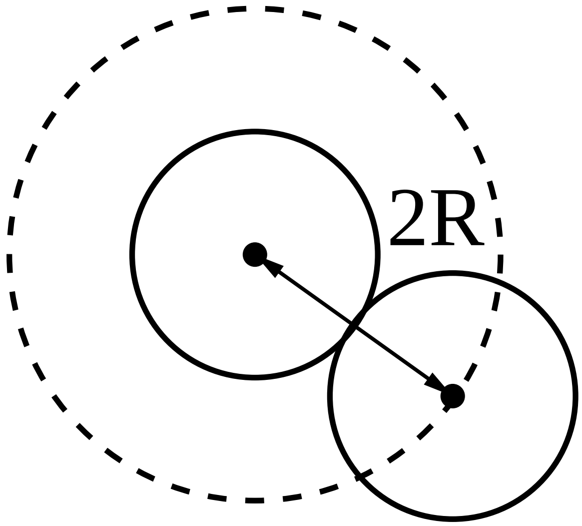

Figure 1: Cross Section.

Chapter 3
3.8 Mean Free Path and Diffusion

In a gas, the molecules collide with one another. Momentum and energy are conserved in these collisions, so the ideal gas law remains valid.

The **mean free path** λ is the average distance a particle travels between collisions. The larger the particles or the denser the gas, the more frequent the collisions are and the shorter the mean free path. If the particle were all by itself, then the mean free path would be infinite. If 2 particles, each of radius R, come within $2R$ of each other, then they collide. The collision cross section is defined as the collision area $\sigma = \pi(2R)^2$ that it presents as it moves through space.

The mean free path λ is related to the cross section σ and the number density n of particles by

$$\lambda \approx \frac{1}{n\sigma} \tag{1}$$

To see this, notice that a particle that undergoes a large number N of collisions will exhibit a zig-zag pattern of total length $L = N\lambda$, since the average distance between collisions is λ. We can think of the particle as sweeping out a volume

$$V = L\sigma = N\lambda\sigma \tag{2}$$

The number density of particles in this volume is n:

$$n = \frac{N}{V} = \frac{N}{N\lambda\sigma} = \frac{1}{\lambda\sigma} \tag{3}$$

where we are assuming that the number of collisions in the volume is the same as the number of molecules in the volume, and that the number density in the volume is the same as the number density in the sample as a whole. We can rewrite this equation as

$$\lambda \approx \frac{1}{n\sigma} \tag{4}$$

which is the desired result. Notice that the mean free path goes down as the number density and the cross section go up, as expected.

Example

Given that the mean radius of an air molecule (either O_2 or N_2) is about R=0.15 nm, what is the approximate mean free path λ of the molecules in air at atmospheric pressure and room temperature? (1 atm $\approx 1.01 \times 10^5$ Pa)

Solution: Use Eq. (4):

$$\lambda \approx \frac{1}{n\sigma} \tag{5}$$

We can obtain the number density n from the ideal gas law:

$$n = \frac{N}{V} = \frac{P}{kT} = \frac{1.01 \times 10^5 \text{ Pa}}{(1.38 \times 10^{-23} \text{ J/K}) \times (300 \text{ K})} = 2.45 \times 10^{25} \text{ m}^{-3} \tag{6}$$

The collision cross section is

$$\sigma = \pi(2R)^2 = 4\pi(0.15 \times 10^{-9} \text{ m})^2 = 2.8 \times 10^{-19} \text{ m}^2 \tag{7}$$

So we have

$$\lambda \approx \frac{1}{n\sigma} = \frac{1}{(2.45 \times 10^{25} \text{ m}^{-3})(2.8 \times 10^{-19} \text{ m}^2)} = 1.4 \times 10^{-7} \text{ m} = 140 \text{ nm} \tag{8}$$

This is about 40 times greater than the average distance between nearest-neighbor molecules in the gas.

The convoluted zig-zag trajectory of a particle is an example of **diffusive motion** or **diffusion**. It is also an example of a **random walk**. Think of a drunk coming out of a bar and staggering around, each step being in a random direction. It turns out that the average magnitude of the displacement D of a particle undergoing a random walk is proportional to the square root of the time t that is has been moving:

$$D_{diff} \propto \sqrt{t} \tag{9}$$

This is in contrast to **ballistic motion** where $D = vt$, i.e., D is proportional to the time of travel:

$$D \propto t \tag{10}$$

To see why the displacement is proportional to $\sqrt{t}$ for a random walk, consider a random walk in 1, 2 or 3 dimensions consisting of steps of length d in random directions described by the vectors $\mathbf{d}_i$. The net displacement is given by

$$\mathbf{D} = \sum_{i=1}^{N} \mathbf{d}_i \tag{11}$$

If we sum these vectors, we'd get zero on average because they are in random directions. If the random walk was in 1D, then we'd be adding positive and negative numbers and they would tend to cancel out, but that doesn't mean the particle doesn't get anywhere. Let's square the displacement so that we are just adding positive numbers. Then we have

$$\begin{aligned} \mathbf{D}\cdot\mathbf{D} = D^2 &= \left(\sum_{i=1}^{N}\mathbf{d}_i\right)\cdot\left(\sum_{j=1}^{N}\mathbf{d}_j\right) \\ &= \sum_{i=1}^{N}\mathbf{d}_i^2 + \sum_{i\neq j}\mathbf{d}_i\cdot\mathbf{d}_j \\ &= Nd^2 + \sum_{i\neq j}\mathbf{d}_i\cdot\mathbf{d}_j \end{aligned} \tag{12}$$

When we take an ensemble average, then the second term cancels out because it is a sum of positive and negative terms. So we get

$$\langle D^2\rangle = Nd^2 \tag{13}$$

The **root-mean-square** average distance D_{rms} is

$$D_{rms} = \sqrt{\langle D^2\rangle} = \sqrt{N}d \tag{14}$$

If we let the mean free path λ be the step size d, then

$$D_{rms} = \sqrt{N}\lambda \tag{15}$$

If τ is the mean time between collisions, then the number of steps is

$$N = \frac{t}{\tau} \tag{16}$$

and

$$D_{rms} = \sqrt{\frac{t}{\tau}}\lambda \propto \sqrt{t} \tag{17}$$

As desired, we see that the rms displacement is proportional to the square root of the time of travel. We can write this in terms of the rms velocity v_{rms} using

$$v_{rms} = \frac{\lambda}{\tau} \tag{18}$$

or

$$\tau = \frac{\lambda}{v_{rms}} \tag{19}$$

$$D_{rms} = \sqrt{\frac{t}{\tau}}\lambda = \sqrt{\frac{v_{rms}t}{\lambda}}\lambda = \sqrt{\lambda v_{rms}}\sqrt{t} \tag{20}$$

From the equipartition theorem,

$$\frac{1}{2}m\langle v^2\rangle = \frac{3}{2}k_B T \tag{21}$$

or

$$v_{rms} = \sqrt{\frac{3k_B T}{m}} \tag{22}$$

so we can write

$$D_{rms} \approx \frac{1}{\sqrt{n\sigma}} \left(\frac{3k_B T}{m}\right)^{1/4} \sqrt{t} \tag{23}$$

This is useful because many of these quantities can be measured experimentally.