Unit 3: Kinetic Theory of Gases

Dr Priya Hasan*
Department of Physics
Maulana Azad National Urdu University
Gachibowli, Hyderabad 500 032

April 16, 2020

Abstract

Derivation of Maxwells law of distribution of velocities and its experimental verification, Mean free path (Zeroth Order), Transport Phenomena: Viscosity, Conduction and Diffusion (for vertical case), Law of equipartition of energy (no derivation) and its applications to specific heat of gases; mono-atomic and diatomic gases.

1 The kinetic theory of gases

The kinetic theory of gases describes a gas as a large number of submicroscopic 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 explains that gas pressure results from particles' collisions with the walls of a container at different velocities.

The theory for ideal gases makes the following assumptions:

- 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. These particles have the same mass.
- The number of molecules is so large that statistical treatment can be applied.
- The rapidly moving particles constantly collide among themselves and with the walls of the container. All these collisions are perfectly elastic. This means the molecules are considered to be perfectly spherical in shape and elastic in nature.
- Except during collisions, the interactions among molecules are negligible.
- 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.
- The elapsed time of a collision between a molecule and the container's wall is negligible when compared to the time between successive collisions.
- There are negligible gravitational force on molecules.

The pressure exerted by a gas is

$$P = \frac{1}{3}\frac{mn\overline{v^2}}{V} = \frac{1}{3}\rho\overline{v^2}$$

where

$$\overline{v^2} = \frac{v_1^2 + v_2^2 + v_3^2 + ... + v_n^2}{n}$$

$$P = \frac{2}{3}\frac{1}{2}\rho\overline{v^2} = \frac{2}{3}(\text{KE of molecule})$$

*e-mail:priya.hasan@gmail.com, priyashasan@yahoo.com

For gas at a temperature T,

$$\frac{1}{2}m\overline{v^2} = \frac{3}{2}kT$$

where $k = 1.38 \times 1 - ^{-23}\ J\ mol^{-1}\ K^{-1} = R/N$ Where R is universal gas constant ($8.314 J\ mol^{-1}\ K^{-1}$) and N is Avogadros Number. This implies that for a gas at T=0, $\overline{v^2} = 0$.

2 Maxwell distribution of velocities

We consider the assumptions of the kinetic theory of gases. Let us consider that the three mutually perpendicular compents of velocity u,v and w are independent of each other and also do not depend on the position or velocities of other molecules. Let us consider the molecules in a velocity diagram where OX,OY and OZ re the three axis. Consider a molecule with a velocity C and its component in the X,Y Z direction be u,v and w, where

$$u^2 + v^2 + w^2 = C^2$$

Consider the velocity element dudvdw in the figure. All molecules that have velocity in the range u, u+du and v, v+dv, and w,w+dw are contained in the element. The probability f(u) that an element has a velocity

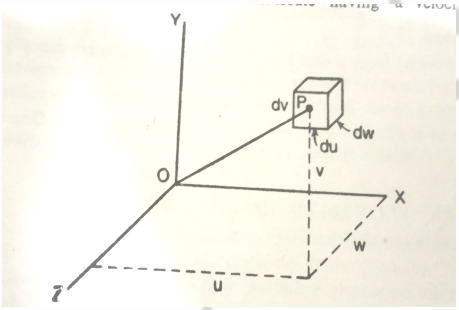

Figure 1: Mean Free Path-2

between u and u+du. Similarly for f(v) and f(w). The total probability that the molecule lies in the element is:

$$f(u)f(v)f(w)dudvdw = \phi(C^2)dudvdw$$

and $\phi(C)$ is the probability that an element has a velocity between C and C+dC.

$$f(u)f(v)f(w)dudvdw = \phi(u^2 + v^2 + w^2)dudvdw$$

Differentiating, we get

$$d\left[f(u)f(v)f(w)\right] = d\left[\phi(C^2)\right] = 0$$

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

Dividing by $f(u)f(v)f(w)$

$$\frac{f^{'}(u)}{f(u)}du + \frac{f^{'}(v)}{f(v)}dv + \frac{f^{'}(w)}{f(w)}dw = 0$$

Also

$$u^2 + v^2 + w^2 = C^2$$

$$2udu + 2vdv + 2wdw = 0$$

$$udu + vdv + wdw = 0$$

Multiplying by λ,

$$\lambda udu + \lambda vdv + \lambda wdw = 0$$

Adding both equations:

$$\left[\frac{f^{'}(u)}{f(u)} + \lambda u\right]du + \left[\frac{f^{'}(v)}{f(v)} + \lambda v\right]dv + \left[\frac{f^{'}(w)}{f(w)} + \lambda w\right]dw = 0$$

Equating each of the coefficients to zero:

$$\left[\frac{f^{'}(u)}{f(u)} + \lambda u\right]du = 0$$

$$\left[\frac{f^{'}(v)}{f(v)} + \lambda v\right] dv = 0$$

$$\left[\frac{f^{'}(w)}{f(w)} + \lambda w\right] dw = 0$$

Now,

$$\left[\frac{f^{'}(u)}{f(u)} = -\lambda u\right] du$$

Integrating,

$$ln\ f(u) = \lambda u^2/2 + ln\ a$$

$$ln\left[\frac{f(u)}{a}\right] = -\lambda u^2/2$$

$$\left[\frac{f(u)}{a}\right] = e^{-\lambda u^2/2} = e^{-bu^2}$$

where $b = \lambda/2$ Similarly,

$$\left[\frac{f(v)}{a}\right] = e^{-bv^2}$$

$$\left[\frac{f(w)}{a}\right] = e^{-bw^2}$$

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

Let n be the number of particles per cc of gas, From the definition of probability,

$$n\int\int\int f(u)f(v)f(w)dudvdw = n$$

$$\int\int\int f(u)f(v)f(w)dudvdw = 1$$

$$\int\int\int a^3 e^{-b(u^2+v^2+w^2)}dudvdw = 1$$

We know

$$\int\int\int e^{-bu^2}du = \sqrt{\frac{\pi}{b}}$$

$$a^3\sqrt{\frac{\pi}{b}}\sqrt{\frac{\pi}{b}}\sqrt{\frac{\pi}{b}} = 1$$

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

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

Thus,

$$a = \sqrt{\frac{b}{\pi}} = \left(\frac{m}{2\pi kT}\right)^{1/2}$$

$$b = \left(\frac{m}{2kT}\right)$$

Thus the number dn of molecules having velocity in the range u, u+du and v, v+dv, and w,w+dw are

$$dn = nf(u)f(v)f(w)dudvdw$$

$$dn = na^3 e^{-b(u^2+v^2+w^2)}dudvdw$$

$$dn = n\left(\frac{m}{2\pi kT}\right)^{3/2} e^{-\left(\frac{m}{2kT}\right)(u^2+v^2+w^2)}dudvdw$$

This is called the Maxwell velocity distribution, because it was discovered by James Clark Maxwell. In terms of C, The volume of the annulus made by a sphere of inner radius C and outer radius C+dC is

$$\frac{4}{3}\pi\left[(C+dC)^3 - C^3\right] = 4\pi C^2 dC$$

$$dn_C = n\left(\frac{m}{2\pi kT}\right)^{3/2} e^{-\left(\frac{m}{2kT}\right)(C^2)} 4\pi C^2 dC$$

$$\frac{dn_C}{n} = 4\pi\left(\frac{m}{2\pi kT}\right)^{3/2} e^{-\left(\frac{m}{2kT}\right)(C^2)} C^2 dC$$

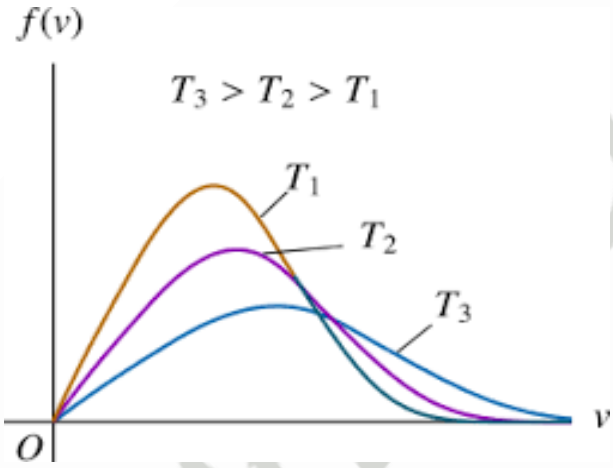

Figure 2: Maxwell velocity distribution

In Fig 2, we see the Maxwell velocity distribution for molecules of a gas at different temperatures. It can be seen that as the temperature increases the area under the curve increases and the peak of the curve increases.

2.1 Equipartition of Energy

$$dn = n\left(\frac{m}{2\pi kT}\right)^{3/2} e^{-\left(\frac{m}{2kT}\right)(u^2+v^2+w^2)} dudvdw$$

The fraction of molecules with velocities between u and u+du is:

$$dn = n\left(\frac{m}{2\pi kT}\right)^{1/2} e^{-\left(\frac{m}{2kT}\right)(u^2)} du$$

The average kinetic energy in the x direction is:

$$\overline{E_x} = \frac{1}{n}\int E_x dn(u)$$

where $E_x = \frac{1}{2}mu^2$

$$\overline{E_x} = \frac{1}{2}m\left(\frac{m}{2\pi kT}\right)^{1/2}\int_{-\infty}^{\infty} e^{-\left(\frac{m}{2kT}\right)(u^2)} u^2 du$$

$$\overline{E_x} = \frac{1}{2}m\left(\frac{b}{\pi}\right)^{1/2}\int_{-\infty}^{\infty} e^{-b(u^2)} u^2 du$$

$$== \frac{1}{2}m\left(\frac{b}{\pi}\right)^{1/2}\left[1/2\sqrt{\frac{\pi}{b^3}}\right]$$

where

$$\int_{-\infty}^{\infty} e^{-b(u^2)} u^2 du = \left[1/2\sqrt{\frac{\pi}{b^3}}\right]$$

$$\overline{E_x} = \frac{1}{4}\frac{m}{b} = \frac{1}{4}\frac{m2kT}{m} = (1/2)kT$$

Similarly

$$\overline{E_y} = \overline{E_z} = (1/2)kT$$

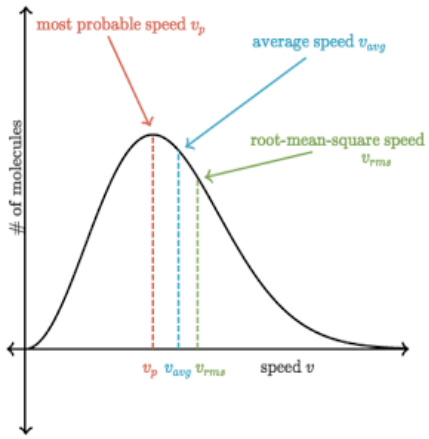

Figure 3: Velocity distribution

2.2 Characteristic speeds

Figure 3 shows the Maxwell velocity distribution as a function of molecular speed in with the most probable speed, mean speed and the root-mean-square speed.

2.2.1 The average speed

The average speed $\overline{C}$ is the speed of all particles divided by the total number of particles.

$$\overline{C} = \int dn_C C dC/n$$

$$= \frac{\int 4\pi n \left(\frac{m}{2kT}\right)^2 e^{-\left(\frac{mC^2}{2kT}\right)}(C^3) dC}{n}$$

$$= 4\pi \left(\frac{b}{\pi}\right)^{3/2} \int_0^\infty e^{-bC^2} C^3 dC$$

Since

$$\int_0^\infty e^{-bC^2} C^3 dC = \frac{1}{2b^2}$$

$$= \sqrt{\frac{4}{\pi b}} = \sqrt{\left(\frac{8kT}{\pi m}\right)} = 1.59\sqrt{\left(\frac{kT}{m}\right)}$$

2.2.2 The most probable speed

The most probable speed is the speed possessed by maximum number of particles. Here

$$\frac{dn_C}{dC} = 0$$

$$\frac{dn_C}{dC} = 4\pi n \left(\frac{m}{2\pi kT}\right)^{3/2} \left[2Ce^{-\left(\frac{mC^2}{2kT}\right)} + C^2 \left(\frac{-2mC}{2kT}\right) e^{-\left(\frac{mC^2}{2kT}\right)}\right] = 0$$

$$= 4\pi n \left(\frac{m}{2\pi kT}\right)^{3/2} e^{-\left(\frac{mC^2}{2kT}\right)} \left[2C - C^2 \left(\frac{mC}{2kT}\right)\right] = 0$$

$$\left[2C - C^2 \left(\frac{mC}{2kT}\right)\right]_{C=C_P} = 0$$

$$\frac{mC_P^2}{kT} = 2$$

$$C_P^2 = \frac{2kT}{m}$$

$$C_P = \sqrt{\frac{2kT}{m}} = 1.41\sqrt{\frac{kT}{m}}$$

2.2.3 RMS Speed

$$\overline{C^2} = \frac{1}{n}\int_0^\infty dn_C C^2 dC$$

$$\overline{C^2} = \frac{1}{n}\int_0^\infty 4\pi n \left(\frac{m}{2\pi kT}\right)^{3/2} e^{-\left(\frac{mC^2}{2kT}\right)} C^4 dC$$

$$= 4\pi \left(\frac{b}{\pi}\right)^{3/2} \int_0^\infty e^{-bC^2} C^4 dC$$

$$= 4\pi \left(\frac{b}{\pi}\right)^{3/2} \frac{3}{8}\sqrt{\frac{\pi}{b^5}}$$

Since

$$\int_0^\infty e^{-bC^2} C^4 dC = \frac{3}{8}\sqrt{\frac{\pi}{b^5}}$$

Now

$$\overline{C^2} = \frac{3}{2b} = \frac{3kT}{m}$$

$$C_{rms} = \sqrt{\overline{C^2}} = \sqrt{\frac{3kT}{m}} = 1.732\sqrt{\frac{kT}{m}}$$

We can see that

$$C_{rms} > \overline{C} > C_p$$

3 Mean Free Path

The mean free path or average distance between collisions for a gas molecule may be estimated from kinetic theory. If the molecules have diameter d, then the effective cross-section for collision can be modeled by using a circle of diameter 2d to represent a molecule's effective collision area while treating the "target" molecules as point masses (Fig. 4).

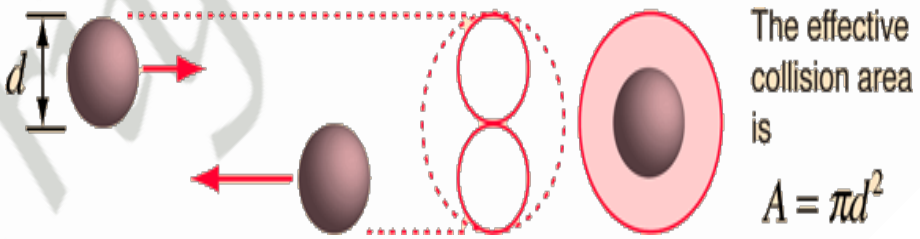

Figure 4: Mean Free Path

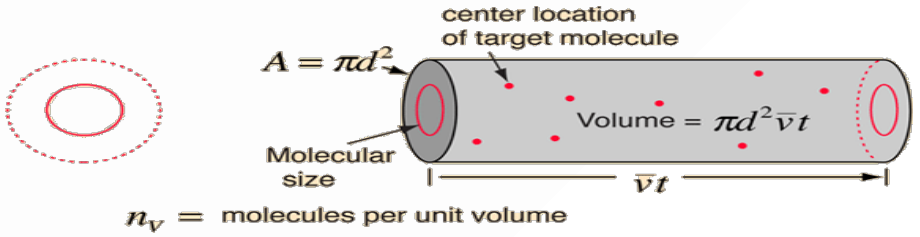

Figure 5: Mean Free Path-2

In time t, the circle would sweep out the volume shown and the number of collisions can be estimated from the number of gas molecules that were in that volume.

$$A = \pi d^2$$

The mean free path could then be taken as the length of the path divided by the number of collisions.

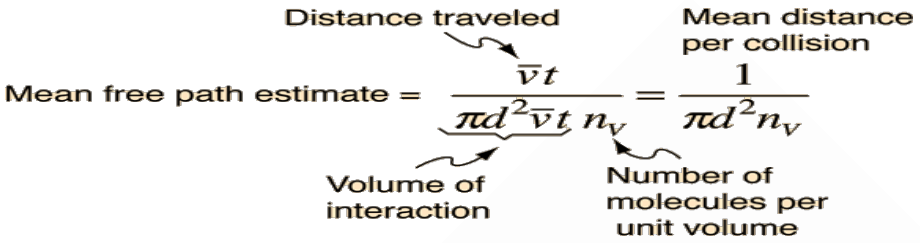

Figure 6: Mean Free Path-2

The problem with this expression is that the average molecular velocity is used, but the target molecules are also moving. The frequency of collisions depends upon the average relative velocity of the randomly moving molecules. And hence Maxwell added a correction factor:

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

$$PV = nRT, n/V = P/RT$$

The mean free path λ is inversely proportional to the pressure of the gas and directly proportional to the Temperature.

4 Transport Phenomema

Transport phenomenon are phenomena involving the movement of various entities, such as mass, momentum, or energy, through a medium, fluid or solid, by virtue of nonuniform conditions existing within the medium. Variations of concentration in a medium, for example, lead to the relative motion of the various chemical species present, and this mass transport is generally referred to as diffusion. Variations of velocity within a fluid result in the transport of momentum, which is normally referred to as viscous flow. Variations in temperature result in the transport of energy, a process usually called heat conduction.

4.1 Viscosity

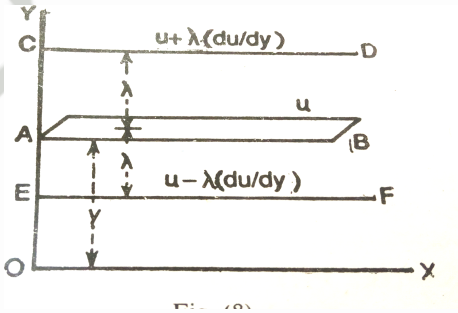

Figure 7: Viscosity

Let a fliud (liquid or gas) flow over a horizontal surface. The velocity of the layer in contact is zero and it gradually increases as we go up from O in Y direction at a uniform rate du/dy. If a layer AB has a velocity u, then a layer at a distance λ above will have a velocity $u + \lambda du/dy$ and a layer EF at a distance λ below will have a velocity $u - \lambda du/dy$. This caues AB to exert an tangential force on the later below to accelerate it and on the layer above to slow it.This force that opposes the motion of gas is called the viscous force. The coefficient of viscosity η is defined as the tangential force per unit area per unit velocity gradient between the layers of the fluid.

$$F = \eta \frac{du}{dy}$$

Let n be the number of molecules per unit volume of the gas and let $\overline{C}$ be the average velocity. Suppose 1/3 molecules are moving in x,y and z directions, then 1/6 are moving upwards, 1/6 are moving downwards. If m is the mass of a molecule, Momentum transferred upwards is $1/6mn\overline{C}(u - \lambda du/dy)$ Momentum transferred

downwards is $1/6mn\overline{C}(u+\lambda du/dy)$ Met momentum transferred upwards is $1/6mn\overline{C}(u+\lambda du/dy)-1/6mn\overline{C}(u-\lambda du/dy)$

$$= 1/3mn\overline{C}(\lambda du/dy)$$

This is the viscous force

$$F = 1/3mn\overline{C}(\lambda du/dy)$$

Coefficient of viscosity is

$$\eta = \frac{1/3mn\overline{C}(\lambda du/dy)}{du/dy} = 1/3mn\overline{C}\lambda = 1/3\rho\overline{C}\lambda$$

where $\rho = mn$ is the density of the gas.

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

Therefore, the coefficient of viscosity is independent of n, directly proportional to $\overline{C}$, directly proportional to $\sqrt{T}$, directly proportional to m and inversely proportional to the diameter of the molecule.

4.2 Conduction

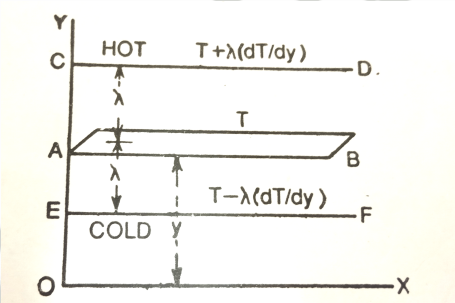

Figure 8: Conduction

Let a fliud (liquid or gas) on a horizontal surface where the temperature layer in contact is low and it gradually increases as we go up from O in Y direction at a uniform rate dT/dy. If a layer AB has a temperature T, then a layer at a distance λ above will have a temperature $T + \lambda dT/dy$ and a layer EF at a distance λ below will have a temperature $T - \lambda dT/dy$. This causes AB to tranfer heat to the layer below to heat it and on the layer above to cool it.This transfer of hear is called conduction. Let n be the number of molecules per unit volume of the gas and let $\overline{C}$ be the average velocity. Let C_V be the specific heat. Suppose 1/3 molecules are moving in x,y and z directions, then 1/6 are moving upwards, 1/6 are moving downwards. If m is the mass of a molecule, Heat Energy transferred upwards is $1/6mn\overline{C}C_V(T - \lambda dT/dy)$ Heat Energy transferred downwards is $1/6mn\overline{C}C_V(T + \lambda dT/dy)$ Net Heat Energy transferred is $1/6mn\overline{C}C_V(T + \lambda dT/dy) - 1/6mn\overline{C}C_V(T - \lambda dT/dy)$

$$= 1/3mn\overline{C}C_V(\lambda dT/dy)$$

$$F = 1/3mn\overline{C}C_V(\lambda dT/dy)$$

Coefficient of heat conduction is

$$K = \frac{1/3mn\overline{C}C_V(\lambda dT/dy)}{dT/dy} = 1/3mn\overline{C}C_V\lambda = 1/3\rho\overline{C}C_V\lambda$$

where $\rho = mn$ is the density of the gas.

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

Therefore, the coefficient of heat conduction is independent of n, directly proportional to $\overline{C}$, directly proportional to $\sqrt{T}$, directly proportional to m and inversely proportional to the diameter of the molecule.

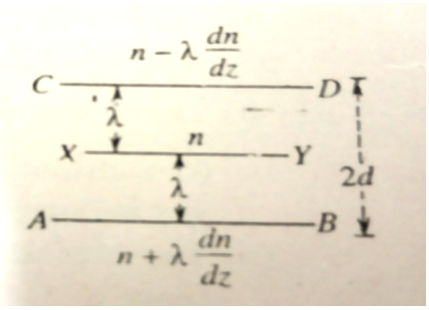

Figure 9: Diffusion

4.3 Diffusion

Consider a fliud (liquid or gas) on a horizontal surface where the concentration gradually increases as we go up from O in Z direction at a uniform rate dn/dz. If a layer AB has a concentration n, then a layer at a distance λ above will have a concentration $n + \lambda dn/dz$ and a layer EF at a distance λ below will have a concentration $n - \lambda dn/dz$. This causes AB to transfer molecules to the layer below to and the layer above. This transfer of molecules is called diffusion. Let n be the number of molecules per unit volume of the gas and let $\overline{C}$ be the average velocity.. Suppose 1/3 molecules are moving in x,y and z directions, then 1/6 are moving upwards, 1/6 are moving downwards. Molecules transferred upwards is $1/6n\overline{C}(n-\lambda dn/dz)$. Molecules transferred downwards is $1/6n\overline{C}(n - \lambda dn/dz)$. Net Molecules transferred transferred is $1/6n\overline{C}(n + \lambda dn/dz) - 1/6n.\overline{C}(n - \lambda dn/dz)$

$$= 1/3\overline{C}(\lambda dn/dz)$$

$$F = 1/3\overline{C}(\lambda dn/dz)$$

Coefficient of diffusion is

$$D = \frac{1/3m\overline{C}(\lambda dn/dz)}{dn/dz} = 1/3\overline{C}\lambda$$

where $\rho = mn$ is the density of the gas.

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

Therefore, the coefficient of diffusion is directly proportional to $T^{3/2}$ and inversely proportional to P.

5 Application of law of equipartition energy in specific heat of a gas

As per the law of equipartition of energy, $kT/2$ is the amount of energy for each degree of freedom. We also know Mayers relation $C_P - C_V = R$ which connects the two specific heats for one mole of an ideal gas, where C_P and C_V are the specific heats at constant pressure and constant volume.

Equipartition law of energy is used to calculate the value of $C_P - C_V$ and the ratio between them $\gamma = C_P/C_V$. Here γ is called the adiabatic exponent.

5.1 Monatomic molecule

Average kinetic energy of a molecule, considering 3 degrees of freedom with $(1/2)kT$ per degree,

$$= \left[\frac{3}{2}kT\right]$$

Total energy of a mole of gas

$$= \frac{3}{2}kT \times N_A = \frac{3}{2}RT$$

$$As, k \times N_A = R$$

For one mole, the molar specific heat at constant volume

$$C_V = \frac{dU}{dT} = \frac{d}{dT}\left[\frac{3}{2}RT\right]$$

$$C_V = \left[\frac{3}{2}R\right]$$

$$C_P = C_V + R = \frac{3}{2}R + R = \frac{5}{2}R$$

The ratio of specific heats,

$$\gamma = \frac{C_P}{C_V} = \frac{\frac{5}{2}R}{\frac{3}{2}R} = \frac{5}{3} = 1.67$$

5.2 Diatomic molecule

Average kinetic energy of a diatomic molecule at low temperature $= (5/2)kT$

Total energy of one mole of gas

$$(5/2)kT \times N_A = (5/2)RT$$

(Here, the total energy is purely kinetic) For one mole Specific heat at constant volume

$$C_V = \frac{dU}{dT} = \left[\frac{5}{2}RT\right] = \frac{5}{2}R$$

$$\text{But } C_P = C_V + R = \frac{5}{2}R + R = \frac{7}{2}R$$

$$\therefore \gamma = \frac{C_P}{C_V} = \frac{\frac{7}{2}R}{\frac{5}{2}R} = 7/5 = 1.40$$

Note that according to kinetic theory model of gases the specific heat capacity at constant volume and constant pressure are independent of temperature. But in reality it is not sure. The specific heat capacity varies with the temperature.