NOTES ON KINETIC THEORY OF GASES by suman sadhukhan.

The **kinetic theory of gases** describes a gas as a large number of sub-microscopic particles(atoms or molecules), all of which are in constant, rapid, random motion. The randomness arises from the particles' many collisions with each other and with the walls of the container.

Kinetic theory of gases explains the macroscopic properties of gases, such as pressure, temperature, viscosity, thermal conductivity, and volume, by considering their molecular composition and motion. The theory posits that gas pressure results from particles' collisions with the walls of a container at different velocities.

Kinetic molecular theory defines temperature in its own way, in contrast with the thermodynamic definition.[1]

Under an optical microscope, the molecules making up a liquid are too small to be visible. However, the jittery motion of pollen grains or dust particles in liquid are visible. Known as Brownian motion, the motion of the pollen or dust results from their collisions with the liquid's molecules.

The theory for ideal gases makes the following assumptions:

1. The gas consists of very small particles known as molecules. This smallness of their size is such that the total volume of the individual gas molecules added up is negligible compared to the volume of the smallest open ball containing all the molecules. This is equivalent to stating that the average distance separating the gas particles is large compared to their size.
2. These particles have the same mass.
3. The number of molecules is so large that statistical treatment can be applied.
4. The rapidly moving particles constantly collide among themselves and with the walls of the container. Collisions between particles and the wall of the container are non-elastic whereas collisions between the particles are elastic. This means the molecules are considered to be perfectly spherical in shape and elastic in nature.
5. Except during collisions, the interactions among molecules are negligible. (That is, they exert no forces on one another.)

   This implies:

   1. Relativistic effects are negligible.
   2. Quantum-mechanical effects are negligible. This means that the inter-particle distance is much larger than the thermal de Broglie wavelength and the molecules are treated as classical objects.
   3. Because of the above two, their dynamics can be treated classically. This means that the equations of motion of the molecules are time-reversible.

6. The average kinetic energy of the gas particles depends only on the absolute temperature of the system. The kinetic theory has its own definition of temperature, not identical with the thermodynamic definition.
7. The elapsed time of a collision between a molecule and the container's wall is negligible when compared to the time between successive collisions.
8. There is negligible gravitational force on molecules.

What is the experimental evidence that it gas consist of particles moving chaotically?

The important evidence in favour of molecule of motion are

1) diffusion and solution. 2) Expansion of gas 3) phenomena of evaporation and vapour pressure
4) and Brownian motion.

Distribution of velocity: Maxwell Boltzmann law of distribution of felicity in an ideal gas and its experimental verification.

What is meant by speed distribution law? Speed distribution law is a particular probability distribution law , defined and used in physics for describing particle speeds in idealized gases where the particles move freely inside a stationary container without interacting with one another, except for very brief collisions in which they exchange energy and momentum with each other or with their thermal environment. Particle in this context refers to gaseous particles (atoms or molecules), and the system of particles is assumed to have reached thermodynamic equilibrium.

Show that the probability that a molecule may speed lying between u & $u+du$ in definite direction is given by $f(u)du = ae^{-bu^2}du$ .....(i) where a, b are constant at temp T. A vessel contains N molecules of a perfect gas at temp T' mass of each molecule is m .Given that $a = \sqrt{\frac{m}{2\pi kT}}$, $b = \frac{m}{2kT}$, Use equation (i) and show that the number of molecules having speed lying between C & $C+dC$ is given by $dN_C = 4\pi N a^3 e^{-bC^2} C^2 dC = F(C)dC$.

Let represent all the gas molecule in velocity space, having OX, OY, OZ as the axes of coordinate with O as origin. Let u, v, w are the components of any vector $\vec{C}$ along the axes then $\vec{C} = u\,\hat{\imath} + v\,\hat{\jmath} + w\,\hat{k}$
or $C^2 = u^2 + v^2 + w^2$.....(i)
A molecule with velocity components u, v, w are represented by a point in the velocity diagram (**figure 1**)
Maxwell assumed that as u, v, w are mutually orthogonal than the distribution of any component is independent of the value of other components. That is the probability of a molecule having velocity components in between u & $u+du$ is $f(u)du$,where $f(u)$is independent of v, w. Similarly, the probability of a molecule having velocity components in between v & $v+dv$ and w & $w+dw$ are $f(v)dv$, $f(w)dw$ [Note that due to assumption of isotropy of velocity distribution the probability functions are same for three mutual orthogonal directions] As velocity components are independent, the probability of a molecule having velocity components in between u & $u+du$, v& $v+dv$ and w & $w+dw$ is $f(u)du \times f(v)dv \times f(w)dw$

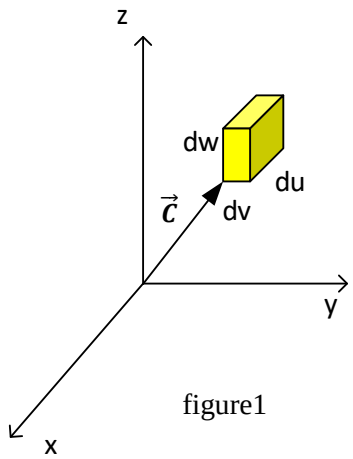


figure1

Out of N molecules the number of molecules having velocity components in between u & $u+du$, v& $v+dv$ and w & $w+dw$ is $dN = N\, f(u)f(v)f(w)dudvdw$.
These molecules will be found in the volume element $dudvdw$.
Hence density of molecules having velocity components in between u & $u+du$, v& $v+dv$ and w & $w+dw$ in velocity space is = $\rho = \frac{dN}{dudvdw} = N\, f(u)f(v)f(w)$

Again the **assumption is that the number density is constant** $d\rho = 0$

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

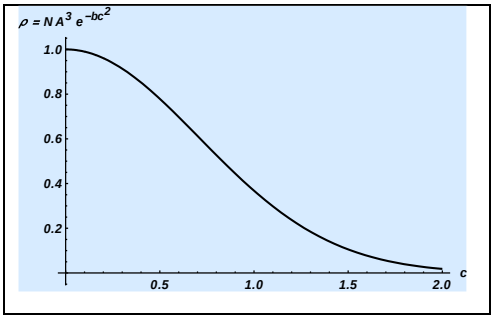
Or, $\frac{f'(u)}{f(u)}du + \frac{f'(v)}{f(v)}dv + \frac{f'(w)}{f(w)}dw = 0$.....(ii)

For constant value of C, du, dv, dw are not independent. From equation (i) we get du, dv, dw , are related by the equation $udu + vdv + wdw = 0$ ..... (iii)

Multiplying equation (iii) by α and adding the product with equation (ii) we get

$\left\{\frac{f'(u)}{f(u)} + \alpha u\right\}du + \left\{\frac{f'(v)}{f(v)} + \alpha v\right\}dv + \left\{\frac{f'(w)}{f(w)} + \alpha w\right\}dw = 0$.....(iv)

[where α is an undetermined multiplier of Lagrange]



(figure 2)

Any two variation can be arbitrary chosen $du = 0\,, dv = 0, dw \neq 0$ so $\left\{\frac{f'(w)}{f(w)} + \alpha w\right\} = 0$ and

similarly , $\left\{\frac{f'(u)}{f(u)} + \alpha u\right\} = 0$ and $\left\{\frac{f'(v)}{f(v)} + \alpha v\right\}$=0……..(v)

Integrating each equation in equation (v) we get $f(u) = A\, e^{-bu^2}\, du$,

$f(v) = A\, e^{-bv^2}\, dv$, $f(w) = A\, e^{-bw^2}\, dw$ [where **b** = $\frac{\alpha}{2}$]

Then molecular density $\boldsymbol{\rho = A^3 e^{-bu^2} e^{-bv^2} e^{-bw^2} = NA^3 e^{-bC^2}}$

Hence the molecular density is a function of C only hence in velocity space the distribution is spherically symmetric.

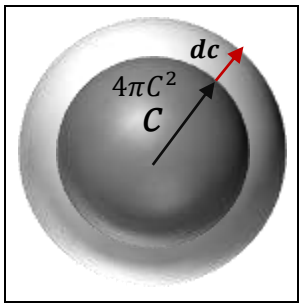


Figure3

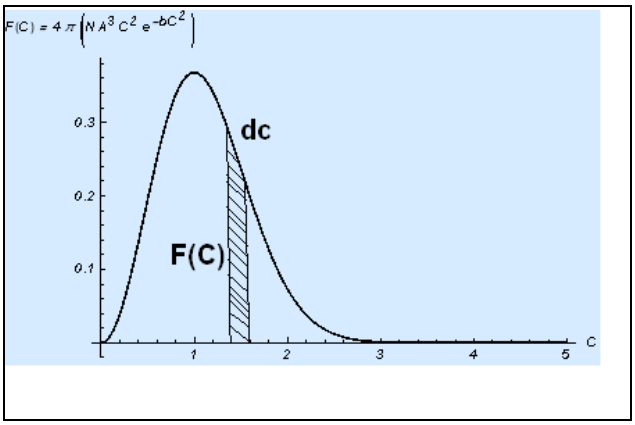
[N.B. ρ falls off exponentially with velocity C and always positive (**figure 2)]**

Then the number of molecule dN_C having velocity in between C & $C + dC$ is ρ times the volume between two spheres (spherical shell) of radius $C\ and\ C + dC$. Plainly the volume of spherical shell $= 4\pi C^2 dC$

Then $\boldsymbol{dN_C} = \rho \times 4\pi C^2 dC = NA^3 e^{-bC^2} dC \times 4\pi C^2 dC$

$= \boldsymbol{4\pi NA^3 e^{-bC^2} C^2 dC}$.= $\boldsymbol{F(C)dC}$

Where $\boldsymbol{F(C) = 4\pi NA^3 e^{-bC^2} C^2}$



The evidence in support of velocity distribution:

1. as Maxwell velocity distribution law gives us the idea that molecules have all velocities ranging from 0 to infinity. A simple consequence of this is that molecules having a velocity greater than escape velocity of any planet will permanently leave the planetary atmosphere. This accounts for either the loss of or rarefied atmosphere in many planets and be moon.
2. We know that the atmosphere has no sharp boundary, is density diminishes with increasing altitude in accordance with the barometric formula. If the molecules had no distribution of velocities but all possessed the same velocity, there would have no atmosphere above a **specific altitude that means there must be abrupt termination of atmosphere.** Which **contradict with observed fact.**

Note that

1. $\int_0^\infty x^n e^{-bx^2} dx = \begin{cases} \frac{(n-1)(n-3).....3.1}{2^{\frac{n}{2}+1} b^{\frac{n}{2}}} \sqrt{\frac{\pi}{b}}. & \textit{for n even} \\ \frac{\left[\frac{1}{2}(n-1)\right]!}{2\, b^{\frac{n+1}{2}}}, & \textit{for n odd} \end{cases}$

Or you may remember $\int_0^\infty e^{-bx^2} dx = \frac{1}{2}\sqrt{\frac{\pi}{b}}$ & $\int_0^\infty x\, e^{-bx^2} dx = \frac{1}{2b}$ **then** $\int_0^\infty x^n e^{-bx^2} dx = \left|\frac{d}{db}\int_0^\infty x^{n-2} e^{-bx^2} dx\right|$

2. $\int_{-\infty}^{\infty} e^{-bx^2+cx} dx = e^{c^2/4b}\sqrt{\frac{\pi}{b}}$

3. $\int_0^\infty e^{ibx^2} dx = \frac{1}{2}\sqrt{\frac{i\pi}{b}}$ & $\int_0^\infty e^{-ibx^2} dx = \frac{1}{2}\sqrt{\frac{\pi}{ib}}$

4. $\int_0^\infty x^{n-1} e^{-x} dx = \Gamma(n)$ $\Gamma(n+1) = n\Gamma(n)$ $\Gamma(1) = 1, \Gamma\left(\frac{1}{2}\right) = \sqrt{\pi},\ \Gamma(0) = 1$

Evaluation of A

Since total number in the assembly is N

then $\iiint_{-\infty}^{\infty} N\ \boldsymbol{A^3} e^{-bu^2} e^{-bv^2} e^{-bw^2}\, du\, dv\, dw = N$

or, $\boldsymbol{A^3} \int_{-\infty}^{\infty} e^{-bu^2}\, du \int_{-\infty}^{\infty} e^{-bu^2}\, du \int_{-\infty}^{\infty} e^{-bu^2}\, du = \mathbf{1}$

or, $\boldsymbol{A^3} \sqrt{\frac{\pi}{b}} \sqrt{\frac{\pi}{b}} \sqrt{\frac{\pi}{b}} = \mathbf{1}$

OR, $\boldsymbol{A} = \sqrt{\frac{b}{\pi}}$

$\therefore \boldsymbol{A} = \sqrt{\frac{b}{\pi}} = \sqrt{\frac{m}{2\pi kT}}$

Evaluation of b

The pressure of the gas is given by $P = 2m \sum_0^{\infty} n_u u^2$

Where n_u = number of molecules per unit volume with velocity between u & $u + du$, then $n_u = nf(u)du$

n is the number of molecules per unit volume.

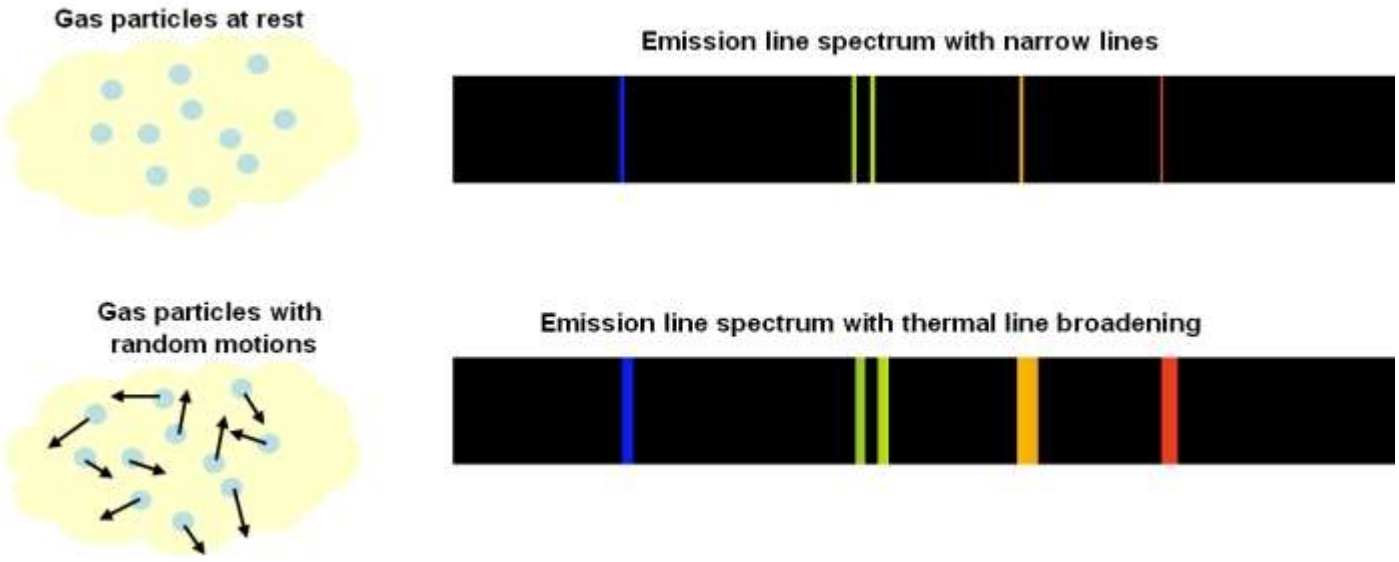
Then $p = 2mnA \int_0^{\infty} \boldsymbol{e^{-bu^2} u^2 dx} = \boldsymbol{2mnA} \times \frac{1}{4} \sqrt{\frac{\pi}{b^3}}$

$= \boldsymbol{2mn} \sqrt{\frac{b}{\pi}} \times \frac{1}{4} \sqrt{\frac{\pi}{b^3}} = \frac{mn}{2b}$

Then $\boldsymbol{b} = \frac{mn}{2p} = \frac{mn}{2nkT} = \frac{m}{2kT}$

Doppler broadening of spectral lines

Doppler broadening is the broadening of spectral lines due to the Doppler effect caused by a distribution of velocities of atoms or molecules. In a gas, the individual atoms, elements or molecules are continuously moving in random directions, with an average speed proportional to the temperature of the gas: $\langle \frac{1}{2} m\, v^2 \rangle = \frac{3}{2} kT$. The term on the left-hand side is the mean kinetic energy. The individual gas particles (with mass *m*) follow a Maxwellian velocity distribution, resulting in a spread of velocities, *v*, about the average value. On the right hand side of the equation, *T* is the temperature of the gas and *k* the Stefan-Boltzmann constant. Compared to a stationary observer, any particular atom, element or molecule could be moving along the line-of-sight, perpendicular to the line-of-sight, or some combination of both. This means that every spectral line emitted is Doppler shifted relative to the observer, resulting in a small change in the observed wavelength. This spreading of a spectral line due to the temperature of the emitting medium is called 'thermal Doppler broadening'.



top: Narrow emissions lines for a gas at "rest" (low temperature means low particle speeds) **bottom:** Emissions lines become broader as gas temperature rises and motions increase.

Thermal Doppler broadening is also possible for **absorption lines**. Particles in the absorbing medium will have random motions, so Doppler shifts in the absorbed **wavelengths** can occur.

For non-relativistic thermal velocities, the Doppler shift in frequency will be: $f = f_0\left(1+\frac{v_f}{c}\right)$

Where f is the observed frequency and f_0 is the rest frequency and v_f is the velocity of the emitter towards the observer and c the velocity of light in free space.

If $f(u)du$ is the fraction of particles with velocity component u & $u+du$ along a line of sight, then the **corresponding distribution of the frequencies** is $P_f(f)df = f(v_f)\frac{dv_f}{df}df$ where $v_f = c\left(\frac{f}{f_0}-1\right)$

In the case of the thermal Doppler broadening, the speed distribution is given by the Maxwell distribution

$$f(u)du = \sqrt{\frac{m}{2\pi kT}}\, e^{-\frac{m}{2kT}u^2}\, du$$

Then $P_f(f)df = \frac{c}{f_0}\sqrt{\frac{m}{2\pi kT}}\, e^{-\frac{m}{2kT}\left\{c\left(\frac{f}{f_0}-1\right)\right\}^2} df$ or, $P_f(f)df = \sqrt{\frac{mc^2}{2\pi kT{f_0}^2}}\, e^{-\frac{mc^2\left(f_0^2-f^2\right)}{2kTf_0^2}} df$

which we immediately recognize as a Gaussian profile with the standard deviation $\sigma_f = \sqrt{\frac{kT}{mc^2}}f_0$

and full width at half maximum (FWHM) $\Delta f_{FWHM} = \sqrt{\frac{8kT\ ln2}{mc^2}}f_0$ (home work)

Experimental verification of maxwell velocity distribution law:

Stern's Experiment:

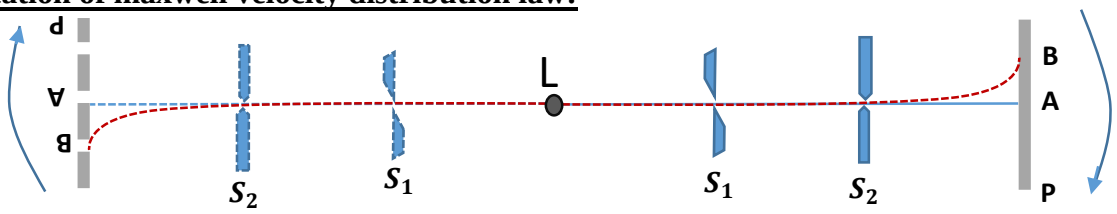


Figure explain the principle of experiment. A platinum wire L coated with silver (represented perpendicular to the plane of the paper in the figure), is heated by an electric current when it emits atomic silver in all direction. The slits, S_1 & S_2 which are parallel to the wire define a stream which condensed on the plate P. The whole system is enclosed in a glass vessel which is highly evacuated so that silver atoms do not suffer any collision in the space. The slits S_1 & S_2 as well as P are rotated together as rigid system about the wire as axis. With the plate at rest the stream towards along LA and forms a deposit at a but when the system is rotating at high speed said clockwise, the deposit will be formed at some point above A, say at B. Faster moving molecules will condense near to A then the slow ones, and thus a velocity spectrum of silver will be obtained. If the relative intensity of the deposit we measured with microphotometer, the ratio of the number of molecules with different velocities can be deduced and the Maxwellian law verified.

The results obtained by Stern were however not quite satisfactory on account of difficulty retaining the vacuum because the spindle of the rotating system has to project outside the vessel for the purpose of coupling it to the driving motor. The dispersion was small and only the distance between two maximum deposits, obtained by reversing the direction of rotation could be measured. Maxwellian law was verified within about 15% stern experiment

Average speed, R. M. S speed and most probable speed

Average speed: $\bar{C} = \frac{\int_0^\infty C\, dN_C}{N} = \int_0^\infty (C)4\pi A^3 e^{-bC^2}C^2dC = 4\pi A^3\int_0^\infty e^{-bC^2}C^3dC = 4\pi A^3\ \frac{1}{2b^2} = \sqrt{\frac{8kT}{m\pi}}$

Hence $\bar{C} = \sqrt{\frac{8kT}{m\pi}}$

R. M. S speed: $C_{r.m.s}^2 = \frac{\int_0^\infty C^2\, dN_C}{N} = \int_0^\infty (C^2)4\pi A^3 e^{-bC^2}C^2dC = 4\pi A^3\int_0^\infty e^{-bC^2}C^4dC = 4\pi A^3\frac{3\sqrt{\pi}}{8b^{\frac{5}{2}}} = \frac{3kT}{m}$

Hence $C_{r.m.s} = \sqrt{\frac{3kT}{m}}$

Most probable speed: We have $\frac{d}{dC}F(C) = \frac{d}{dC}4\pi NA^3 e^{-bC^2}C^2 = 4\pi NA^3\left[2Ce^{-bC^2} + C^2(-2Cb)e^{-bC^2}\right]$

Now if C_m the most probable speed then at most probable speed C_m, $\frac{d}{dC}F(C) = 0$ that means $\frac{d}{dC}F(C)\Big|_{C=C_m} = 0$

$2C_m e^{-bC_m{}^2} + C_m{}^2(-2C_m b)e^{-bC_m{}^2} = 0$

or, $C_m{}^2 b = 1$ [As $2C_m e^{-bC_m{}^2} \neq 0$] or, $C_m = \sqrt{\frac{1}{b}} = \sqrt{\frac{2kT}{m}}$

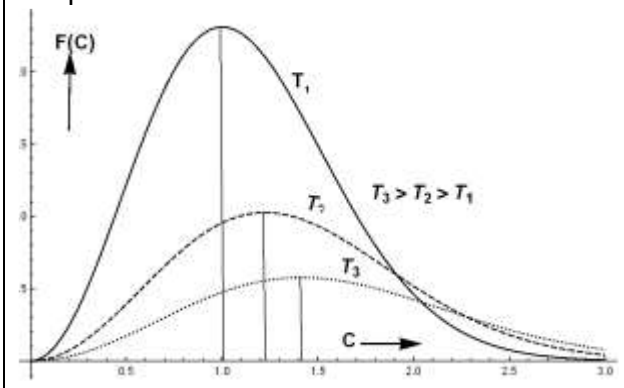
Hence $C_m = \sqrt{\frac{2kT}{m}}$

Temperature dependence of velocity distribution law and the reduce form:

Since the area under the curve is fixed(N), the curve get broadened with increasing temperature. The broadening will naturally depend on the mass value of the molecules. Hence temperature may thus be taken as a maze of broadness of the distribution curve.

If we express speed as a fraction of most probable speed. That means if we express the speed in a unit of most probable speed, the Maxwell speed distribution law becomes independent of temperature.

Brodaning of speed distribution curve with temperature



$C_r = \frac{C}{C_m} = \frac{C}{\sqrt{\frac{2kT}{m}}}$ Then $C = \sqrt{\frac{2kT}{m}}\, C_r$ or, $dC = \sqrt{\frac{2kT}{m}}\, dC_r$

$dN_C = \boldsymbol{4\pi NA^3 e^{-bC^2} C^2 dC}$

Then, $dN_{C_r} = \boldsymbol{4\pi N\left(\frac{m}{2\pi kT}\right)^{3/2} e^{-b\left(\sqrt{\frac{2kT}{m}}C_r\right)^2}}\left(\sqrt{\frac{2kT}{m}}\, C_r\right)^2 \sqrt{\frac{2kT}{m}}\, dC_r = \frac{4}{\sqrt{\pi}} N e^{-C_r{}^2} C_r{}^2 dC_r$ ……*(I)*

Equation *(I)* is independent of parameter A & b hence, dN_{C_r} is independent of temperature.

Equation (I) is known as reduced form of Maxwell's speed distribution.

Q. If u is a certain component of the molecular velocity (say x- axis) show that the ratio of the square of the velocity of sound in air (ideal gas) to the mean square value of u equals to the ratio of specific heat at constant pressure to the specific heat at constant volume.

If we assume gas molecule obey Maxwell's distribution then out of N number of molecules the number of molecules having velocity between u & u+ du is given by $dN_u = N A e^{-bu^2} du$

[where $A = \left(\frac{m}{2\pi kT}\right)^{\frac{1}{2}}$, $b = \frac{m}{2kT}$, m = mass of gas molecule, k = Boltzmann constant, T =absolute tempareturte]

Then $< u^2 > = \frac{\int_{-\infty}^{+\infty} u^2\, N A e^{-bu^2} du}{\int_{-\infty}^{+\infty} N A e^{-bu^2} du} = A\int_{-\infty}^{+\infty} u^2 e^{-bu^2} du = A\frac{1}{2}\sqrt{\left(\frac{\pi}{b^3}\right)} = \frac{kT}{m} = \frac{kN_A T}{mN_A} = \frac{RT}{M}$

[where N_A = Avogadro's number ,M = molar mass ; R = universal gas constant]

Again the square of the velocity of sound in air $v^2 = \frac{\gamma P}{\rho} = \frac{\gamma PV}{\rho V} = \frac{\gamma RT}{M}$

[Where P = pressure of the gas, V = molar volume of the gas, γ = the ratio of specific heat at constant pressure to the specific heat at constant volume.]

Then $\frac{< u^2 >}{v^2} = \gamma$ (proved)

Q. **Define degrees of freedom of a system.**

Degrees of freedom is meant the number of independent co-ordinates necessary for specifying the position and configuration in space of a dynamical system

OR, Degrees of freedom is meant by the number of independent quadratics variables (square terms) by which the ener4gy of the system is determined.

Q. State the classical Equipartition law. ***apply the theorem to calculate (i) the internal energy of one mole perfect gas (ii)molar specific heat of the gas at constant volume***

The classical equipartition law - ***T***he energy of a dynamical system in thermal equilibrium is equally partitioned of divided amongst its different degrees of freedom and for each degree of freedom it is equal to $\frac{kT}{2}$
where k =Boltzmann and T = absolute temp.

(i)For perfect gas degrees of freedom per molecule$= 3.$ Hence energy per molecule = $\frac{3kT}{2}$

Hence internal energy per gram mole =$N_A \frac{3kT}{2}$ = $\frac{3RT}{2}$ [where $N_A = Avogrado's\ Number$]

(ii) As here for one gram mole internal energy E= $\frac{3RT}{2}$

The molar specific heat at constant volume is $C_V = (\frac{dE}{dT})_V = \frac{3R}{2}$