

Study Material - Sem. 3 - CGT - Kinetic

Theory of Gases - Dr. T. Kar - Class 2

## Average velocity

If  $n_1$  molecules have velocity  $c_1$ ,  $n_2$  molecules have velocity  $c_2$  and so on, then average velocity is given by

$$\bar{c} = \frac{n_1 c_1 + n_2 c_2 + \dots}{n_1 + n_2 + \dots}$$
$$= \frac{\sum_i n_i c_i}{n} = \frac{\int_0^{\infty} c \, dn}{n}$$

Now,  $dn = 4\pi n a^3 e^{-bc^2} c^2 \, dc$

$$\therefore \bar{c} = \frac{4\pi n a^3 \int_0^{\infty} e^{-bc^2} c^3 \, dc}{n} = 4\pi a^3 \int_0^{\infty} e^{-bc^2} c^3 \, dc$$

$$= 4\pi a^3 \int_0^{\infty} e^{-z} \left(\frac{z}{b}\right) \left(\frac{dz}{2b}\right)$$

$$= \frac{2\pi a^3}{b^2} \int_0^{\infty} e^{-z} z^{2-1} \, dz$$

Let  $bc^2 = z$

$\therefore 2bc \, dc = dz$

$\therefore c \, dc = \frac{dz}{2b}$

$c^2 = \frac{z}{b}$

$$\therefore \bar{c} = \frac{2\pi a^3}{b^2} \Gamma(2) = \frac{2\pi a^3}{b^2} \Gamma(1) = \frac{2\pi a^3}{b^2}$$

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

$$= 2^{1+2-\frac{3}{2}} \pi^{1-\frac{3}{2}} m^{\frac{3}{2}-2} (kT)^{2-\frac{3}{2}}$$

$$= 2^{3/2} \pi^{-1/2} m^{-1/2} (kT)^{1/2}$$

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

### Mean Square velocity

It is defined as,

$$\bar{c^2} = \frac{n_1 c_1^2 + n_2 c_2^2 + \dots}{n_1 + n_2 + \dots} = \frac{\sum_0^{\infty} n_i c_i^2}{n} = \frac{\int_0^{\infty} c^2 dn}{n}$$

$$dn = 4\pi n a^3 e^{-bc^2} c^2 dc$$

$$\bar{c^2} = 4\pi a^3 \int_0^{\infty} e^{-bc^2} c^4 dc$$

$$= \frac{4\pi a^3}{b^{3/2}} \int_0^{\infty} e^{-z} z^{3/2} \left(\frac{dz}{2b}\right)$$

$$= \frac{2\pi a^3}{b^{5/2}} \int_0^{\infty} e^{-z} z^{5/2-1} dz$$

$$= \frac{2\pi a^3}{b^{5/2}} \Gamma\left(\frac{5}{2}\right) = \frac{2\pi a^3}{b^{5/2}} \left(\frac{3}{2}\right) \Gamma\left(\frac{3}{2}\right)$$

$$= \frac{2\pi a^3}{b^{5/2}} \left(\frac{3}{2}\right) \left(\frac{1}{2}\right) \Gamma\left(\frac{1}{2}\right) = \frac{2\pi a^3}{b^{5/2}} \left(\frac{3}{4}\right) \sqrt{\pi} = \left(\frac{3}{2}\right) \frac{\pi^{3/2} a^3}{b^{5/2}}$$

Let,  $bc^2 = z$

$$\therefore 2bc dc = dz$$

$$\therefore c dc = \frac{dz}{2b}$$

$$c = \left(\frac{z}{b}\right)^{1/2}$$

$$\frac{5}{2} = 1 + \frac{3}{2}$$

$$\frac{3}{2} = 1 + \frac{1}{2}$$

$$\overline{c^2} = \left(\frac{3}{2}\right) \pi^{3/2} \left(\frac{m}{2\pi kT}\right)^{3/2} \frac{1}{\left(\frac{m}{2\pi kT}\right)^{5/2}}$$

$$= \left(\frac{3}{2}\right) \pi^{3/2} \left(\frac{m}{2\pi kT}\right)^{3/2} \left(\frac{2\pi kT}{m}\right)^{5/2}$$

$$= (3) \left(2^{5/2 - 3/2 - 1}\right) \pi^{3/2 - 3/2} m^{3/2 - 5/2} (kT)^{5/2 - 3/2}$$

$$= \frac{3kT}{m}$$

$\therefore$  Root mean square velocity =  $C_{rms}$

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

Most Probable Velocity:

It is that value of  $c$  for which  $F$  is maximum.

$$\text{Now, } F = 4\pi a^3 c^2 e^{-bc^2}$$

Differentiating w.r.t.  $c$ ,

$$\frac{dF}{dc} = 8\pi a^3 c e^{-bc^2} - 8\pi b a^3 c^3 e^{-bc^2}$$

For stationary values,  $\frac{dF}{dc} = 0$

Suppose  $c = c_m$  is that value for which  $\frac{dF}{dc} = 0$

Then,

$$8\pi a^3 c_m e^{-bc_m^2} = 8\pi b a^3 c_m^3 e^{-bc_m^2}$$

$$\therefore 1 = bc_m^2 \quad \therefore c_m = \sqrt{\frac{1}{b}} = \sqrt{\frac{2kT}{m}}$$

## Distribution of energy among the molecules

We want to find out the number of molecules having kinetic energy between  $E$  and  $E+dE$ .

$$\text{Kinetic energy, } E = \frac{1}{2} mc^2$$

$$\begin{aligned} \therefore dE &= mc \, dc \quad \text{or} \quad dc = \frac{dE}{mc} = \frac{dE}{m \left( \frac{2E}{m} \right)^{1/2}} \\ &= \frac{dE}{\sqrt{2mE}} \end{aligned}$$

From Maxwell's law, no. of molecules moving with velocity between  $c$  and  $c+dc$  is —

$$dn = 4\pi n \left( \frac{m}{2\pi kT} \right)^{3/2} e^{-\frac{mc^2}{2kT}} c^2 dc$$

$\therefore$  The no. of molecules having energy between  $E$  and  $dE$  is —

$$dn = 4\pi n \left( \frac{m}{2\pi kT} \right)^{3/2} e^{-\frac{(2E/m)m}{2kT}} \left( \frac{2E}{m} \right) \frac{dE}{\sqrt{2mE}}$$

$$= 8\pi n \left( \frac{m}{2\pi kT} \right)^{3/2} e^{-\frac{E}{kT}} \left( \frac{E}{m} \right) \frac{dE}{\sqrt{2mE}}$$

$$= \left[ 2^{3 - \frac{3}{2} - \frac{1}{2}} \pi^{1 - 3/2} m^{3/2 - 1 - \frac{1}{2}} E^{1 - \frac{1}{2}} e^{-E/kT} \right] (kT)^{-3/2} dE$$

$$= 2 \pi^{-1/2} m^0 e^{-E/kT} \sqrt{E} dE (kT)^{-3/2}$$

$$= 2 \sqrt{\frac{E}{\pi}} (kT)^{-3/2} e^{-E/kT} dE$$

# Experimental Verification of Maxwell-Boltzmann Velocity Distribution Law

By Zartman & Ko :

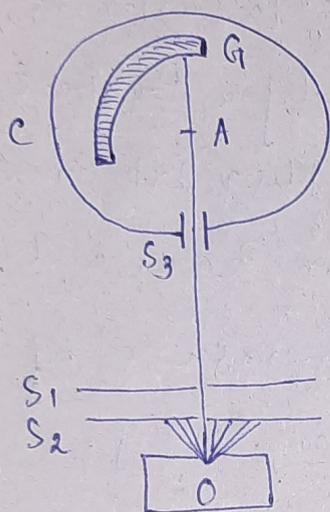


Fig. 1.

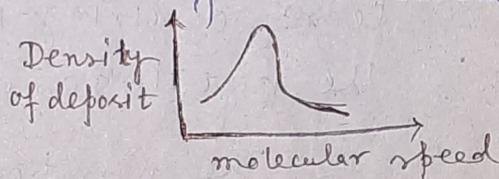
The essentials of the apparatus used by these two workers are shown in Fig. 1. 'O' is an electrically heated oven containing a vapour which comes out of it. There are two slits  $S_1$  &  $S_2$  defining a molecular beam. 'C' is a cylinder which can be rotated at 1000 rpm about an axis passing through A.

It has a hole that comes directly above the slits in each turn. If the cylinder is at rest, the molecular beam would pass through  $S_3$  to the cylinder and strike a curved glass-plate (G) at the right end as shown in the figure. The molecules stick to the glass plate causing darkening of the plate. The number arriving at any portion is determined by removing the glass plate and measuring the resultant darkening by a microphotometer.

When the cylinder is rotated the molecules can enter it only a short interval of time during which the slit is in the line with the opening

In the cylinder. If the motion is clockwise as shown in the figure, the glass plate moves towards the right while molecules cross diametrically across the cylinder. The molecules, therefore, strike more and more towards the left of the direct point of impact; the greater the velocity of the molecules nearer to the direct point of impact they strike the glass, and lower the velocity, further and further to the left they fall, thus giving rise to different amount of darkening/blackening on the glass plate.

The blackening of the plate is a measure of the 'velocity spectrum' of the molecular beam.



## Degrees of Freedom

If a particle moves in a straight line, say, along  $x$ -direction, only one coordinate is necessary to specify the position of the particle. We say it has one degree of freedom. But if it moves in a plane, then to specify the position two coordinates  $x$  and  $y$  are necessary to specify the position and then the particle has two degrees of freedom.

But when it flies in space, three coordinates  $x, y, z$  are needed to specify the position and the particle has three degrees of freedom. So, by degree of freedom we mean the number of independent coordinates necessary to specify the position or configuration of a dynamical system.

Again, the kinetic energy of the particle in the first instance is given by  $\frac{1}{2} m \dot{x}^2$ , that in the second by  $\frac{1}{2} m (\dot{x}^2 + \dot{y}^2)$  and in the third by  $\frac{1}{2} m (\dot{x}^2 + \dot{y}^2 + \dot{z}^2)$ . So, we can define the degrees of freedom as also the number of squared terms occurring in the expression for the kinetic energy of the system.

The number of degrees of freedom depends on the geometrical shape of the body or system and on the number of constraints imposed on the motion of the body.

Now we have to differentiate two types of motion of a system—  
(i) free motion and (ii) constrained motion.

Let us consider the motion of a

particle in  $xy$  plane. If the particle is moving freely, it can occupy any position  $(x, y)$  in the plane and its position is completely defined as soon as we know coordinates  $(x, y)$ . Now, we impose the condition that the particle must always move on the circumference of the circle,  $x^2 + y^2 = a^2$ .

Then the coordinates  $(x, y)$  of the position cannot be any arbitrary number, for they must satisfy the equation  $x^2 + y^2 = a^2$ . We thus see the difference between the two types of motion. In the former case, the particle is said to have free motion, in the second case, it has constrained motion; the circle itself is called the constraint. It means that if the motion is subjected to certain restrictions, then the restraining conditions which indirectly regulate the motion are known as constraints. In general, if a dynamical system consists of  $N$  particles with  $p$  constraints to obey, then the number of degrees of freedom will be  $(3N - p)$ .

## Law of Equipartition of Energy

This law states that "The total energy of a dynamical system in Thermal equilibrium is equally partitioned (i.e, divided) among all The degrees of freedom and The energy per molecule per degree of freedom is equal to  $\frac{1}{2}KT$  where  $K$  = Boltzmann constant and  $T$  = equilibrium temperature in absolute scale.

This law is also known as Boltzmann law of equipartition of energy and it is true for all degrees of freedom — translational, rotational or vibrational.

If a dynamical system has  $f$  degrees of freedom, Then total energy of a molecule is  $\frac{1}{2}fKT$ . If we consider one mole gas, Then total energy =  $\frac{1}{2}fKTN$ ,  $N$  = Avogadro's Number  
=  $\frac{1}{2}fRT$

## Relation Between Degrees of Freedom and Ratio of Two Specific Heats of a Gas

Let us assume that The number of

degrees of freedom of each molecule of the gas is  $f$ . Then, the kinetic energy of one mole gas is —

$$E = \frac{1}{2} f K T N = \frac{1}{2} f R T \quad \left[ \begin{array}{l} \text{energy/molecule/deg.} \\ \text{of freedom} = \frac{1}{2} K T \end{array} \right]$$

$\therefore$  molar specific heat at constant volume

$$\text{is } C_v = \frac{dE}{dT} = \frac{1}{2} f R$$

$$\text{But, } C_p - C_v = R$$

$$\therefore, C_p = R + C_v = R + \frac{1}{2} f R = R \left( 1 + \frac{f}{2} \right)$$

$$\therefore \gamma = \frac{C_p}{C_v} = \frac{R \left( 1 + \frac{f}{2} \right)}{R \left( \frac{f}{2} \right)} = \frac{2}{f} \left( 1 + \frac{f}{2} \right) = 1 + \frac{2}{f}$$

$$\therefore \boxed{\gamma = 1 + \frac{2}{f}}$$

Now, let us take particular cases —

### Case I. Monatomic Gas

In a monatomic gas/molecule, there is a single atom. The degrees of freedom in such case is —

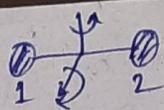
$f = 3N - p = (3 \times 1) - 0 = 3$ , i.e., there are three translational degrees of freedom.

$$\therefore \gamma = 1 + \frac{2}{3} = \frac{5}{3} = 1.66$$

### Case II. Diatomic Gas

Each molecule consists of 2 atoms which are subject to the constraint that the atomic

distance is fixed.



$$\therefore f = 3N - p = (3 \times 2) - 1 = 5$$

Of these five degrees of freedom, three correspond to translational degrees of freedom and two correspond to rotational degrees of freedom. [Rotation about an axis at right angles to the line joining two atoms.]

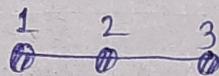
$$\therefore \gamma = 1 + \left(\frac{2}{5}\right) = \frac{7}{5} = 1.40$$

### Case III. Triatomic molecule

Here the ~~two~~ three atoms can have two types of arrangements — (a) linear, (b) at the vertices of a triangle/Triangular

If case (a), The number of constraints are two.

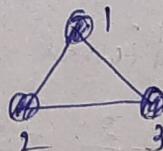
$$\therefore f = (3 \times 3) - 2 = 9 - 2 = 7$$



$$\therefore \gamma = 1 + \frac{2}{7} = \frac{9}{7} = 1.28$$

In case (b), Here The number of constraints are 3.

$$\therefore f = (3 \times 3) - 3 = 6$$



$$\therefore \gamma = 1 + \frac{2}{6} = 1.33$$

## Doppler Broadening of Spectral lines

In atomic physics, Doppler broadening is the broadening of spectral lines due to the Doppler effect caused by a distribution of velocities of atoms or molecules. Different velocities of the emitting particles result in different Doppler shifts, the cumulative effect of which is the line broadening. The resulting line profile is known as a Doppler profile. A particular case is the Thermal Doppler broadening due to the thermal motion of the particles. Then, the broadening depends on the frequency of the spectral line, the mass of the emitting particles, and their temperature, and therefore can be used for inferring the temperature of an emitting body.

When thermal motion causes a particle to move towards the observer, the emitted radiation will be shifted to a higher frequency. Likewise, when the ~~emitter~~ emitter moves away, the frequency will be lowered. For non-relativistic thermal velocities, the

Doppler shift in frequency will be:

$$f = f_0 \left(1 + \frac{v}{c}\right)$$

where,  $f \rightarrow$  observed frequency

$f_0 \rightarrow$  rest frequency

$v \rightarrow$  velocity of the emitter towards the observer

$c \rightarrow$  velocity of light

Since there is a distribution of speeds both towards and away from the observer in any volume element of the radiating body, the net effect will be to broaden the observed line. If  $P_0(v) dv$  is the fraction of particles with velocity component  $v$  to  $v+dv$  along a line of sight, then the corresponding distribution of the frequencies is —

$P_f(f) df = P_0(v_f) \frac{dv}{df} df$  where  $v_f = c \left(\frac{f}{f_0} - 1\right)$  is the velocity towards the observer corresponding to the shift of the rest frequency ' $f_0$  to ' $f$ '. ~~Therefore~~ Therefore,

$$P_f(f) df = \frac{c}{f_0} P_0 \left[ c \left(\frac{f}{f_0} - 1\right) \right] df$$

In case of the thermal doppler broadening, the velocity distribution is given by the Maxwell distribution —

$$P_v(v) dv = \sqrt{\frac{m}{2\pi kT}} \exp\left(-\frac{mv^2}{2kT}\right) dv$$

where,  $m \rightarrow$  mass of the emitting particle

$T \rightarrow$  Temperature

$k \rightarrow$  Boltzmann constant

Then,  $\oint$

$$P_f(f) df = \left(\frac{c}{f_0}\right) \sqrt{\frac{m}{2\pi kT}} \exp\left[-\frac{m\left[\frac{c}{f_0}(f-f_0)\right]^2}{2kT}\right] df$$

$$= \sqrt{\frac{mc^2}{2\pi kT f_0^2}} \exp\left[-\frac{mc^2(f-f_0)^2}{2kT f_0^2}\right] df$$

In astronomy and plasma physics, the thermal Doppler broadening is one of the explanations for the broadening of spectral lines and as such gives an indication for the temperature of observed material. Doppler broadening is also used to determine the velocity distribution of interstellar gas clouds. Doppler broadening is also used in designing high temperature nuclear reactor.