

§3. Collisions.

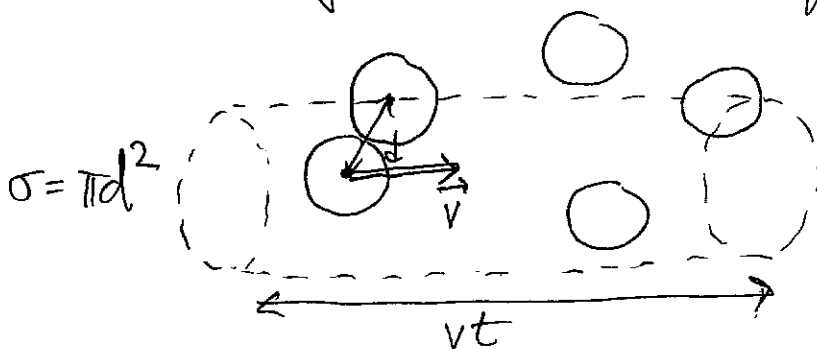
Treating gas as being in equilibrium involved assuming that molecules collide a suff. # of times for the initial conditions to be forgotten — this means there are certain constraints on the timescales on which we can believe the eq. distribution (how long do we wait for gas to Maxwellianise?) and on the spatial scales of the systems in which we can think of gas as being in collisional equilibrium:

e.g. size of container \rightarrow $t \gg \tau_c$ "collision time" \bullet $\nu_c = \frac{1}{\tau_c}$ "coll. rate" (# of coll-s per unit time)
 $l \gg \lambda_{mfp}$ "mean free path"

[recall that in the treatment of effusion, we needed a "small" hole, $d \ll \lambda_{mfp}$, to be able to snatch indiv. molecules w/o altering the gas as a collective]

3.1. Cross-section

Assume particles are hard spheres of diameter d . So they collide if their centres approach within distance d of each other — so particle with velocity



\vec{v} sweeps volume σvt
 \uparrow cross section

and will collide with anything in that volume.

3.2. Collision rate

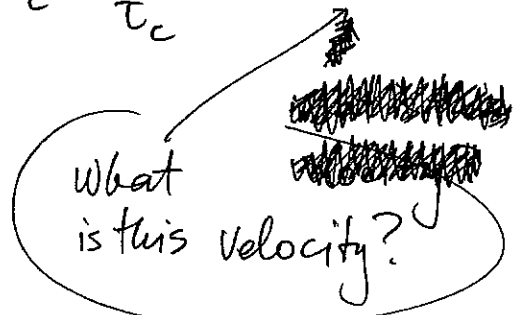
Avg # of particles in volume σvt is

coll. time $\sigma vt n$

$t = \tau_c$ if $\sigma v \tau_c n = 1$ (one collision)

or, coll. rate is

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



Obviously, by order of magnitude,

$v \sim \langle v \rangle \sim v_{rms} \sim v_{th}$

So, a quick estimate is simply

$\tau_c \sim \frac{1}{\sigma n v_{th}} \sim \frac{1}{\sigma n} \sqrt{\frac{m}{T}}$

3.3 Mean free path

Can immediately define

$\lambda_{mfp} \sim v \tau_c \sim \frac{1}{\sigma n} = \frac{k_B T}{\sigma p}$

independent of temperature!

So all we need to know about microphysics is

- size of molecules to get λ_{mfp}
- also their way to get τ_c

NB: can generalize σ to 1) particles of diff. diameters d_1, d_2 Ex.

2) "squashy" particles (not hard spheres) - then

smaller σ at higher v

3) particles that act on each other with some force, e.g.

Coulomb's pot. for charged ("Rutherford x-section")

↳ Ex. look it up!

We can refine our definitions of τ_c and λ_{mp} somewhat - although we do this just to understand the physics a bit better because fundamentally they are order-of-mag. quantities and it's not very meaningful to assign particularly precise values to them.

We had $v_c = \sigma n v$ ← velocity of particle travelling through gas of other particles.

So average over particle distribution: } But other particles are also moving, so actually it is relative velocity! $v = v_r$

$$\langle v_c \rangle = \sigma n \langle v_r \rangle$$

This involves velocities of 2 particles: $v_r = |\vec{v}_1 - \vec{v}_2|$
and so we need joint distribution $f(\vec{v}_1, \vec{v}_2)$:

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

$$= \iint d^3\vec{v}_1 d^3\vec{v}_2 |\vec{v}_1 - \vec{v}_2| \underbrace{f(\vec{v}_1) f(\vec{v}_2)}_{\text{assume independent}} \frac{1}{(\pi v_{th}^2)^3} e^{-v_1^2/v_{th}^2 - v_2^2/v_{th}^2}$$

Change variables: $(\vec{v}_1, \vec{v}_2) \rightarrow (\vec{V}, \vec{v}_r)$

$$\vec{V} = \frac{\vec{v}_1 + \vec{v}_2}{2}, \quad \vec{v}_r = \vec{v}_1 - \vec{v}_2$$

Ex. Show using this

that $\langle v_r \rangle = \sqrt{2} \langle v \rangle$

Conv. speed of the Maxwellian distribution

Proof. $v_1^2 + v_2^2 = 2V^2 + \frac{1}{2}v_r^2$

Jacobian $\frac{\partial(\vec{v}_1, \vec{v}_2)}{\partial(\vec{V}, \vec{v}_r)} = 1$

So ~~the distribution of relative velocities is given by~~

~~$f(\vec{v}_1, \vec{v}_2) d^3\vec{v}_1 d^3\vec{v}_2 = d^3\vec{V} d^3\vec{v}_r \frac{e^{-\frac{2V^2 + \frac{1}{2}v_r^2}{v_{th}^2}}}{(\pi v_{th}^2)^3}$~~

Then the distr. of relative velocities is

$f(\vec{V}, \vec{v}_r)$

$f(\vec{v}_r) = \int d^3\vec{V} f(\vec{V}, \vec{v}_r) = \text{const} e^{-\frac{v_r^2}{2v_{th}^2}}$

~~avg of relative velocity~~

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

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

So $\langle v_r \rangle = \sqrt{2} \langle v \rangle$

~~the distribution of relative velocities is given by~~

So, we have ~~the~~ $v_c = \sqrt{2} \sigma n \langle v \rangle = \frac{1}{\tau_c}$

and $\lambda_{\text{mfp}} = \langle v \rangle \tau_c = \frac{1}{\sqrt{2} \sigma n}$

So we pick up a numerical factor - not a big deal (but many books like keep this particular prefactor)

Note. We could have decided to define these quantities in terms of rms speeds:

$$v_c = \sigma n \langle v_r^2 \rangle^{1/2} = \sqrt{2} \sigma n \langle v^2 \rangle^{1/2}$$

$$\langle \vec{v}_1 \rangle \cdot \langle \vec{v}_2 \rangle = 0$$

~~the~~ because

$$\langle v_r^2 \rangle = \langle |\vec{v}_1 - \vec{v}_2|^2 \rangle = \langle v_1^2 \rangle + \langle v_2^2 \rangle - 2 \langle \vec{v}_1 \cdot \vec{v}_2 \rangle = 2 \langle v^2 \rangle$$

Then $\lambda_{\text{mfp}} = \langle v^2 \rangle^{1/2} \tau_c = \frac{1}{\sqrt{2} \sigma n}$ again.