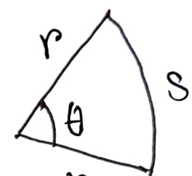
Lecture 8

We found that the number of molecules per unit volume travelling with speeds between v and $v+dv$ is given by $F(v)dv$. Let's try to find the distribution function of molecules travelling in different directions.

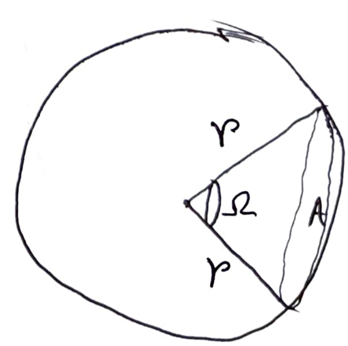
Solid angles



An angle θ in a circle is defined by dividing the arc length s which the angle subtends by radius r, so that,

$$\theta = \frac{s}{r}$$

The angle is measured in radians. The angle subtended by whole circle is then $= \frac{2\pi r}{r} = 2\pi$.



Similarly, a solid angle Ω in a sphere is defined by dividing the surface area A which the solid angle subtends by the radius squared, so that,

$$\Omega = \frac{A}{r^2}$$

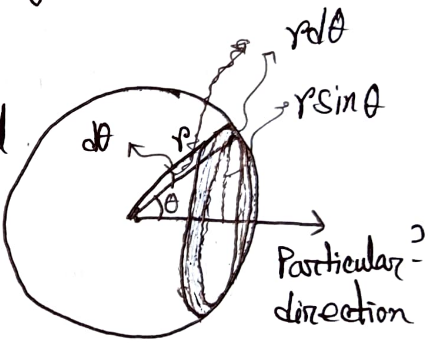
The solid angle is measured in steradians (sr). The ... angle subtended by the whole sphere is then $= \frac{4\pi r^2}{r^2} = 4\pi$.

The number of molecules travelling in a certain direction at a certain speed

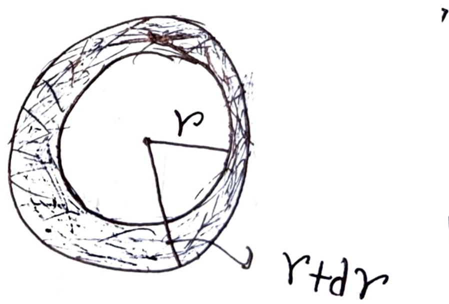
Since the molecules travels in random directions, the fraction whose trajectory lie in the elemental solid angle $d\Omega$ will be given by $\frac{d\Omega}{4\pi}$.

If we choose a particular ~~angle~~ direction, then we can find the solid angle corresponding to molecules travelling at angles between θ and $\theta + d\theta$.

This basically corresponds to infinitesimal area between circles with radius $r\sin\theta$ and $r\sin\theta + r\,d\theta$.



The infinitesimal area (shaded region) between circles with radius r and $r+dr$ will be given by,



$$dA = \pi(r+dr)^2 - \pi r^2 = \pi r^2 + 2\pi r\,dr + \pi dr^2 - \pi r^2$$

$$= 2\pi r\,dr$$

Ignoring the dr^2 term.

So, in our case, the area of shaded region

is $= 2\pi\, r\sin\theta \cdot r\,d\theta = 2\pi r^2 \sin\theta\, d\theta$

$\therefore$ The infinitesimal solid angle, $d\Omega = \frac{2\pi r^2 \sin\theta \, d\theta}{r^2}$

$= 2\pi \sin\theta \, d\theta$

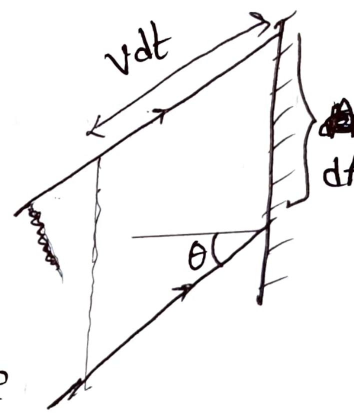
$$\therefore \frac{d\Omega}{4\pi} = \frac{1}{2}\sin\theta \, d\theta$$

So, the fraction of molecules travelling between θ and $\theta + d\theta$ is given by $\frac{1}{2}\sin\theta \, d\theta$. So, total number of molecules per unit volume travelling at angles between θ and $\theta+d\theta$, having speeds between v and $v+dv$ is given by,

$$F(v)\,dv \, \frac{1}{2}\sin\theta \, d\theta$$

The number of molecules hitting the wall

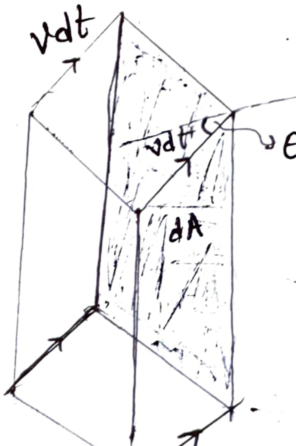
Let us now consider our particular direction, up until now arbitrarily choosen, be perpendicular to the wall of area dA. In a small time dt, the molecules travelling at an angle normal to the wall sweep out an oblique parallelepiped, as shown in the figure. The volume is given by



$= \text{Base area} \times \text{height}$

$= dA \times v\,dt \cos\theta$

$= dA \, v\,dt \cos\theta$



Shaded region is the wall.

Any gas particle outside of this parallelepiped will miss to hit this area. If we now multiply this volume with the number of molecules travelling with ~~velocity~~ speed between v and $v+dv$, and in the direction between θ and $\theta+d\theta$, then the number of particles in these ranges is hitting the wall of area dA found, which is -

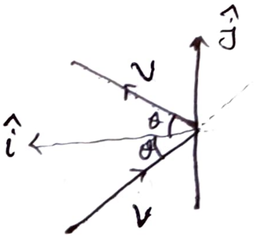
$$dA\, v\, dt \cos\theta \; F(v)\, dv \, \frac{1}{2} \sin\theta \, d\theta$$

Hence, the number of molecules hitting the wall per unit area per unit time is given by -

$$v \cos\theta \; F(v) \, \frac{1}{2} \sin\theta \; dv \, d\theta$$

Now, each molecule hitting the wall at an angle θ will bounce back at the same angle after the elastic collision. So, the change in momentum,

$\cancel{\Delta\vec{P} = -mv\cos\theta}\,\hat{i}$



$$\Delta\vec{P} = \vec{P}_f - \vec{P}_i = (mv\cos\theta\,\hat{i} + mv\sin\theta\,\hat{j}) - (-mv\cos\theta\,\hat{i} + mv\sin\theta\,\hat{j})$$

$$\therefore\ \Delta\vec{P} = 2mv\cos\theta\,\hat{i}$$

The momentum change is hence totally in the normal direction to the wall.

Now, the pressure is defined as the force per unit area, which is basically change in momentum per unit time per unit area.

If we multiply the magnitude of momentum change for a particle with the number of particles hitting the wall per unit time per unit area in the range v and v+dv and θ and θ+dθ, then integrate over all possible range of v and θ, we should get the pressure.

$$\therefore p = \int_0^\infty \int_0^{\pi/2} (2mv\cos\theta)\ v\cos\theta\ F(v)\frac{1}{2}\sin\theta\, dv\, d\theta$$

$$= m\int_0^\infty dv\ v^2 F(v) \int_0^{\pi/2} \cos^2\theta \sin\theta\, d\theta$$

$$= mn\int_0^\infty v^2 F'(v)dv \times \frac{1}{3}$$

$$\int_0^\infty v^2 F'(v)\, dv = \langle v^2 \rangle$$

$$= \frac{1}{3}mn\langle v^2\rangle$$

$$\boxed{\therefore p = \frac{1}{3}mn\langle v^2\rangle}$$

$$n = \frac{N}{V}$$

$$\Rightarrow p = \frac{1}{3}m\cdot\frac{N}{V}\langle v^2\rangle$$

$$\Rightarrow pV = \frac{1}{3}mN\langle v^2\rangle$$

$$\langle v^2\rangle = \sqrt{\frac{3K_BT}{m}}$$

$$\boxed{\therefore PV = \frac{1}{3}NK_BT}$$

This is the ideal gas equation.

You can also write, $P = \frac{N}{V} K_B T = n K_B T$

This means the pressure does not depend on the mass of the molecules in a gas, rather only on the number of molecules per unit volume and the temperature T. Think about why mass of the molecule doesn't affect pressure.

Again, $PV = n_m N_A K_B T$ | $n_m = \frac{N}{N_A}$ number of moles

$$\therefore \boxed{PV = n_m RT}$$

with $R = N_A K_B = 8.31447 \ JK^{-1} mol^{-1}$, called the gas constant.

Dalton's law

If one has a mixture of gases in thermal equilibrium, then the total pressure is simply the sum of the pressure due to each component.

Total pressure, $P = n K_B T$, with $n = \sum_i n_i$

Then, $P = \sum n_i K_B T = \sum P_i$

where $P_i = n_i K_B T$ is the partial pressure of the i^{th} type molecule. The observation that $p = \sum_i p_i$ is known as Dalton's law.

Molecular effusion

Effusion is the process by which a gas escapes ~~from~~ through a very small hole. The empirical relation, Graham's law of effusion states that, the rate of effusion is inversely proportional to the square root of mass of the molecule. We are going to show this using our calculations from above.

Flux

The flux quantifies the flow of particles, or the flow of energy or the flow of momentum, depending on the context. In our current context, molecular flux Φ is defined to be the number of molecules ~~per~~ ~~unit~~ striking unit area per unit time.

$$\therefore \text{Molecular flux} = \frac{\text{number of molecules}}{\text{area} \times \text{time}}$$

The unit of molecular flux is then $m^{-2}s^{-1}$. We did calculate the number of particles hitting a wall per unit area per unit time in the range v and $v+dv$ and θ and $\theta+d\theta$. So, we will just integrate over the ranges of v and θ to find the molecular flux.

$$\therefore \phi = \int_0^{\infty}\int_0^{\pi/2} v\cos\theta\, F(v)\, \tfrac{1}{2}\sin\theta\, dv\, d\theta$$

$$= \frac{n}{2}\int_0^{\infty} v\, F'(v)\, dv \int_0^{\pi/2} \sin\theta\cos\theta\, d\theta$$

$$= \frac{n}{2}\langle v\rangle \cdot \frac{1}{2}$$

$$\boxed{\therefore \phi = \frac{1}{4} n\langle v\rangle}$$

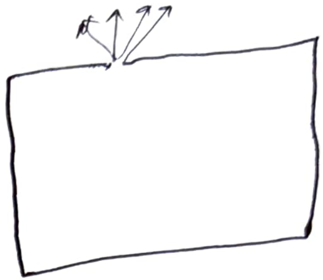
Now, $P = nk_BT \Rightarrow n = \dfrac{P}{k_BT}$

and $\langle v\rangle = \sqrt{\dfrac{8k_BT}{\pi m}}$

$$\boxed{\therefore \phi = \frac{P}{\sqrt{2\pi m k_B T}}}$$

And as we can see, the flux $\phi \propto \frac{1}{\sqrt{m}}$, and since the rate of effusion will be proportional to this flux, it is proportional to the inverse of square root of m.

Effusion rate



Consider a container of gas with a small hole of area A in the side. The gas will obviously leave (effuse) out of the container through the hole. The hole has to be small enough so that the equilibrium of gas is not disturbed. Now, the number of molecules escaping per unit time is given by the molecular flux times the area.

$$\therefore \text{Effusion rate} = \Phi A = \frac{pA}{\sqrt{2\pi m k_B T}}$$