ASME231 Atmospheric Thermodynamics NC A&T State U
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Lecture 7 Kinetic Theory of Gases

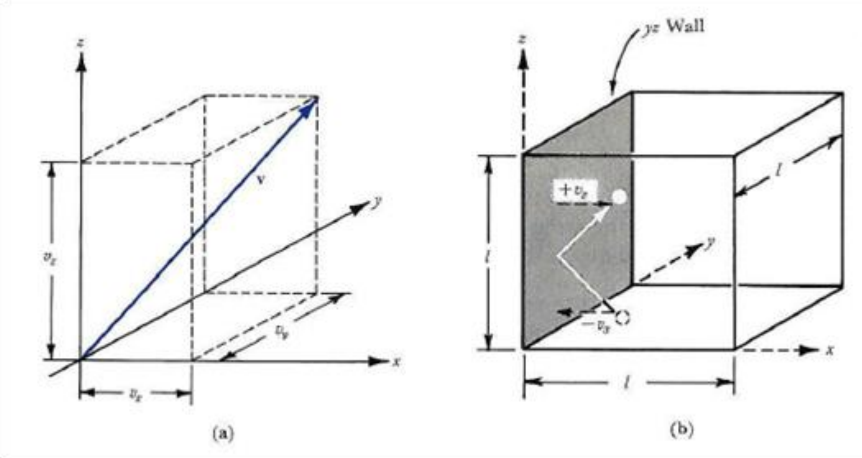
(Ch. 3 First Law of Thermodynamics: 3.2b Kinetic Theory of Gasses)

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 (Fig. 8.1), which contains a large number of molecules, *N*.

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

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

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

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

where

N = the total number of molecules
n = number of molecules in *kmoles*
$N_A = N/n$ = 1 *kmole* = 10^3 moles = $6.022\text{x}10^{26}$ molecules,
i.e. the *Avogadro's constant*
$k = R^*/N_A = 1.38\text{x}10^{-23}$ $J\,K^{-1}$ 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

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

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

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

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

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

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

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

$$\Delta t = \frac{\bar{l}}{v_{rms}}. \tag{3.14}$$