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CHAPTER

1

The Kinetic Theory of Gases

1.0 Kinetic Theory, Classical and Quantum Thermodynamics

Two important components of the universe are: the matter and the energy. Interplay between them creates a variety of processes and phenomenon. In order to understand and appreciate the vast spectrum of happenings around us, it is required to know more intimately the properties of the different forms of matter and their interactions with energy. This may be approached in two different ways. In the first approach, often called the microscopic approach, some assumptions about the nature of the matter present in the universe is made and then the well-known and well-established laws of interaction are applied between the assumed entities of the matter to explain the observed natural phenomenon. The kinetic theory of matter and the statistical mechanics (or quantum statics) are the examples of the microscopic approach. In kinetic theory of matter it is assumed that matter is made of elements, which in turn are made of molecules that are in motion. Molecules of an element are all alike, while molecules of different elements are different. Molecules are themselves assumed to be made of atoms. Having made assumptions about the constitution of the matter, the kinetic theory applies the laws of Newtonian mechanics, like the law of conservation of energy, law of conservation of liner momentum, the law that states that the rate of change of momentum is equal to force, etc. to the molecules and obtain expressions for average properties of the system, like the pressure exerted by a gas, etc.

In the case of quantum statics or statistical mechanics, it is assumed that matter is made of different kinds of identical particles or entities; the number of each type of entity in a given piece of matter is very large and, therefore, the entities follow the laws of quantum statistics. In quantum statistics , the entities can have different discrete energies and their energy distributions are given by distribution laws. The average properties of a given piece of matter may be obtained by the application of the relevant quantum distribution law.

In the second approach, called the macroscopic approach, some very general laws obeyed by macroscopic systems are derived by observing their behavior over a sufficiently long period of time. These laws, that are not specific to any system, are then used to drive the average properties of specific systems. This macroscopic approach is historically called the thermodynamics. In thermodynamics, no assumption about the microscopic constitution of the matter is made, and, therefore, it is immaterial whether the matter is made of molecules or not. This approach has evolved over a considerable period of time, out of the experiments carried out in entirely different contexts. The implications of the laws obeyed by large macroscopic systems were realized much later. There had been controversies about calling this branch of science as thermodynamics, or thermostatic, or equilibrium thermodynamics,

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etc. which will be discussed in details later. It may, however, be remarked that thermodynamics is a branch of science based entirely on experiments and hence empirical in nature.

1.1 Kinetic Theory of Gases

Out of the three prominent states of matter, solid, liquid and gas, the kinetic theory of gases is perhaps the most developed and complete. Further, under suitable boundary conditions, the kinetic theory of gases may be applied to the solid and the liquid states as well.

1.1.1 What do we expect from a good theory of gases?

Any good theory of gases must be able to explain satisfactorily all experimentally observed facts about gases, like the Boyle's law, Charles' law, Gay-Lussac's law, Graham's law of effusion, Daltons law of partial pressure, magnitudes of specific thermal capacities and their ratios for different gases, their temperature dependence, thermal conductivity and viscosities of gases, etc. The simple classical theory, called the kinetic theory of gases, detailed below, brings out the main properties of gases remarkably well. It, however, fails to explain some finer points as regards to the temperature dependence of some gas properties. It is also not expected that such a simple theory will explain all details of complex gas systems. Laws of quantum statistics, also called statistical mechanics applied to gaseous systems, explain most of the properties that remained unexplained by the kinetic theory.

The first step toward the development of the kinetic theory of gases is to define an ideal gas. An ideal gas is a hypothetical or imaginary gas, properties of which are defined through the following assumptions of the kinetic theory of gases.

1.1.2 Assumptions or postulates of the kinetic theory

1. Gases are made up of molecules. In any given measurable or macroscopic volume there is large number of molecules of the gas.
2. The molecules of a gas are in state of continuous motion and the relative separation between the molecules is much larger than their own dimensions.
3. Molecules exert no force on one another except when they collide. The molecules, therefore, travel in straight lines between collisions with each other or with the wall of the container.
4. Molecules undergo elastic collisions with each other and with the walls of the container. If it is further assumed that the walls of the container are perfectly smooth then during the collisions with the walls the tangential component of the velocity of the molecule will remain unaltered.
5. The molecules are uniformly distributed over the volume of the container.
6. The molecular speeds, that is the magnitudes of the molecular velocities, have values from zero to infinity.
7. The directions of the molecular velocities are uniformly distributed in space.

1.1.3 Justifications and implications of assumptions

According to Avogadro's law, one mole of every gas occupies 22.4 liter of volume at standard temperature and pressure (STP) and contains 6.03×10^{23} molecules of the gas. Since 1 liter of volume

$= 1 \times 10^{-3}$ m^3, there are $\approx 10^{16}$ molecules per cubic millimeter of the volume of a container at (STP) which is a very large number. This justifies the first assumption.

Assumption that the size of molecules is much smaller than the distance of their separation essentially means that large space around each molecule is empty or there is vacuum around each molecule. Molecules in this force-free space move in straight lines till they encounter a collision either with another molecule or with the wall of the container. Assuming that molecules are uniformly distributed, the volume of space that may be associated with each molecule of the gas at STP $\approx \frac{22.4 \times 10^{-3} \text{ m}^3}{6.03 \times 10^{23}} \approx 3 \times 10^{-26} \text{ m}^3$. Now the size or the diameter of an average molecule is of the order of 10^{-10} m. Taking molecule to be a sphere of radius 0.5×10^{-10} m, the actual volume of the molecule comes out to be $\frac{4}{3}\pi\left(0.5 \times 10^{-10}\right)^3$ m $\approx 5 \times 10^{-31}$ m^3. It may now be observed that out of the volume of space of 3×10^{-26} m^3 that each molecule has around it, the actual volume of the molecule is only 5×10^{-31} m^3. It means that space of volume $\frac{3 \times 10^{-26}}{5 \times 10^{-31}} = 6 \times 10^4$ times the actual volume of the molecule is available to each molecule as free space or vacuum where there is no other molecule. This justifies the second assumption.

Assumption 3, that molecules exert no force on each other, is not true in case of a real gas and is a major point of difference between a real gas and the hypothetical ideal gas. It may be treated as the first approximation that may be dropped later. Assumptions that collisions are elastic and the container walls are smooth are required to carry out the calculations of momentum transfer in molecular collisions with the walls.

Suppose the total number of gas molecules in the container of volume V is N. The number density of molecules 'n', which is the number of molecules per unit volume, is then $n = N/V$. Therefore, in any volume element ΔV the number of molecules, $N_{\Delta V} = n\,\Delta V$. Now it may be argued that the assumption of uniform distribution of molecules may break down if one selects the volume element ΔV to be so small that there is no molecule in this volume. It may, however, be realized that elements of infinitesimal small size are taken to carry out operations of differentiation and integration. The term 'infinitesimal' is a relative term. For example, if there is a gas container of 1cubic meter volume, a volume of 1/1000 cubic millimeter is infinitesimally small in comparison to the size of the container. The number of gas molecules at STP in a volume of 1/1000 cubic millimeter is still of the order of 10^6. It may, thus, be seen that the assumption of uniform distribution of gas molecules is valid and does not break down even for the relatively infinitesimal small volumes.

Assumption that molecular speeds vary from zero to infinity is quite justified as even if one starts from the assumption that initially all molecules have same speed, the intra molecular collisions will soon produce a spectrum of speeds. The upper limit of the speed spectrum may remain a question, since no material particle can attain speeds greater than the speed of light. It will, however, be shown that the actual value of the upper limit whether it is infinity or the speed of light does not matter because the speed distribution curve falls almost exponentially for very high values of speeds. Another assumption that the directions of molecular velocities are uniformly distributed in space ensures their randomness, and as many molecules go away from a particular location in the container, on an average same number of molecules reaches there from some other part of the container keeping the average number density of molecules constant in the container. Figure 1.1 (a) shows the velocity

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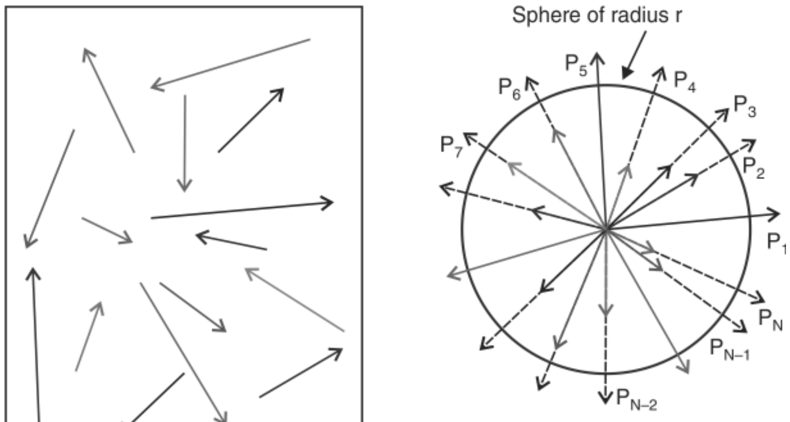
vectors of some gas molecules in the container. Actually there should be N such vectors, one for each of the N gas molecules. These velocity vectors are transported parallel to themselves such that they originate from the common point O, in Fig. 1.1 (b). A sphere of radius r is then drawn taking O as the center. The velocity vectors, either themselves or on extension (shown by dotted lines in Fig. 1.1 (b)), cut the surface of the sphere at points P_1, P_2, P_3, … P_N . Each of these points of intersection indicates a different direction of the motion of the gas molecule. Now in case the directions of motion of gas molecules are uniformly distributed in space then the points of intersection (P's) should also be uniformly distributed on the surface of the sphere of radius r. The total number of points of intersection is N, one for each molecule and the total surface area of the sphere of radius r is $4\pi r^2$. Therefore, for the uniform distribution of the directions of molecular velocities in space, the number of intersection points per unit surface area should be $\frac{N}{4\pi r^2}$. On the other hand if we consider a surface area, ΔS, then the number of intersection points on this area will be $\frac{N}{4\pi r^2}\Delta S$.



(a) Vectors indicating the velocities of some gas molecules in the container

(b) Molecular velocity vectors transported to the centre O of a sphere of radius r

Fig. 1.1 (a) shows the velocity vectors for some molecules of the gas in a container. In Fig. 1.1 (b) these velocity vectors are transported parallel to themselves to the origin O, which is the center of a sphere of radius r. The velocity vectors cut the surface of the sphere either themselves or on extension (dotted lines) at points P_1, P_2, P_3,……P_N , each of which gives the direction of motion of a gas molecule. The directions of motion of gas molecules will be uniformly distributed in space if the points of intersection are uniformly distributed on the surface of the sphere.

It is now clear that the number of intersection points on a given area on the spherical surface is equal to the number of gas molecules moving in the direction of that surface area. An element of surface (i.e., a small surface area) on the spherical surface may be conveniently defined in spherical polar coordinates, with the origin of the coordinate system at the center of the sphere as is shown in Fig. 1.2

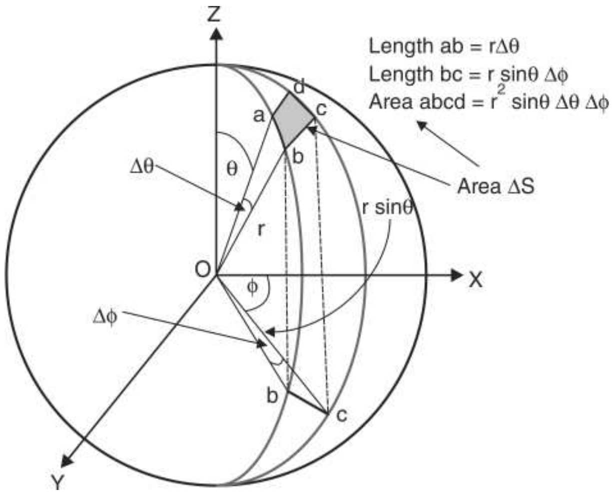


Fig. 1.2 Definition of an element of area in spherical polar coordinates

As is clear from Fig. 1.2, the small element of surface area ΔS is given by the expression,

$$\Delta S = r^2 \sin\theta\,\Delta\theta\,\Delta\varphi \qquad 1.1$$

The number $N^{(\theta,\varphi)}$ of molecules moving in the direction θ and $(\theta + \Delta\theta)$ and φ and $(\varphi + \Delta\varphi)$ and hitting the shaded area ΔS normally, is equal to the points of intersection on surface, ΔS, and is given by,

$$N^{(\theta,\varphi)} = \frac{N}{4\pi r^2}\Delta S = \frac{N}{4\pi r^2} r^2 \sin\theta\,\Delta\theta\,\Delta\varphi = \frac{N}{4\pi}\sin\theta\,\Delta\theta\,\Delta\varphi \qquad 1.2\text{ (a)}$$

We divide both sides of this equation by the volume V of the container to get,

$$n^{(\theta,\varphi)} = \frac{n}{4\pi}\sin\theta\,\Delta\theta\,\Delta\varphi \qquad 1.2\text{ (b)}$$

Here n, and $n^{(\theta,\varphi)}$ are, respectively, the number density of gas molecules (N/V) and the number density $(N^{(\theta,\varphi)}/V)$ of molecules moving in direction θ & $(\theta + \Delta\theta)$; φ & $(\varphi + \Delta\varphi)$.

The velocity vectors of these $N^{(\theta,\varphi)}$ molecules are in the direction θ within a small spread $\Delta\theta$, and φ within a small spread $\Delta\varphi$, but these molecules may have all possible speeds from zero to infinity. We now select out of $N^{(\theta,\varphi)}$ only those molecules that are moving in the direction θ & $(\theta + \Delta\theta)$ and φ & $(\varphi + \Delta\varphi)$ and have their velocities between v and $(v + \Delta v)$ and denote them by $N^{(\theta,\varphi,v)}$. The velocity vectors of these $N^{(\theta,\varphi,v)}$ molecules will all be confined within two concentric spheres of radii v and $(v + \Delta v)$ as shown in Fig.1.3. The number density of (θ, φ, v) molecules is given by,

$$n^{(\theta,\varphi,v)} = \left(\frac{\Delta n^v}{4\pi}\sin\theta\,\Delta\theta\,\Delta\varphi\right) \qquad 1.2\text{ (c)}$$

where, Δn^v is the number density of molecules with velocities in the range v to $(v + \Delta v)$.

Since we will consider the molecules that are moving in the direction θ and $(\theta + \Delta\theta)$ and φ and $(\varphi + \Delta\varphi)$, we simply refer them as $n^{(\theta,\varphi)}$, the molecules moving in direction (θ, φ) and will understand that there are spreads of $\Delta\theta$ and $\Delta\varphi$ in the directions without specifying it repetitively. It follows from Eq. 1.2(c) that;

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$$n^{(\theta,\varphi)} = \frac{n}{4\pi}\sin\theta\,\Delta\theta\,\Delta\phi \qquad 1.3$$

Similarly, $N^{(\theta,\varphi,v)}$ will indicate molecules moving in the direction (θ, φ) with velocities between v and $(v + \Delta v)$ and will be called molecules moving in direction θ, φ with velocity v.

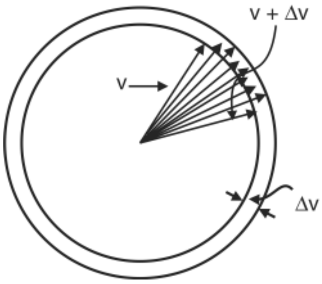

Fig.1.3 Bunch of molecules moving in direction θ and $(\theta + \Delta\theta)$, φ and $(\varphi + \Delta\varphi)$ with velocities between v and $(v + \Delta v)$

1.1.4 Molecular flux

The flux of a system of moving particles is defined as the number of particles crossing an imaginary unit area per unit time. In case of the N ideal gas molecules that are in random motion and are held in a container of volume V, if ΔN molecules cross an imaginary area ΔS in time Δt, then the molecular flux Φ may be given as,

$$\Phi = \frac{\Delta N}{\Delta S.\Delta t} \qquad 1.3\ (a)$$

In case the imaginary area is taken somewhere within the volume of the container, then there will be two molecular fluxes through the area. One will be the flux of gas molecules crossing the imaginary area from one side of the surface (from right to left in Fig. 1.4 a) to the other and the other of gas molecules crossing the area in the opposite direction (from left to right in Fig. 1.4 a). The two fluxes will also be equal in magnitude because the number density of molecules in the container is constant on an average. If we choose the area on the wall of the container (lower part in Fig. 1.4 a), then also there will be two fluxes: one of gas molecules hitting the area from left to right and the other flux of molecules rebounded by the area on the wall and moving from right to left. Again, the two fluxes will be equal. In case when the area in consideration is at the wall of the container, the flux of molecules reflected from the wall will be related to the flux of incident molecules through the laws of elastic scattering. No such relationship between the two molecular fluxes will exist in case the area is taken somewhere in the volume of the gas.

We now calculate the flux $\Phi^{(\theta,\varphi,v)}$ of (θ, φ, v) molecules through an imaginary area ΔS inside the volume of the ideal gas held in a container of volume V as shown in Fig. 1.4 (b). As shown in Fig. 1.4 (b), the normal to the area ΔS is contained in the shaded plane and makes an angle θ with the direction of motion of (θ, φ, v) molecules. The angle φ is also indicated in the figure. We now construct a cylinder with area ΔS as the base and slant lengths of magnitude $(v\,\Delta t)$ as sides, as shown in the Fig. 1.4 (b). A large number of gas molecules will be contained in this cylindrical volume which may be categorized as

(a) Molecules moving in direction θ & $(\theta + \Delta\theta)$, φ & $(\varphi + \Delta\varphi)$, with their velocities in the range of v & $(v + \Delta v)$. These are the molecules of our interest.
(b) Molecules moving in direction θ & $(\theta + \Delta\theta)$, φ & $(\varphi + \Delta\varphi)$, with their velocities NOT in the range of v & $(v + \Delta v)$. We are not interested in these molecules.
(c) Molecules having their velocities in the range of v & $(v + \Delta v)$ but NOT moving in the direction θ & $(\theta + \Delta\theta)$, φ & $(\varphi + \Delta\varphi)$. These molecules are also not of interest to us.

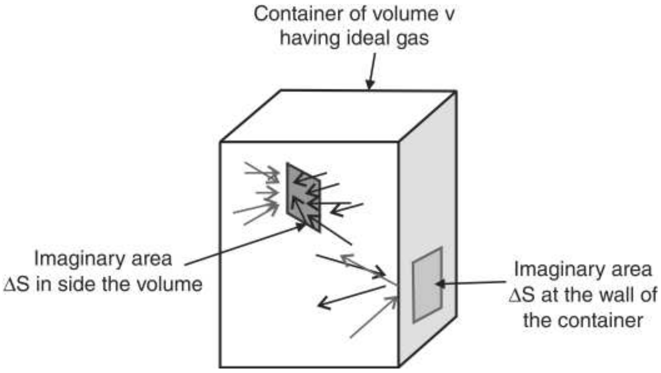

Fig. 1.4 (a) Gas molecules crossing an imaginary area inside the volume

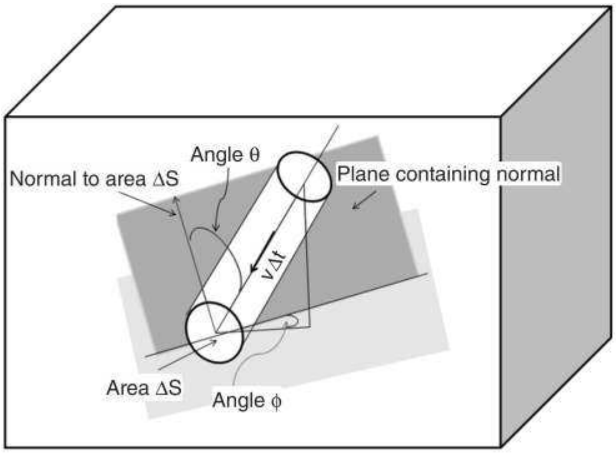

Fig. 1.4 (b) All molecules moving in direction θ, φ with velocity v contained in the cylindrical volume will cross the area ΔS in time Δt

If collisions between molecules contained in the cylindrical volume are neglected, then all the (θ, φ, v) molecules contained within the volume of the cylinder will definitely cross through the area ΔS. It is because all the (θ, φ, v) molecules that are at the other edge of the cylinder, moving with velocity v in direction (θ, φ) will cover a distance $(v\Delta t)$ in time Δt and will cross the area ΔS. The number $N^{(\theta, \varphi, v)}$ of (θ, φ, v) molecules that will pass through the area ΔS is equal to the volume V^{cyl} of the cylinder multiplied by the number density $n^{(\theta, \varphi, v)}$ of (θ, φ, v) molecules. Since $V^{cyl} = (\Delta S \cos\theta).v\Delta t$; therefore,

$$N^{(\theta,\,\varphi,\,v)} = n^{(\theta,\varphi,v)} \cdot \Delta S \cos\theta \, v \, \Delta t \tag{1.3 (b)}$$

Hence,

$$\Phi^{(\theta,\,\varphi,\,v)} = \frac{N^{(\theta,\varphi,v)}}{\Delta S \, \Delta t} = \frac{n^{(\theta,\varphi,v)} \cdot \Delta S \cos\theta \, v \, \Delta t}{\Delta S \, \Delta t}$$

or

$$\Phi^{(\theta,\,\varphi,\,v)} = n^{(\theta,\varphi,v)} \, v \cos\theta \tag{1.3 (c)}$$

or

$$\Phi^{(\theta,\,\varphi,\,v)} = \frac{\Delta n^{v}}{4\pi} v \cos\theta \, \sin\theta \, \Delta\theta \, \Delta\varphi \tag{1.4}$$

In Eq. 1.4, $\Delta\theta$ and $\Delta\varphi$ are infinitesimally small elements of angle θ and φ and may be replaced by their corresponding differential elements dθ and dφ. Further, the angles θ and φ in polar coordinates may vary, respectively, from 0 to $\frac{\pi}{2}$ and 0 to 2π. Integration of Eq. 1.4 over all values of φ will yield the molecular flux of those molecules that have velocities in the range v to $(v + \Delta v)$ coming from direction θ to $(\theta + \Delta\theta)$ with all values of φ (from 0 to 2π).

$$\Phi^{(v,\,\theta)} = \frac{\Delta n^{v}}{4\pi} v \cos\theta \sin\theta \, d\theta \int_{0}^{2\pi} d\varphi = \frac{\Delta n^{v}}{2} v \cos\theta \sin\theta \, d\theta \tag{1.4 (a)}$$

and the flux Φ^{θ} of molecules of all velocities coming in direction θ may be obtained by summing Eq. 1.4 (a) over all values of $\Delta n^{v} v$.

$$\Phi^{\theta} = \frac{1}{2} \cos\theta \sin\theta \, d\theta \sum \Delta n^{v} \, v \tag{1.4 (b)}$$

On the other hand

$$\Phi^{v} = \iint \Phi^{(\theta,\varphi,v)} d\theta \, d\varphi = \frac{\Delta n^{v}}{4\pi} v \int_{0}^{\pi/2} \cos\theta \sin\theta \, d\theta \int_{0}^{2\pi} d\varphi$$

or

$$\Phi^{v} = \frac{\Delta n^{v}}{4\pi} v \left(\frac{1}{2}\right) (2\pi) = \frac{v \Delta n^{v}}{4} = \frac{1}{4} v \, \Delta n^{v} \tag{1.5}$$

Equation 1.5 tells that the flux of molecules having their velocities between v and $(v + \Delta v)$, coming from any direction, is one fourth of the multiplication of the velocity v with their number density. If it is required to find the total flux Φ of all molecules, coming from all directions and having all possible velocities, then it may be found by summing Eq.1.5 over all values of velocities. i.e.,

$$\Phi = \frac{1}{4} \sum v \, \Delta n^{v} \tag{1.6 (a)}$$

There are molecules of velocity say v_1 with number density Δn^{v_1}, v_2 with number density Δn^{v_2}, v_3 with number density Δn^{v_3}, and so on, then expression 1.6 (a) may be expended as;

$$\Phi = \frac{1}{4} \sum [v_1 \, \Delta n^{v_1} + v_2 \, \Delta n^{v_2} + v_3 \, \Delta n^{v_3} + v_4 \, \Delta n^{v_4} + \ldots] \tag{1.6 (b)}$$

We multiply both the numerator and the denominator of Eq. 1.6 (b) by $n\left(= \frac{N}{V}\right)$ the number density of molecules in the container.

$$\Phi = \frac{n}{4}\sum[\frac{v_1\,\Delta n^{v_1} + v_2\,\Delta n^{v_2} + v_3\,\Delta n^{v_3} + v_4\,\Delta n^{v_4} + \dots}{n}]$$

or
$$\Phi = \frac{1}{4}n\bar{v} \qquad 1.6\ (c)$$

where the average velocity (speed) $\bar{v} = \sum[\frac{v_1\,\Delta n^{v_1} + v_2\,\Delta n^{v_2} + v_3\,\Delta n^{v_3} + v_4\,\Delta n^{v_4} + \dots}{n}]$ 1.6 (d)

or
$$\bar{v} = \frac{1}{n}\sum\Delta n^{v}\,v \qquad 1.6\ (e)$$

Equation 1.6 (c) shows that the molecular flux at any place inside the container is proportional to the average or mean velocity, $\bar{v}$.

Substitution of $n\bar{v} = \sum\Delta n^{v}\,v$ from Eq. 1.6 (e) into Eq. 1.4 (b), the molecular flux in direction θ may be written as

$$\Phi^{\theta} = \frac{1}{2}\cos\theta\,\sin\theta\,d\theta\sum\Delta n^{v}\,v = \frac{1}{2}n\bar{v}\,\cos\theta\sin\theta\,d\theta \qquad 1.6\ (f)$$

1.1.5 Pressure exerted by an ideal gas

Randomly moving ideal gas molecules when hit the walls of the container get elastically scattered and reflected back. As a result of reflection, the directions of motion of molecules get changed and so also their linear momentum. However, rate of change of momentum is equal to force. Molecules colliding with the container walls exert a force on the wall. The average force exerted per unit area of the walls is equal to the pressure exerted by the gas.

In Fig. 1.5 an area of unit dimension at the wall of the container is shown. The normal to the unit area is also shown in the figure. A group of molecules with velocity v moving in the direction θ with the normal to the unit area hit the unit area and are elastically scattered. The velocity vector of both the incident and the scattered molecules may be resolved in to two mutually perpendicular components as shown in the figure. The tangential component $v\sin\theta$ remains unaltered after scattering as the container walls and hence the surface of the unit area is assumed to be smooth. The normal component $v\cos\theta$ after scattering from the surface becomes ($-\,v\cos\theta$). Thus the scattered particles move out making an angle θ with the normal, as shown in the figure. The number of (v, θ) particles hitting the unit area per unit time is equal to the flux $\Phi^{(v,\,\theta)}$. If the mass of each molecule is m, then the change in the linear momentum Δp per unit time of $\Phi^{(v,\,\theta)}$. molecules will be,

$$\Delta p = \left\{mv\,\cos\theta - \left(-mv\,\cos\theta\right)\right\}\Phi^{(v,\theta)} \qquad 1.7\ (a)$$

Hence the force $F^{(v,\,\theta)}$ exerted by $\Phi^{(v,\,\theta)}$ molecules when they are elastically scattered by the unit area on the container wall is given by;

$$F^{(v,\,\theta)} = \left\{2mv\cos\theta\right\}\Phi^{(v,\theta)} \qquad 1.7\ (b)$$

But from Eq. 1.4 (a), $\Phi^{(v,\,\theta)} = \frac{\Delta n^{v}}{2}v\cos\theta\sin\theta\,d\theta$; therefore,

$$F^{(v,\,\theta)} = \{2m\,v\cos\theta\}\frac{\Delta n^{v}}{2}\,v\cos\theta\sin\theta\,d\theta$$

$$= m\,\Delta n^{v} v^{2}\cos^{2}\theta\sin\theta\,d\theta \qquad 1.7\ (\text{c})$$

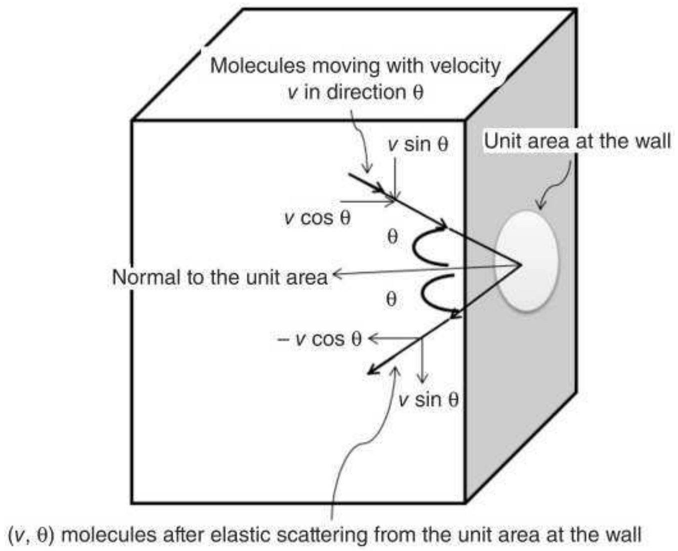

Fig. 1.5 Gas molecules moving with velocity v in direction θ are elastically scattered by the unit area at the wall of the container

In order to find the force $F^{(v)}$ exerted on the unit surface at the wall of the container by all molecules with velocity v coming from all directions may be obtained by integrating Eq. 1.7 (c) over θ from 0 to $\frac{\pi}{2}$. Integration becomes easy if the substitution $\cos\theta = t$ is made so that $dt = -\sin\theta\,d\theta$ and the integration in the given limits results in

$$F^{(v)} = \frac{1}{3}m\,v^{2}\Delta n^{v} \qquad 1.7\ (\text{d})$$

The total force F exerted by all the gas molecules coming from all directions having all possible velocities and hitting the unit area may be obtained by summing Eq. 1.7 (d) over all velocities. You may wonder why we do not integrate the above equation over v as we have done it in case of θ and φ. The reason is that if the expression is integrated over v it will give infinite value as the upper limit for v is ∞. To avoid this we sum it over all values of v.

Force F experienced by the unit area on the container wall by all gas molecules hitting the area

$$= \frac{1}{3}m\sum v^{2}\Delta n^{v} = \frac{n}{3}m\sum\frac{v_1^{\,2}\nabla n^{v_1} + v_2^{\,2}\nabla n^{v_2} + v_3^{\,2}\nabla n^{v_3} + v_4^{\,2}\nabla n^{v_4} + \ldots}{n}$$

Force per unit area is pressure; hence pressure P (= F) may be written as

$$\text{or } P = \frac{1}{3}mn\left(v^{2}\right)_{average} = \frac{1}{3}mn\overline{v^{2}} = \frac{1}{3}\rho\ \overline{v^{2}},\ \rho \text{ is the density of the gas} \qquad 1.8$$