5.3 MEAN FREE PATH

Unlike ideal gases the molecules of real gases interact with each other and collide which changes their momenta. The average distance traveled by a molecule between collisions is called the mean free path. To get a useful estimate of the **mean free path**, we model molecules as spheres of diameter d, and look at the collision cross-section between two molecules A and B as shown in Fig. 5.5, which is drawn in the rest frame of B. Let v_{rel} be average relative speed between two molecules.

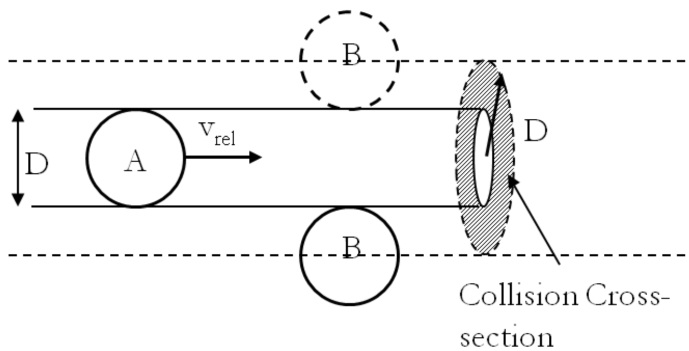

Figure 5.5: Collision of molecules A and B in the rest frame of B. Molecules A and B will collide if they are within the circle of radius D, which is taken to be the diameter of one molecule.

Molecule A will collide with molecule B if latter's center is within a distance D of the center of the molecule A as shown in Fig. 5.5. Therefore the cross-section for collision is equal to πD^2. The number of collisions suffered by a molecule will depend on the density of molecules and the relative speed. Although after each collision the direction of motion of the molecule will change, but in each direction it is the same cross-sectional area. Therefore the number of collisions in some duration Δt will equal the number of molecules in the volume of a cylinder of the cross-sectional area πD^2 and length $v_{rel}\Delta t$, the distance traveled by the molecule shown as A (Fig. 5.6).

$$\text{Number of collisions in } \Delta t = \frac{N}{V}\left(\pi D^2 v_{rel}\Delta t\right) \tag{5.15}$$

$$\text{Distance traveled in } \Delta t = <v> \Delta t \tag{5.16}$$

where $<v>$ is the average speed of the molecule, N is the total number of molecules occupying volume V. It can be shown that the average speed is related to the average relative speed as follows.

$$v_{rel} = \frac{<v>}{\sqrt{2}} \tag{5.17}$$

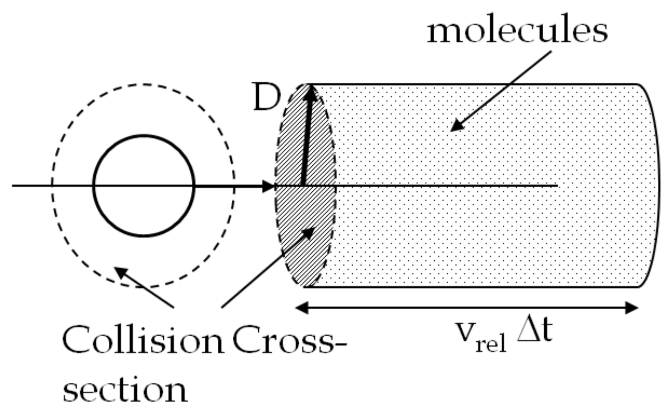

Figure 5.6: Molecules in the enclosed cylinder will collide with a selected molecule

Hence, mean free path λ is

$$\boxed{\text{Mean free path, } \lambda = \frac{\text{Distance traveled}}{\text{Number of Collisions}} = \frac{1}{\sqrt{2}\,\pi D^2}\frac{V}{N}.} \quad (5.18)$$

Because most real gases at high temperature and low density behave as ideal gas, sometimes we can use the ideal gas law even for real gases. In that case we can replace V/N and obtain mean free path in terms of temperature and pressure.

Approximately Ideal Gas Behavior:

$$\boxed{\lambda = \frac{k_B}{\sqrt{2}\,\pi D^2}\frac{T}{p}.} \quad (5.19)$$

You might call this "ideal gas" mean free path. In a strict sense a true ideal gas will have $\lambda = \infty$ since the molecules of an ideal gas do not interact with each other. This formula is a mixture of ideas from the real gas and the ideal gas and the final mean free path formula is often called the "ideal gas mean free path".

Example 5.3.1. Mean Free Path

Find the mean free path for an "ideal gas" at standard temperature and pressure (STP), i.e. a temperature T=300 K and a pressure $p = 1$ atmosphere for a molecule of size 0.4 nm and compare it to the average distance between molecules.

Solution. We use the formula for mean free path for an ideal gas given in terms of T and p to obtain

$$\lambda_{\text{ideal}} = \frac{k_B}{\sqrt{2}\,\pi D^2}\frac{T}{p} = 52 \text{ nm}.$$

Average separation between molecules can be obtained from the average space occupied by one molecule. If the average space occupied by one molecule as a sphere of radius R, The average separation between molecules will be $2R$.

$$\text{Average separation between molecules } = 2\left(\frac{3k_BT}{4\pi p}\right)^{1/3} = 3.3 \text{ nm.}$$

Thus, at standard temperature and pressure (STP) mean free path $\lambda >>$ average distance between molecules as shown in Fig. 5.7.

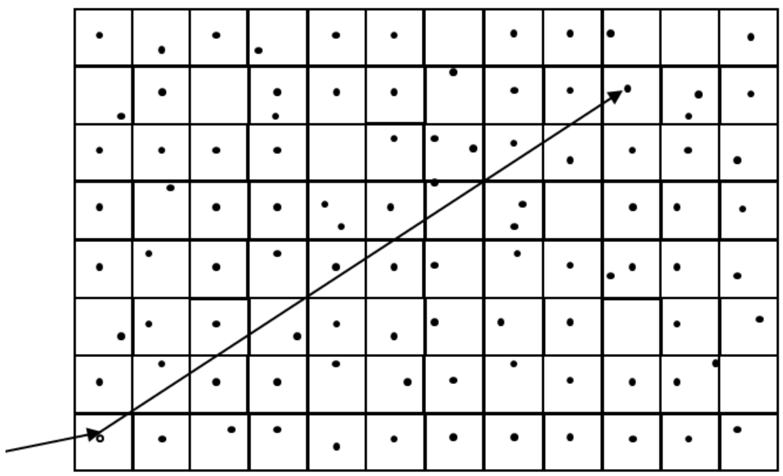

Figure 5.7: Molecular size, the separation of molecules and the mean free path illustrated approximately to scale in an "ideal gas" at 300 K and 1 atm.