

Lecture 7 Kinetic Theory of Gases

(Ch. 3 First Law of Thermodynamics: 3.2b Kinetic Theory of Gases)

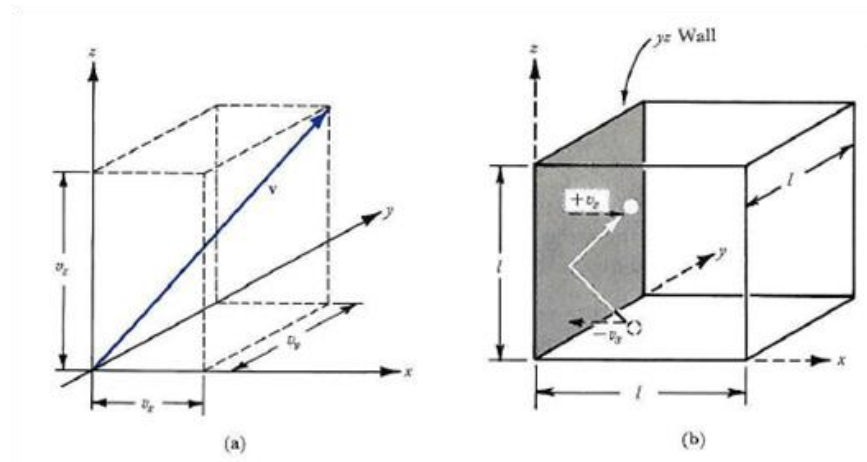
To a high degree of accuracy, the following **assumptions** are made for a volume of gas in the Kinetic Theory of Gases:

- (1) The volume occupied by the molecules can be neglected.
- (2) The motion of the molecules is completely random.
- (3) The collisions are elastic (i.e. KE and momentum are conserved)
- (4) The time of any collision is very small compared to the time between collisions.
- (5) The collisions obey Newton's laws.

The above assumptions apply to an ideal gas. Now, let us consider a cube of side l , which contains a large number of molecules, N .

(Fig. 8.1)

The pressure exerted on the inner walls of the box is caused by collisions of the molecules. For a single molecule, the average force exerted over the



time between the right and left walls (collisions) is given by

$$F_x = ma_x = \frac{d(mv_x)}{dt} \approx \frac{\Delta(mv)}{\Delta t} = \frac{2mv_x}{2l/v_x} = \frac{mv_x^2}{l}.$$

Thus, the total force due to all molecules is

$$F_x = \sum_{i=1}^N \frac{mv_{xi}^2}{l} = \frac{mN}{l} \overline{v_x^2},$$

and the total pressure may be expressed as

$$P_x = \frac{F_x}{l^2} = \frac{mN}{l^3} \overline{v_x^2}.$$

Since the motion is completely random, similar relationships can be obtained,

$$P_y = \frac{F_y}{l^2} = \frac{mN}{l^3} \overline{v_y^2}, \quad P_z = \frac{F_z}{l^2} = \frac{mN}{l^3} \overline{v_z^2}$$

and

$$\overline{v_x^2} = \overline{v_y^2} = \overline{v_z^2} = \frac{1}{3} \overline{v^2}.$$

Therefore, the pressure on any face of the cube is

$$P = \frac{1}{3} \frac{mN}{l^3} \overline{v^2} = \frac{1}{3} \frac{mN}{V} \overline{v^2}, \quad \text{or} \quad PV = \frac{1}{3} mN \overline{v^2}. \quad (3.10)$$

Now, we may apply the equation of state for ideal gases,

$$PV = nR^*T,$$

to the above equation,

$$nR^*T = \frac{1}{3}mN\overline{v^2},$$

$$\frac{3}{2}\left(\frac{n}{N}\right)R^*T = \frac{3}{2}\left(\frac{R^*}{N_A}\right)T = \frac{3}{2}kT = \frac{1}{2}m\overline{v^2},$$

or

$$\frac{3}{2}kT = \frac{1}{2}m\overline{v^2} \quad (3.11)$$

where

N = the total number of molecules

n = number of molecules in *kmoles*

$N_A = N/n = 1 \text{ kmole} = 10^3 \text{ moles} = 6.022 \times 10^{26}$ molecules,

i.e. the *Avogadro's constant*

$k = R^*/N_A = 1.38 \times 10^{-23} \text{ J K}^{-1} \text{ molecule}^{-1}$,

i.e. the **universal gas constant per molecule** or
the *Boltzmann's constant*

Thus, temperature is a measure of the average *KE* of the molecules.

For 1 molecule ($N = 1$), Eq. (3.10) may be rewritten as

$$v_{rms}^2 = \overline{v^2} = \frac{3p}{\rho}, \quad (3.12)$$

which gives us a way to estimate the so called *root-mean-square molecular speed*, v_{rms} . For example, $v_{rms} = 500 \text{ m s}^{-1}$ for a gas with $p=1000 \text{ mb}$ and $\rho=1.2 \text{ kg m}^{-3}$.

The distance between 2 molecular collisions, the *mean free path*, can also be estimated,

$$\bar{l} = \frac{M}{\pi\sqrt{2}\rho N_A d^2}, \quad (3.13)$$

where d is the *molecular diameter* and M is the *molecular weight*.

For example, the mean free path is about $2.3 \times 10^{-7} \text{ m}$ for $d = 2 \times 10^{-10} \text{ m}$, $\rho = 1.2 \text{ kg m}^{-3}$, $M_d = 29 \text{ kg kmol}^{-1}$, and $N_A = 6.022 \times 10^{26}$.

In addition, *the time between 2 collisions* (i.e., distance divided by speed) can be estimated by

$$\Delta t = \frac{\bar{l}}{v_{rms}}. \quad (3.14)$$