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B.Sc. (Prog), Thermal Physics
Chapter-3
Kinetic Theory of Gases

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> **Kinetic Theory of Gases:** Derivation of Maxwell's 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.

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Que 1: Derive Maxwell Speed Distribution Directly from Boltzmann Distribution

Ans: Fundamental to our understanding of classical molecular phenomena is the Boltzmann distribution, which tells us that the probability that any one molecule will be found with energy E decreases exponentially with energy; i.e., any one molecule is highly unlikely to grab much more than its average share of the total energy available to all the molecules. Mathematically, the Boltzmann distribution can be written in the form

We will take it as a postulate here and show that the Maxwell speed distribution follows from it.

Velocity Distribution in One Dimension

If the energy in the Boltzmann distribution

is just one-dimensional kinetic energy, then the expression becomes

But this must be normalized so that the probability of finding it at some value of velocity is one. This is accomplished by integrating the probability from minus to plus infinity and setting it equal to one. Making use of the definite integral form

with the substitution

allows us to normalize the function:

This normalizes the distribution function to

Converting this relationship to one which expresses the probability in terms of speed in three dimensions gives the Maxwell speed distribution:

Speed distribution as a sum over all directions

To put the three-dimensional energy distribution into the form of the Maxwell speed distribution, we need to sum over all directions.

Direct mathematical approach is to make the conversion of the cartesian volume element to spherical polar coordinates

Que 2: Explain and calculate Most probable speed, mean speed and Root mean square speed/velocity.

Ans: There are actually three ways to quantify typical speeds of a distribution of particles in thermal equilibrium and our back of the envelope calculation only gives us one of them. The first typical speed is the easiest to calculate: the most probable speed.

Most Probable speed

The most probable speed occurs when f(v) is maximum. To calculate this we set the derivative to zero:

$$\frac{df(v)}{dv} = 4\pi \left(\frac{m}{2\pi kT}\right)^{3/2} \left(2v \exp\left(-\frac{mv^2}{2kT}\right) - v^2 \frac{mv}{kT} \exp\left(-\frac{mv^2}{2kT}\right)\right) = 0$$

$$\tilde{v} = \sqrt{2kT/m}$$

Mean speed

The next speed we will find is the mean speed, $\bar{v}$. To find this, we find the expectation value of v:

$$\bar{v} = \int_0^\infty f(v)v\,dv = \int_0^\infty 4\pi \left(\frac{m}{2\pi kT}\right)^{3/2} v^3 \exp\left(-\frac{mv^2}{2kT}\right) dv$$

Using the result that:

$$\int_0^\infty x^3 exp(-x^2/a^2) = a^4/2$$

we get:

$$\bar{v} = 4\pi \left(\frac{m}{2\pi kT}\right)^{3/2} \frac{1}{2} \left(\frac{2kT}{m}\right)^2$$

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

It turns out this is slightly greater than the most probably speed ($\sqrt{8/\pi} > \sqrt{2}$).

Root Mean square velocity

The last speed we will find is the root mean square velocity (v_{rms}). We define $v_{rms}^2 \equiv \overline{v^2}$. To find $\overline{v^2}$:

$$\overline{v^2} = \int_0^\infty f(v)v^2 dv = \int_0^\infty 4\pi \left(\frac{m}{2\pi kT}\right)^{3/2} v^4 \exp\left(-\frac{mv^2}{2kT}\right) dv$$

Using the result that:

$$\int_0^\infty x^4 exp(-x^2/a^2) = \frac{3\sqrt{\pi}a^5}{8}$$

we get:

$$\overline{v^2} = 4\pi \left(\frac{m}{2\pi kT}\right)^{3/2} \frac{3\sqrt{\pi}}{8} \left(\frac{2kT}{m}\right)^{5/2}$$

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

Thus, we find that: Support by Donating alllabexperiments.com

$$v_{rms} = \sqrt{\frac{3kT}{m}}$$

Here is a plot showing the Maxwell speed distribution and the three typical velocities. We can see from this plot that the Maxwell speed distribution is skewed to the right.

Que 3: An ideal gas A is at 27°C initially. The temperature of the gas is increased to 927°C.Find the ratio of final V$_{rms}$ to the initial V$_{rms}$.

Ans: $V_{rms} = \sqrt{3RT/M}$
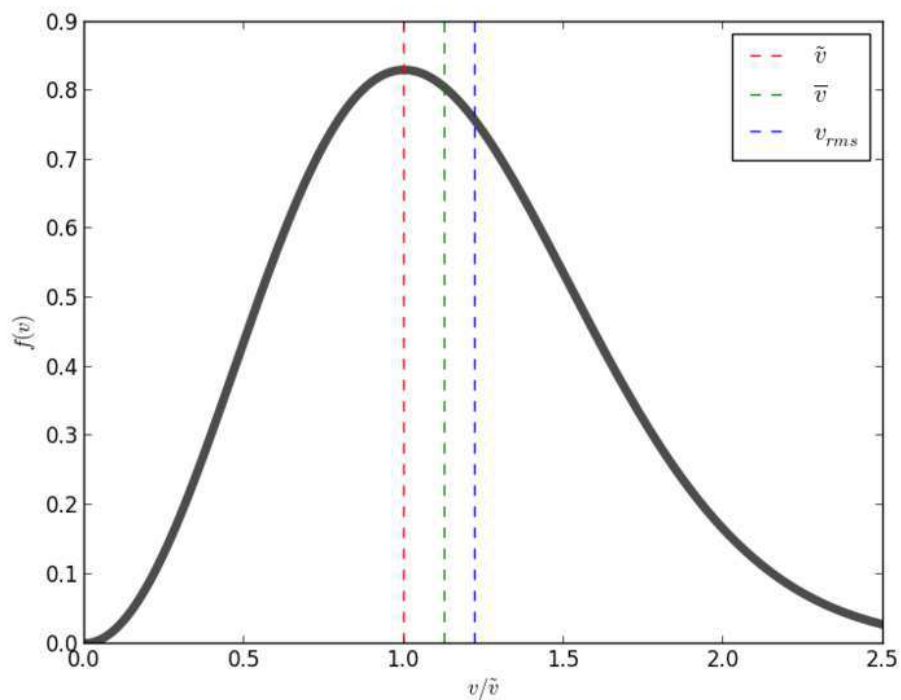
So it is proportional to Temperature

Now

T1=27°C =300K

T2=927°C =1200K

So initial $V_{rms} = k\sqrt{300}$

Final $V_{rms} = k\sqrt{1200}$

ratio of final to initial = 2:1

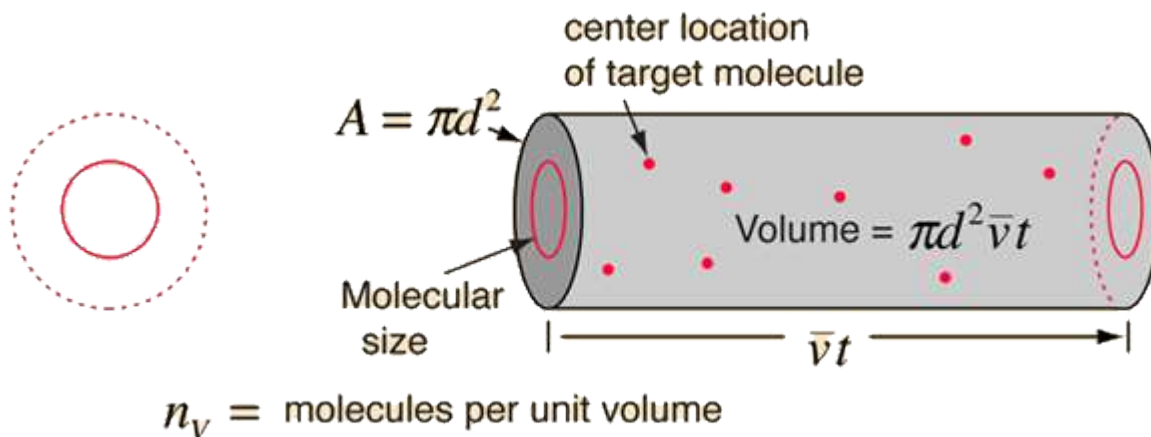**Que 4: Define mean free path for a molecule/particle.**

Ans: In physics, the mean free path is the average distance traveled by a moving particle (such as an atom, a molecule, a photon) between successive impacts (collisions), which modify its direction or energy or other particle properties.

Que 5 : Estimate Mean Free Path using Kinetic Theory of gases.

Ans: The mean free path or average distance between collisions for a gas molecule may be estimated from kinetic theory. Serway's approach is a good visualization - if the molecules have diameter d, then the effective cross-section for collision can be modeled by

The effective collision area is

$$A = \pi d^2$$
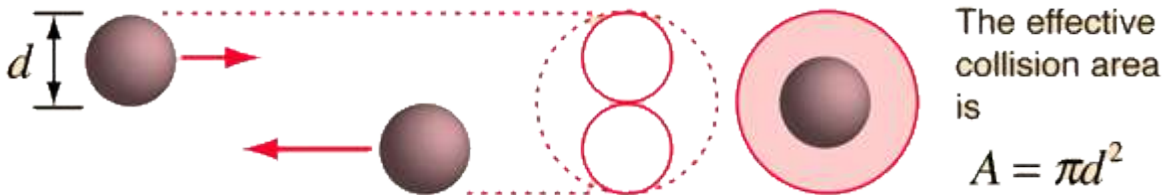
using a circle of diameter 2d to represent a molecule's effective collision area while treating the "target" molecules as point masses. In time t, the circle would sweep out the volume shown and the number of collisions can be estimated from the number of gas molecules that were in that volume

center location of target molecule

$$A = \pi d^2$$

Volume $= \pi d^2 \bar{v} t$

Molecular size

$$\bar{v} t$$

$$n_V = \text{molecules per unit volume}$$

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

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Distance traveled   Mean distance per collision

$$\text{Mean free path estimate} = \frac{\overline{v}t}{\underbrace{\pi d^2 \overline{v}t}\, n_V} = \frac{1}{\pi d^2 n_V}$$

Volume of interaction

Number of molecules per unit volume

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.

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which revises the expression for the effective volume swept out in time t

Effective volume of targets swept $\pi d^2 \sqrt{2}\, \overline{v}t$

The number of collisions is $\sqrt{2}$ times the number with stationary targets.

The resulting mean free path is

$$n_V = \frac{nN_A}{V} = \frac{nN_A}{\frac{nRT}{P}} = \frac{N_A P}{RT}$$

Mean free path

$$\lambda = \frac{RT}{\sqrt{2}\pi d^2 N_A P}$$

Que6 : Explain Diffusion, Viscosity and Thermal conductivity in gases and derive the mathematical expressions.

Ans:

Diffusion

Now if we consider gas with a concentration gradient it should be clear that molecules will move from the more concentrated to the less concentrated regions via a process of collision/random walk. This is diffusion process. If over distance dx concentration change is dn the concentration gradient is dn/dx. The number of molecules crossing A normal to gradient per second can then be written as:

$$\frac{dN}{dt} = -D\frac{dn}{dx}A \qquad \left(j = \frac{dN}{Adt} = -D\frac{dn}{dx} \right) \quad \text{Fick's Law}$$

Where D is called the coefficient of self-diffusion and the negative sign implies flow in the direction of smaller concentration.

Consider the following situation:
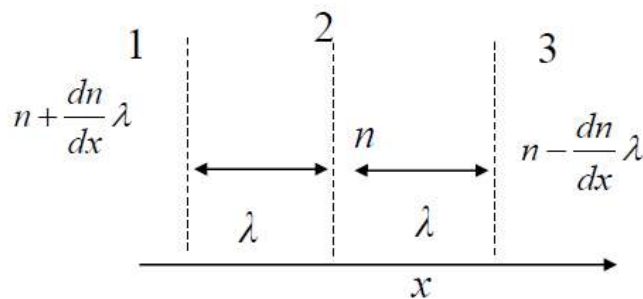
We would then have the number of molecules per second crossing from 1

$$= \frac{1}{6}\left(n + \frac{dn}{dx}\lambda \right)\bar{v}A$$

and from 3

$$= \frac{1}{6}\left(n - \frac{dn}{dx}\lambda \right)\bar{v}A$$

There will also be molecules leaving on each side of 2 of number $\qquad = \frac{1}{6}n\bar{v}A$

So the net transfer is then

$$-\frac{1}{6}\left(n+\frac{dn}{dx}\lambda\right)\bar{v}A+\frac{1}{6}\left(n-\frac{dn}{dx}\lambda\right)\bar{v}A-\frac{1}{6}n\bar{v}A+\frac{1}{6}n\bar{v}A=-\frac{1}{3}\frac{dn}{dx}\lambda\bar{v}A=-D\frac{dn}{dx}A$$

hence

$$\boxed{D=\frac{\lambda\bar{v}}{3}=\frac{\bar{v}}{3\pi n\sigma^2}}$$
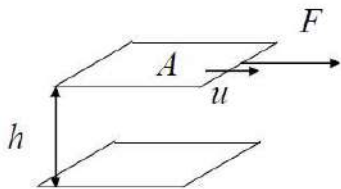
For air at STP σ=0.3nm, $\lambda\approx$100nm, v=450m/s, n $\approx 3*10^{25}$m^{-3}

which gives D of order 10^{-2} m^2/s

also

$$\bar{v}=\left(\frac{8k_BT}{\pi m}\right)^{1/2}$$

hence D can be related with macroscopic T and also P and V through n
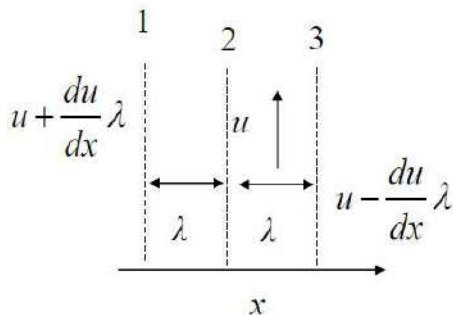
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Viscosity

F must be applied to maintain constant flow. F is proportional to A and u/h.

$$\boxed{F=\eta A\frac{du}{dx}}$$

We further assume: (i) $u\!<\!<\!v$, (ii) the only molecules reaching 2 are those that just made their collision at a distance λ. Thus the number of molecules crossing A is $\frac{1}{6}n\bar{v}A$ per second and from 3 this molecules bring to 2 net horizontal momentum

$$m\left(u-\frac{du}{dx}\lambda\right)\frac{n\bar{v}}{6}A$$

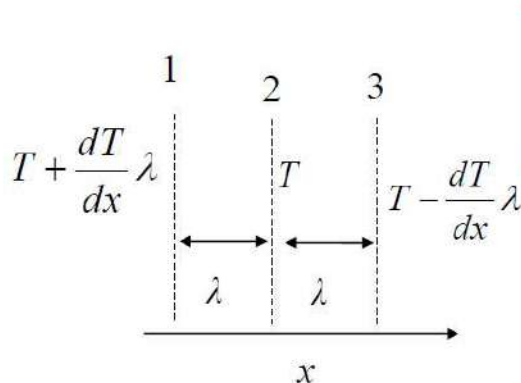Similarly fro 1 to 2 $\quad m\left(u+\frac{du}{dx}\lambda\right)\frac{n\bar{v}}{6}A$

But 2 sends $\frac{1}{6}n\bar{v}A$ both ways too

Thus the total momentum transfer per second (i.e. force) is

$$F=\frac{m\lambda n\bar{v}}{3}A\frac{du}{dx}\Rightarrow\boxed{\eta=\frac{1}{3}m\lambda n\bar{v}=\frac{1}{3}\frac{m\bar{v}}{\pi\sigma^2}}$$

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Thermal conductivity

$$Q = -KA\frac{dT}{dx}$$

where K is the thermal conductivity

Now the rate of transport, this time of thermal energy ($dQ = C_v dT$), is from 1

$$\frac{n\bar{v}A}{6}c_v\left(T+\frac{dT}{dx}\lambda\right)$$

from 3 $\dfrac{n\bar{v}A}{6}c_v\left(T-\dfrac{dT}{dx}\lambda\right)$ so the net transfer at 2 is $\dfrac{n\bar{v}A}{3}c_v\left(\dfrac{dT}{dx}\lambda\right)$

hence $Q = -\dfrac{n\bar{v}A}{3}c_v\lambda\dfrac{dT}{dx} \Rightarrow K = \dfrac{n\bar{v}\lambda}{3}c_v$

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Que 7: State the law of equipartition of energy.

Ans: Each independent degree of freedom has an equal amount of energy equal to (1/2) kT , where the constant k is called the Boltzmann constant and is equal to

$$k = 1.3806505 \times 10^{-23}\ \text{J} \cdot \text{K}^{-1}.$$

The total internal energy of the ideal gas is then

$$E_{\text{internal}} = N(\text{\# of degrees of freedom})\frac{1}{2}kT.$$

This equal division of the energy is called the equipartition of the energy.

Que 8: Derive Specific heat at constant volume and at constant pressure for an ideal gas.

Ans: The specific heats of gases are generally expressed as molar specific heats. For a monoatomic ideal gas, the internal energy is all in the form of kinetic energy, and kinetic theory provides the expression for that energy, related to the kinetic temperature. The expression for the internal energy is

Two specific heats are defined for gases, one for constant volume (CV) and one for constant pressure (CP). For a constant volume process with a monoatomic ideal gas the first law of thermodynamics gives:

$$Q = C_v n \Delta T \qquad Q = \Delta U + P \Delta V = \Delta U$$

$$C_v = \frac{1}{n} \frac{\Delta U}{\Delta T} = \frac{3}{2} R$$

Further application of the ideal gas law and first law gives the relationship

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This value agrees well with experiment for monoatomic noble gases such as helium and argon, but does not describe diatomic or polyatomic gases since their molecular rotations and vibrations contribute to the specific heat. The equipartition of energy predicts

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