A. Schekochihin
Kinetic Theory - MT12
Oxford

§4. Collisions.

We argued (on plausibility/symmetry grounds) that in equilibrium, we expect the pdf to be Maxwellian for an ideal gas.

This meant that initial conditions were forgotten, i.e., in practice, molecules had collided a sufficient # of times.

So, there are certain constraints on the time scales on which we can believe that the gas is in equilibrium (how long do we wait for gas to "Maxwellianise"?) and on the spatial scales of the system if we are to describe it in these terms. Namely,

$$t \gg \tau_c \text{ "collision time" } \left(\nu_c = \frac{1}{\tau_c} \text{ "collision rate" \# of collisions per unit time}\right)$$

$$l \gg \lambda_{mfp} \text{ "mean free path"}$$

typical scale, e.g. size of container (for homogeneous systems)

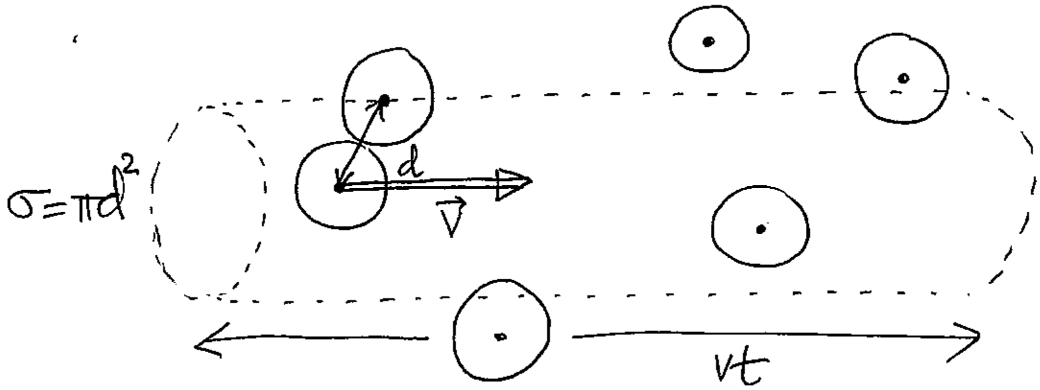
[recall that in the treatment of effusion, we required a "small hole" $d \ll \lambda_{mfp}$ to be able to snatch individual molecule w/o affecting the gas as a collective]

What are these quantities?

In order to estimate them, we will have to bring in some information and some assumptions about the microscopic properties of the gas and the nature of collisions.

4.1 Cross-section

Assume particles are <u>hard spheres of diameter d</u>. They will collide if their centres of mass approach each other within this distance d.



So, a particle with velocity $\vec{v}$ is moving through a cylinder with cross-section $\boxed{\sigma = \pi d^2} \perp \vec{v}$ and will collide with any other particle whose centre is within this cylinder. σ is the <u>collisional x-section</u>

NB: This is a useful way of parametrising the general situation when particles are <u>not</u> hard spheres but interact with e.a. via some potential (e.g. charged particles via Coulomb). One can then talk about "effective cross-section" (how close they have to get to have a "collision")

4.2 Collision time

Over time t, particle sweeps volume $\sigma v t$ (length of cylinder $= vt$).

Avg. # of particles in this volume $= \sigma v t n$

Clearly, if this is > 1, there will be at least one collision during this time.

Thus, we define <u>collision time</u> $t = \tau_c$ so that

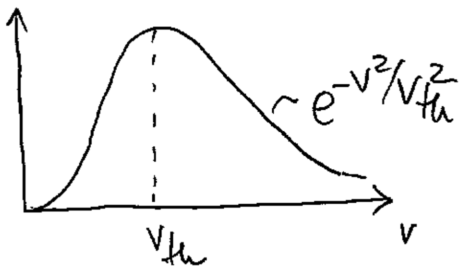
$$\sigma v \tau_c n = 1$$

$$\boxed{\tau_c = \frac{1}{\sigma n v}}$$

But what is this v? (1)

a collision rate $\boxed{\nu_c = \frac{1}{\tau_c} = \sigma n v}$

Particles are expected to have a Maxwellian distribution of speeds. Thus, typical speeds are



$$v \sim \underbrace{\overset{\frac{2}{\sqrt{\pi}} v_{th}}{\langle v \rangle} \sim \overset{\sqrt{\frac{3}{2}} v_{th}}{v_{rms}} \sim v_{th}}$$

NB: all these quantities have different numerical coefficients, but that does not matter for our order-of-magnitude estimates.

Thus, we define the collision time as

$$\boxed{\tau_c = \frac{1}{\nu_c} = \frac{1}{\sigma n v_{th}} = \frac{1}{\sigma n} \sqrt{\frac{m}{2 k_B T}}}$$ (2)

microscopic properties of molecules

macroscopic properties of gas

4.3 Mean free path

So the typical distance particle travels between collisions is

$$\boxed{\lambda_{mfp} = v_{th} \tau_c = \frac{1}{\sigma n}}$$ independent of temperature! (3)

$\left(\lambda \propto \frac{k_B T}{p} \propto p^{-1} @ \text{const}\, T\right)$

(alternatively, we could have just said the length of cylinder s.t. it contains at least one particle is ~~seta~~ $l = \lambda_{mfp}$:

$\sigma \cdot \lambda_{mfp} \cdot n = 1$)

4.4 Relative speed.

If you are a suspicious student, you might worry that the arguments above are somewhat dodgy: indeed, we effectively assumed that while our chosen particle is moving through its $\sigma v t$ cylinder all other particles are sitting there waiting to be collided with. Surely what matters is, in fact, the relative speed of the particles?

So $\quad \nu_c = \sigma n \langle v_r \rangle \quad$, where $\quad v_r = |\vec{v}_1 - \vec{v}_2| \qquad (4)$

It's sort of obvious that $\langle v_r \rangle \sim v_{th}$ by order of magnitude (what else can it possibly be?!) but let us convince ourselves of this anyway:

$$\langle v_r \rangle = \int d^3\vec{v}_1 \int d^3\vec{v}_2 \; |\vec{v}_1 - \vec{v}_2| \; \underbrace{f(\vec{v}_1, \vec{v}_2)}$$

Here we make a key assumption: $\vec{v}_1$ and $\vec{v}_2$ are independent, so $f(\vec{v}_1, \vec{v}_2) = f(\vec{v}_1)\, f(\vec{v}_2)$

joint distribution (i.e. pdf that $\vec{v}_1$ is in $d^3\vec{v}_1$ interval and $\vec{v}_2$ in $d^3\vec{v}_2$)

both Maxwellian!

(recall: ideal gas — non-interacting particles)

between collisions

Then

$$\langle v_r \rangle = \iint d^3\vec{v}_1\, d^3\vec{v}_2 \; |\vec{v}_1 - \vec{v}_2| \; \frac{e^{-\frac{v_1^2}{v_{th}^2} - \frac{v_2^2}{v_{th}^2}}}{(\pi v_{th}^2)^3} = \sqrt{2}\langle v \rangle \qquad (5)$$

just maths (Ex.)

<u>Proof.</u> Change variables: $(\vec v_1, \vec v_2) \to (\vec V, \vec v_r)$

$$\vec V = \frac{\vec v_1 + \vec v_2}{2} \quad \text{centre of mass}$$

$$\vec v_r = \vec v_1 - \vec v_r$$

Then $v_1^2 + v_2^2 = 2V^2 + \frac{1}{2} v_r^2$ and $d^3\vec v_1\, d^3\vec v_2 = d^3\vec V\, d^3\vec v_r$

$$\langle v_r \rangle = \int d^3\vec v_r\, v_r \int d^3\vec V\, \frac{e^{-2V^2/v_{th}^2 - v_r^2/2v_{th}^2}}{(\pi v_{th}^2)^3} =$$

$$\int d^3\vec V\, e^{-2V^2/v_{th}^2} = (\pi v_{th}^2/2)^{3/2} \quad \left(\begin{array}{l}\text{integrating out the distribution}\\ \text{of c.-of-m. velocities}\end{array}\right)$$

$$= \int d^3\vec v_r\, v_r \underbrace{\frac{e^{-v_r^2/2v_{th}^2}}{(2\pi v_{th}^2)^{3/2}}}_{= f(\vec v_r) \text{ distribution of relative velocities}} = \sqrt{2}\langle v \rangle \quad \text{where}$$

$$\langle v \rangle = \int d^3\vec v\, v\, \frac{e^{-v^2/v_{th}^2}}{(\pi v_{th}^2)^{3/2}}$$

q.e.d.

Hint: This is in fact much easier to show than $\langle v_r \rangle = \sqrt{2}\langle v \rangle$ — you can prove this in <u>1 line</u>.

So, we have $\langle v_r \rangle = \sqrt{2}\langle v \rangle = \frac{v_{th}}{\sqrt{2\pi}} = \sqrt{\frac{k_B T}{\pi m}}$

and

$$\boxed{\nu_c = \sqrt{2}\,\sigma n \langle v \rangle} = \frac{1}{\tau_c} \quad (6)$$

$$\boxed{\lambda_{mfp} = \langle v \rangle \tau_c = \frac{1}{\sqrt{2}\,\sigma n}} \quad (7)$$

not relative because this is just particle travelling at avg speed for time τ_c

This is <u>not</u> in any sense more precise because these are order-of-magnitude quantities, but many books like to define λ_{mfp} in this way

<u>Ex.</u> Prove $\langle v_r^2 \rangle \stackrel{?}{=} 2\langle v^2 \rangle$ so $v_{r,rms} = \sqrt{2}\, v_{rms}$ (coincidence)
so if we defined ν_c using $\langle v_r^2 \rangle^{1/2}$ and $\lambda_{mfp} = \langle v^2 \rangle^{1/2} \tau_c$
we would again get $\lambda_{mfp} = 1/\sqrt{2}\,\sigma n$