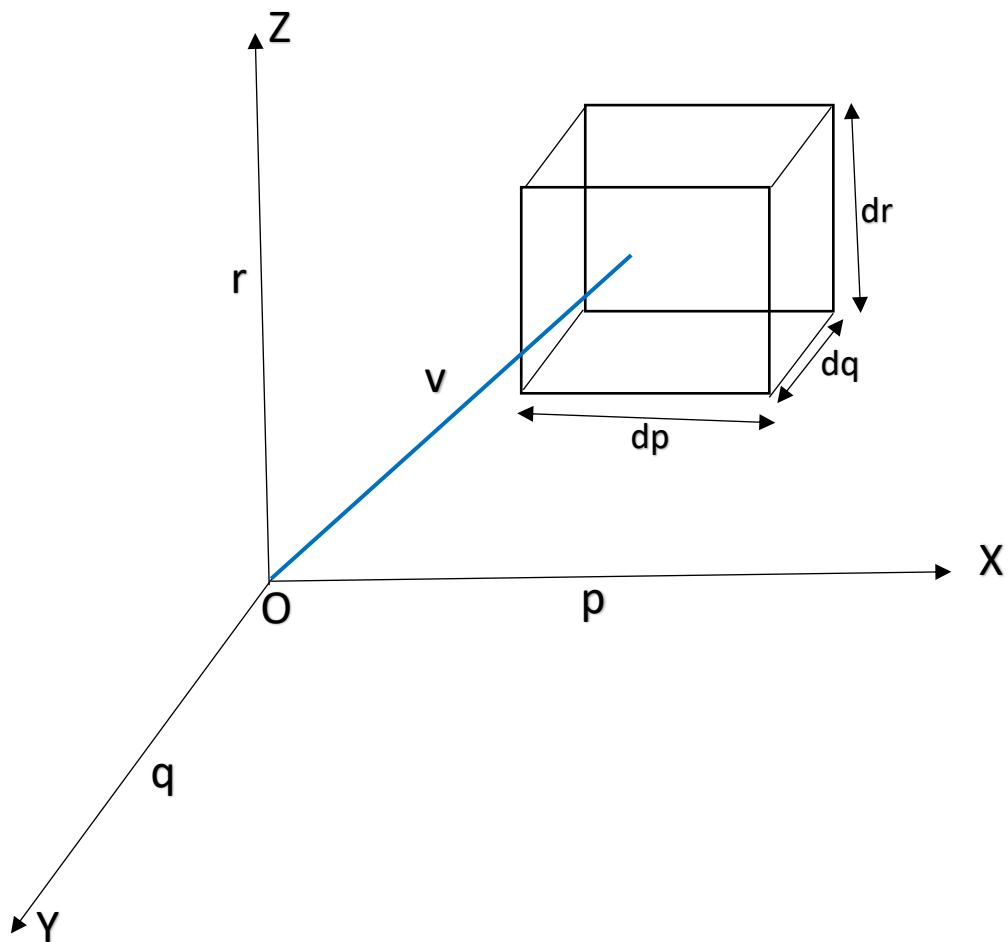
[This is the product of individual probabilities. The probability of finding a molecule with velocity component  $p$  doesn't affect the probability of finding that molecule with velocity component  $q$ . So, finding a molecule with a velocity component along any axis is an independent event]

Hence, the number of molecules per c.c. having velocity components lying between  $p$  and  $p+dp$ ,  $q$  and  $q+dq$ ,  $r$  and  $r+dr$  is

$$n f(p) f(q) f(r) dp dq dr.$$

## Velocity Diagram

Let us draw the velocity diagram and represent all the molecules in it.



In this diagram a molecule with velocity  $\mathbf{v}$  and velocity components  $p, q, r$  is represented by a point whose coordinates are  $(p, q, r)$ . This point is called velocity point.

All the molecules with velocity components lying between  $p$  and  $p+dp$ ,  $q$  and  $q+dq$ ,  $r$  and  $r+dr$  will lie inside the volume element  $dpdqdr$ .

The number of molecules having velocity components lying between  $p$  and  $p+dp$ ,  $q$  and  $q+dq$ ,  $r$  and  $r+dr$  is  $n f(p) f(q) f(r) dpdqdr$ .

Hence, the number of molecules inside the volume element  $dpdqdr$  is  $n f(p)f(q)f(r) dpdqdr$ .

Now these molecules with velocity components p,q,r have resultant velocity  $\mathbf{v}$  [ $v^2=p^2+q^2+r^2$ ].

Hence, the number of molecules inside the volume element  $dpdqdr$  can be written as  $n F(\mathbf{v}) dpdqdr$ .

[ $F(\mathbf{v})$  is some function of  $\mathbf{v}$ . If we randomly select a molecule then the probability that the molecule has velocity  $\mathbf{v}$  is  $F(\mathbf{v})$ .  $F(\mathbf{v})$  doesn't depend upon the inclination of  $\mathbf{v}$  to the axes as the directions of the axes are quite arbitrary.]

$$\therefore n f(p)f(q)f(r) = n F(\mathbf{v}) = n \phi(v^2) \quad [\text{As } v^2=p^2+q^2+r^2]$$

We want to find out how many molecules are there with a particular velocity  $\mathbf{v}$  [velocity components p,q,r].

For a fixed value of v,  $\phi(v^2)$  is constant.

$$\therefore d[\phi(v^2)] = 0$$

$$\therefore d[f(p)f(q)f(r)] = 0$$

$$\therefore f'(p)dp f(q)f(r) + f(p) f'(q)dqf(r) + f(p) f(q)f'(r)dr$$

Dividing this by  $f(p)f(q)f(r)$  we get,

$$\frac{f'(p)}{f(p)} dp + \frac{f'(q)}{f(q)} dq + \frac{f'(r)}{f(r)} dr = 0 \quad \dots\dots\dots (1)$$

Now,  $v^2=p^2+q^2+r^2$

So, for a fixed value of v,  $p^2+q^2+r^2 = \text{constant}$ .

$$\therefore pdp + qdq + rdr = 0 \quad \dots\dots\dots (2)$$

Let us solve (1) and (2) by Laplace's method of undetermined multiplier.

Let us multiply (2) with  $\alpha$  and add it with (1)

From (1) +  $\alpha$  \*(2) we get,

$$\left\{ \frac{f'(p)}{f(p)} + \alpha p \right\} dp + \left\{ \frac{f'(q)}{f(q)} + \alpha q \right\} dq + \left\{ \frac{f'(r)}{f(r)} + \alpha r \right\} = 0 \quad \dots\dots\dots(3)$$

$dp, dq, dr$  are completely arbitrary. Hence, their coefficients in (3) must vanish.

$$\therefore \frac{f'(p)}{f(p)} + \alpha p = 0$$

$$\therefore \frac{f'(p)}{f(p)} = -\alpha p$$

Integrating both sides with respect to p we get,

$$\log f(p) = -\frac{\alpha p^2}{2} + \log a \quad \text{['a' is integration constant]}$$

$$\therefore f(p) = a e^{-\frac{\alpha p^2}{2}} = a e^{-\beta p^2}$$

Similarly,  $f(q) = a e^{-\beta q^2}$  and  $f(r) = a e^{-\beta r^2}$

$$\therefore f(p)f(q)f(r) = a^3 e^{-\beta p^2} e^{-\beta q^2} e^{-\beta r^2}$$

Let us try to determine the value of a and  $\beta$ .

### Value of a

Total number of molecules per c.c. in n.

The number of molecules per c.c. having velocity components lying between p and p+dp, q and q+dq, r and r+dr is  $n f(p) f(q) f(r) dpdqdr$ .

$$\therefore \iiint_{-\infty}^{+\infty} n f(p) f(q) f(r) dpdqdr = n$$

$$\therefore \iiint_{-\infty}^{+\infty} f(p) f(q) f(r) dpdqdr = 1$$

$$\therefore a^3 \iiint_{-\infty}^{+\infty} e^{-\beta p^2} e^{-\beta q^2} e^{-\beta r^2} dpdqdr = 1$$

$$\therefore a^3 \int_{-\infty}^{+\infty} e^{-\beta p^2} dp \int_{-\infty}^{+\infty} e^{-\beta q^2} dq \int_{-\infty}^{+\infty} e^{-\beta r^2} dr = 1$$

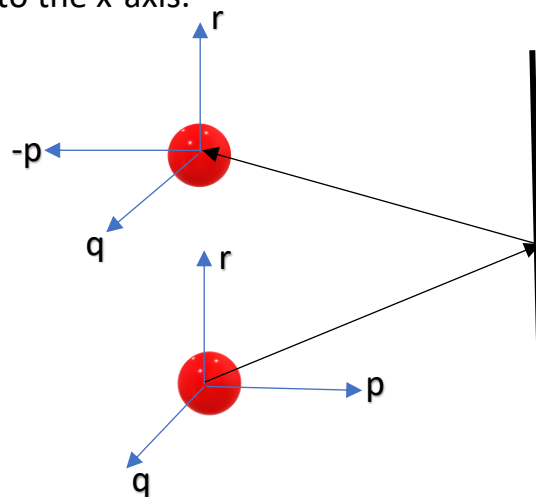
$$\therefore a^3 * \sqrt{\frac{\pi}{\beta}} * \sqrt{\frac{\pi}{\beta}} * \sqrt{\frac{\pi}{\beta}} = 1$$

$$\therefore a = \sqrt{\frac{\beta}{\pi}} \dots\dots\dots(4)$$

## Pressure exerted on a wall

Let us consider a perfect gas enclosed in a container and take the x-axis to be perpendicular to one surface of the container.

A molecule moving with x-component of velocity 'p' towards the wall collides with the latter. From the principle of conservation of energy and momentum we know that after the collision the x-component of velocity will be '-p'. Other components (y and z components) of velocity will not suffer a change, as the wall is perpendicular to the x-axis.



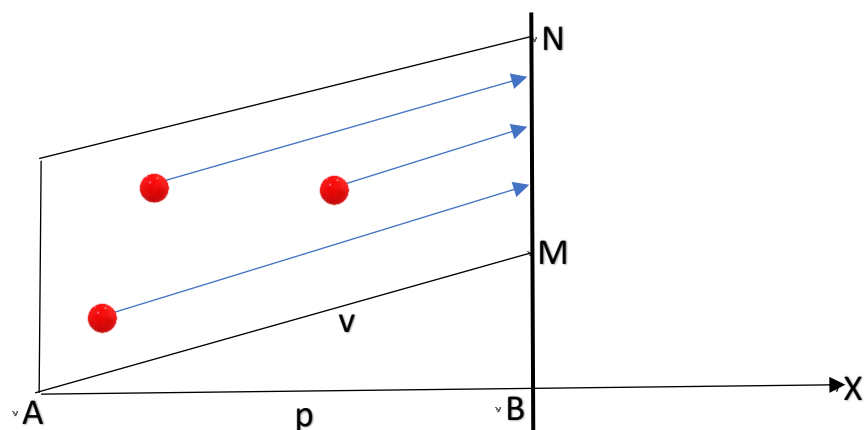
Hence the change in momentum suffered by that molecule during collision is  $2mp$  [  $m$  is the mass of the gas molecule]. The other components of velocity do not suffer any change. So, they do not contribute to pressure.

Now pressure is equal to force per unit area.

Force is equal to the rate of change of momentum.

Therefore, pressure is equal to the change of momentum suffered by molecules striking unit area of the wall per second.

So, the pressure  $P = 2mp \times$  number of impacts delivered on unit surface area of the wall.





Let us focus on a portion MN of wall.

Surface area of MN =  $\delta A$

The molecules having x-component of velocity  $p$ , striking the area MN in time  $\delta t$  are contained inside the cylinder whose base area is MN, axis is  $AM=v \delta t$  and vertical height is  $AB=p \delta t$ . Any molecule outside this cylinder will not be able to deliver any impact on the surface area MN.

Volume of this cylinder is  $p \delta t \delta A$ .

Hence, the number of molecules having x-component of velocity  $p$  inside this cylinder is  $n_p p \delta t \delta A$ .

The total change of momentum experienced by these molecules is  $2mp * n_p p \delta t \delta A$ .

Total change of momentum =

Force X time during which the change takes place =

Pressure X Area X time during which the change takes place

Hence,  $\mathbf{P} \delta A \delta t = 2mp * n_p p \delta t \delta A$

$$\therefore \mathbf{P} = 2mp^2 n_p$$

Now pressure on the wall under consideration is caused by all the molecules having positive x-component of velocity.

[As the wall is perpendicular to the positive X-axis. Molecules with negative x-component of velocity will not strike on this wall]

$$\therefore \mathbf{P} = 2m \sum_0^{\infty} p^2 n_p$$

$$n_p = nf(p) = nae^{-\beta p^2} = n \sqrt{\frac{\beta}{\pi}} e^{-\beta p^2}$$

$$\therefore \mathbf{P} = 2m n \sqrt{\frac{\beta}{\pi}} \sum_0^{\infty} (p^2 e^{-\beta p^2})$$

Replacing the sign of summation by the sign of integration we get,

$$\mathbf{P} = 2m n \sqrt{\frac{\beta}{\pi}} \int_0^{\infty} p^2 e^{-\beta p^2} dp = \frac{mn}{2\beta}$$

We know at temperature T,  $P = nkT$  [k is Boltzmann constant]

$$\therefore \frac{mn}{2\beta} = nkT$$

$$\therefore \beta = \frac{m}{2kT}$$

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

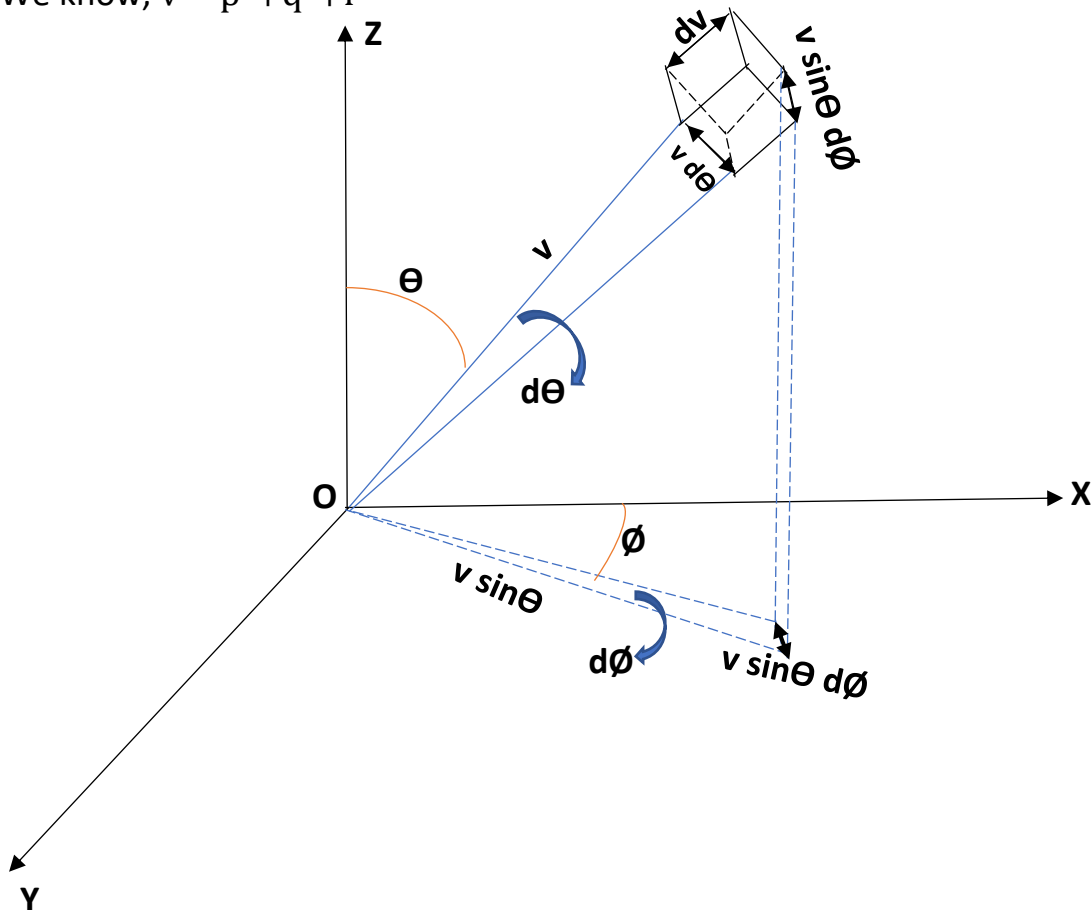
Hence, the number  $dn_p$  of molecules per c.c. having velocity components lying between  $p$  and  $p+dp$ ,  $q$  and  $q+dq$ ,  $r$  and  $r+dr$  is

$$dn_p = n \left( \frac{m}{2\pi kT} \right)^{\frac{3}{2}} e^{-\frac{m}{2} \left( \frac{p^2 + q^2 + r^2}{kT} \right)} dpdqdr$$

This is Maxwell's distribution law.

Now let us try to find out the number of molecules having velocities lying between  $v$  and  $v+dv$ .

We know,  $v^2 = p^2 + q^2 + r^2$



Let us consider the molecule which has velocity components lying between  $p$  and  $p+dp$ ,  $q$  and  $q+dq$ ,  $r$  and  $r+dr$  in Cartesian coordinate system.

The same molecule has velocity components lying between  $v$  and  $v+dv$ ,  $\Theta$  and  $\Theta+d\Theta$ ,  $\Phi$  and  $\Phi+d\Phi$  in Spherical polar coordinate system.

Hence, the element of volume  $dpdqdr$  in velocity space in Cartesian coordinate system, can be replaced by the element of volume lying between  $v$  and  $v+dv$ ,  $\Theta$  and  $\Theta+d\Theta$ ,  $\Phi$  and  $\Phi+d\Phi$  in Spherical polar coordinate system.

This element of volume can be written as  $dv \cdot v \, d\Theta \cdot v \sin\Theta \, d\Phi$

$$= v^2 \sin\Theta \, dv \, d\Theta \, d\Phi$$

Therefore, the number  $dn_{v,\Theta,\Phi}$  of molecules per c.c. having velocity components lying between  $v$  and  $v+dv$ ,  $\Theta$  and  $\Theta+d\Theta$ ,  $\Phi$  and  $\Phi+d\Phi$  is

$$dn_{v,\Theta,\Phi} = n \left( \frac{m}{2\pi kT} \right)^{\frac{3}{2}} e^{-\frac{m}{2} \left( \frac{p^2 + q^2 + r^2}{kT} \right)} v^2 \sin\Theta \, dv \, d\Theta \, d\Phi$$

$$= n \left( \frac{m}{2\pi kT} \right)^{\frac{3}{2}} e^{-\frac{mv^2}{2kT}} v^2 \sin\Theta \, dv \, d\Theta \, d\Phi$$

What is the the number  $dn_v$  of molecules per c.c. having velocity components lying between  $v$  and  $v+dv$ ?

To find the number  $dn_v$  of molecules per c.c. having velocity components lying between  $v$  and  $v+dv$ , we have to integrate the above expression for all possible values of  $\Theta$  and  $\Phi$ .

$$\therefore dn_v = \int_{\Theta=0}^{\pi} \int_{\Phi=0}^{2\pi} dn_{v,\Theta,\Phi} = n \left( \frac{m}{2\pi kT} \right)^{\frac{3}{2}} e^{-\frac{mv^2}{2kT}} v^2 \, dv \int_{\Theta=0}^{\pi} \sin\Theta \, d\Theta \int_{\Phi=0}^{2\pi} d\Phi$$

$$\therefore dn_v = 4\pi n \left( \frac{m}{2\pi kT} \right)^{\frac{3}{2}} e^{-\frac{mv^2}{2kT}} v^2 \, dv \quad \left[ \int_{\Theta=0}^{\pi} \sin\Theta \, d\Theta = 2 \text{ and } \int_{\Phi=0}^{2\pi} d\Phi = 2\pi \right]$$

