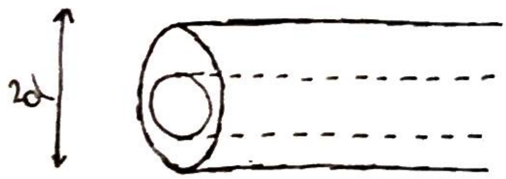
Mean Free Path

Consider a gas with free moving particles. What is the average distance a particle can travel before it collides?



We can start by constructing a cylinder. If the particle has a diameter d, then the cylinder is constructed with diameter $2d$. Therefore the cross-sectional area is πd^2.

Since the cylinder diameter is twice the diameter of a particle, if another particle has its centre within the cylinder, it will definitely be collided with.

The volume swept by the cylinder over a time t is given by: $\text{volume} = \underline{\underline{\pi d^2 v t}}$ where v is the velocity of the particle.

The number of particles in this volume is given by:

$$\text{number} = \text{number density} \times \text{volume} = \underline{\underline{n \pi d^2 v t}}$$

It might seem simple now to then say that the collision rate R is just number of particle in the volume per unit time

$$R = \frac{n\pi d^2 v t}{t} = n\pi d^2 v$$ so average time between collisions is $\frac{1}{R} = \tau = \frac{1}{n\pi d^2 v}$

But this is <u>wrong</u>! We have forgotten the motion of the other particles! So we have to use relative velocity, not just the velocity of the particle we are following.

$$\underline{v}_{relative} = \underline{v}_1 - \underline{v}_2 \Rightarrow \langle v_{relative} \rangle = \langle |\underline{v}_1 - \underline{v}_2| \rangle$$

$$= \sqrt{\langle |\underline{v}_1|^2 + |\underline{v}_2|^2 - 2\underbrace{\underline{v}_1 \cdot \underline{v}_2}_{\simeq 0} \rangle}$$

Therefore $\langle v_{relative} \rangle = \langle \underline{v}_1^{\,2} + \underline{v}_2^{\,2} \rangle$

$$= \sqrt{2\langle v \rangle^2} = \sqrt{2}\,\langle v \rangle$$

We can therefore replace v with $\sqrt{2\langle v\rangle^2} = \sqrt{2}\,\langle v\rangle$.

$\boxed{R = \sqrt{2}\, n\pi d^2 \langle v\rangle}$	Rate of collisions
$\boxed{\tau = \dfrac{1}{\sqrt{2}\, n\pi d^2 \langle v\rangle}}$	Average time between collisions
$\boxed{\lambda = \dfrac{1}{\sqrt{2}\, n\pi d^2}}$	Mean free path, the average distance a particle can travel before it collides

This is very interesting since it shows that if the volume of the gas is kept constant, the mean free path is independent of the temperature. Note, volume needs to be kept constant to keep n constant.

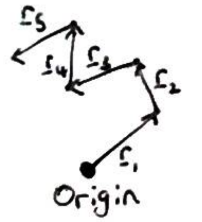
Diffusion

Diffusion is the process by which a molecule travels over a distance through a succession of random collisions. The diffusion of one type of molecules through another type of molecules follows Fick's Law, which as the same form as Fourier's Law:

$$\boxed{\frac{dN}{dt} = -DA\frac{dn}{dx}}$$

Fick's Law: The number of molecules per unit time crossing an area A is proportional to the gradient in number density.

The equation also defines D, called the diffusion coefficient.



Consider a particle bouncing off other particles randomly. Each bounce alters its direction of motion. What is its position after a certain interval of time?

If within the interval, there are N_c number of collisions, then final position is given by:

$$\underline{\underline{\underline{R} = \sum_i^{N_c} \underline{r}_i}}$$

Since there is no external force acting on the molecules, there is no reason for the molecule to "drift" a certain way.

So for an isotropic system, i.e of uniform number density:

$$\langle \underline{R} \rangle = \sum_i^{N_c} \langle \underline{r}_i \rangle = 0$$

The expectation value of the final position is at the origin where the particle started.

What is more interesting is the expectation value of the squared displacement. This is a measure of the width of the volume explored by the particle.

$$\langle R^2 \rangle = \langle |\underline{R}|^2 \rangle = \langle (\sum_i^{N_c} r_i) \cdot (\sum_j^{N_c} r_j) \rangle$$

$$= \langle |\underline{r}_1|^2 + |\underline{r}_2|^2 + \dots + \overbrace{2\underline{r}_1 \cdot \underline{r}_2 + 2\underline{r}_1 \cdot \underline{r}_3 + \dots}^{=0 \text{ since in random directions so average is } 0} \rangle$$

$$= \langle |\underline{r}_1|^2 + |\underline{r}_2|^2 + |\underline{r}_3|^2 + \dots \rangle$$

$$= \sum_i^{N_c} \langle |\underline{r}_i|^2 \rangle = \sum_i^{N_c} \langle r_i^2 \rangle$$

$$= \underline{\underline{N_c 2 \lambda^2}}$$

$$\therefore \boxed{\langle R^2 \rangle = N_c 2 \lambda^2}$$

$\langle |\underline{r}|^2 \rangle = 2\lambda^2$ is a proof we haven't done yet.

The time taken for N_c collisions is $t = \tau N_c$ and $\lambda = \tau \langle v \rangle$ so that $N_c = \frac{t}{\tau} = \frac{t \langle v \rangle}{\lambda}$

$$\therefore \langle R^2 \rangle = \frac{t \langle v \rangle}{\lambda} 2\lambda^2 \qquad \sqrt{\langle R^2 \rangle} = \boxed{R_{RMS} = \sqrt{2 \langle v \rangle \lambda t}}$$

If we take a look at Fick's Law again:

$$\frac{dN}{dt} = -DA\frac{\partial n}{\partial x}$$, we see that one possible solution is:

$$n(\underline{r},t) \approx e^{-|\underline{r}|^2/12Dt}$$

This gives $R_{RMS} = \sqrt{6Dt}$. This is a little hand-wavey but the derivation is not really important. The result is, for an ideal gas, the Diffusion Coefficient is:

$$\boxed{D = \frac{1}{3}\langle v\rangle\lambda}$$