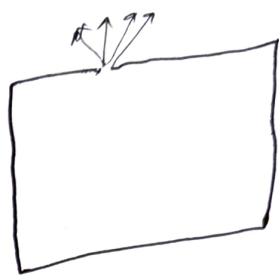


Effusion rate

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.



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

~~If the container had mass M , then~~

Say the mass of the total container is given by M . Now, the rate of change of the mass of the container, $\frac{dM}{dt}$ is simply equal to $-m\Phi A$. This is because ΦA gives number of molecules escaping the box per second. Then, $m \times \Phi A$ must be the mass loss per second.

$$\therefore \left| \frac{dM}{dt} \right| = m\Phi A$$

$$\Rightarrow \left| \frac{dM}{dt} \right| = m \frac{pA}{\sqrt{2\pi m k_B T}}$$

$$\therefore p = \sqrt{\frac{2\pi k_B T}{m}} \cdot \frac{1}{A} \left| \frac{dM}{dt} \right|$$

This equation is used to calculate the vapour pressure p from a liquid, called the Knudsen method.

Now, effusion preferentially selects faster molecules. Hence, the speed distribution of the effusing molecules is not Maxwellian. This is because faster molecules travel more quickly and hence, has a greater chance of reaching the hole. This can be seen from the fact that, we previously found, number of molecules hitting a wall per unit area per unit time in the ranges v and $v+dv$ and θ and $\theta+d\theta$ is,

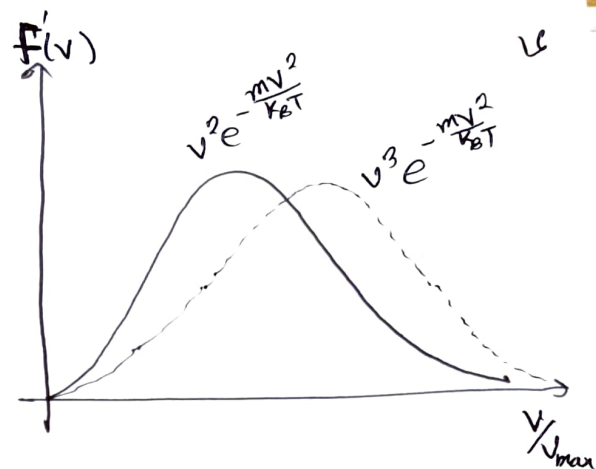
$$v \cos\theta F(v) \frac{1}{2} \sin\theta dv d\theta$$

So, the distribution function is proportional to,

$$v F'(v) dv$$

which is, proportional to $v^3 e^{-\frac{mv^2}{k_B T}} dv$. The distributions are shown graphically in the figure.

You can find the mean kinetic energy of the effusing particles by finding $\langle v^2 \rangle$.



$$\langle v^2 \rangle = \frac{\int_0^{\infty} v^2 \cdot v^3 e^{-\frac{mv^2}{k_B T}} dv}{\int_0^{\infty} v^3 e^{-\frac{mv^2}{k_B T}} dv}$$

Let, $u = \frac{mv^2}{2k_B T} \Rightarrow \frac{du}{dv} = \frac{m}{k_B T} 2v$

$v=0, u=0$
 $v=\infty, u=\infty$

The denominator just gives you the normalization factor.

$$\therefore \langle v^2 \rangle = \frac{\int_0^{\infty} v^5 e^{-\frac{mv^2}{2k_B T}} dv}{\int_0^{\infty} v^3 e^{-\frac{mv^2}{2k_B T}} dv} = \frac{\frac{1}{2} \int_0^{\infty} \left(\frac{k_B T}{m}\right)^{5/2} u^{5/2} e^{-u} \left(\frac{k_B T}{m}\right)^{1/2} du}{\frac{1}{2} \int_0^{\infty} \left(\frac{k_B T}{m}\right)^{3/2} u^{3/2} e^{-u} \left(\frac{k_B T}{m}\right)^{1/2} du}$$

$$= \left(\frac{k_B T}{m}\right)^{3-2} \frac{\int_0^{\infty} u^2 e^{-u} du}{\int_0^{\infty} u e^{-u} du}$$

$$\int_0^{\infty} x^n e^{-x} dx = n! \quad \text{at}$$

$$= \left(\frac{k_B T}{m}\right) \frac{2!}{1!} = 4 \frac{k_B T}{m}$$

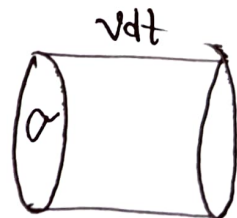
$$\therefore \text{Average kinetic energy} = \frac{1}{2} m \langle v^2 \rangle$$

$$\text{which is } \frac{4}{3} \text{ times the mean kinetic energy of the all molecules.} = \frac{1}{2} m \times \frac{4k_B T}{m} = 2k_B T$$

Mean free paths and collisions

Mean collision time

Let us try to calculate average time between molecular collisions. We will start with simple situations, and later make proper corrections. Consider a molecule moving with speed v where all other gas molecules in the container are stationary. Let us attribute a collision cross-section σ to each molecule, which we define as the cross sectional area that will correspond to the collision with other molecules. In a time dt , the molecule will sweep ~~an area~~ a volume of $\sigma v dt$. If another molecule lie in this volume, there will be a collision.



If there are n molecules per unit volume, then the probability of a collision in this time $= n \sigma v dt$

Let's define $P(t)$ to be the probability of a molecule not colliding up to time t .

$$\text{Now, } \frac{dP}{dt} = \frac{P(t+dt) - P(t)}{dt}$$

But $P(t+dt)$ is also the probability of the molecule not colliding up to time t multiplied by the probability of not colliding in subsequent time dt .

$$\therefore P(t+dt) = P(t) (1 - n\sigma v dt)$$

$$\therefore P(t) + \frac{dP}{dt} dt = P(t) - P(t) n\sigma v dt$$

$$\Rightarrow \frac{1}{P(t)} \frac{dP}{dt} = -n\sigma v$$

$$\Rightarrow \int \frac{dP}{P} = \int -n\sigma v dt \quad \Rightarrow \ln P(t) = -n\sigma v t + C$$

$$\text{At } t=0, \quad \ln P(0) = C$$

But $P(0)=1$, since at $t=0$ the ~~part~~ molecule certainly won't collide.

$$\therefore C = \ln 1 = 0$$

$$\therefore \ln P(t) = -n\sigma v t$$

$$\therefore P(t) = e^{-n\sigma v t}$$

Now, the probability of surviving up to time t without collision and colliding in next dt is $= P(t) n\sigma v dt = e^{-n\sigma v t} n\sigma v dt$

This is a proper probability since,

$$\begin{aligned} \text{Take, } x &= n\sigma v t \\ \Rightarrow \frac{dx}{dt} &= n\sigma v \end{aligned}$$

$$\int_0^{\infty} e^{-n\sigma v t} n\sigma v dt = \int_0^{\infty} e^{-x} dx = 0! = 1$$

$$\therefore P(t) = e^{-n\sigma v t} n\sigma v dt$$

Now, the average time elapsed between collisions for a given molecule, called the mean collision time,

$$\tau = \int_0^{\infty} t P(t) dt = \int_0^{\infty} t e^{-n\sigma v t} n\sigma v dt$$

Again, $x = n\sigma v t$

$$\Rightarrow \frac{dx}{dt} = n\sigma v$$

$$\therefore \tau = \int_0^{\infty} \frac{x}{n\sigma v} \cdot e^{-x} dx$$

$$= \frac{1}{n\sigma v} \int_0^{\infty} x e^{-x} dx = \frac{1}{n\sigma v} 1!$$

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

$$\boxed{\therefore \tau = \frac{1}{n\sigma v}}$$

Mean free path

The mean free path, the average path for a molecule without collision is then simply,

$$\lambda = \langle v \rangle \tau = \frac{\langle v \rangle}{n\sigma v}$$

But, what is v ? We have considered v as

as the speed of the molecule considering all other molecules to be stationary. But this is obviously wrong. We should have considered the relative velocity v_r , and the quantity v in the denominator should really be $\langle v_r \rangle$, since we are taking average over all the molecules.

Now,
$$\vec{v}_r = \vec{v}_1 - \vec{v}_2$$

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

$$\begin{aligned} \Rightarrow \langle v_r^2 \rangle &= \langle v_1^2 \rangle + \langle v_2^2 \rangle - 2\langle \vec{v}_1 \cdot \vec{v}_2 \rangle \\ &= \langle v_1^2 \rangle + \langle v_2^2 \rangle - 2\langle v_1 v_2 \cos \theta \rangle \end{aligned}$$

But, $\langle \cos \theta \rangle = 0$ over the range of all possible θ .

$$\begin{aligned} \therefore \langle v_r^2 \rangle &= \langle v_1^2 \rangle + \langle v_2^2 \rangle = \langle v^2 \rangle + \langle v^2 \rangle \\ &= 2\langle v^2 \rangle \end{aligned}$$

We needed $\langle v_r \rangle$, but we have $\langle v_r^2 \rangle$. But we can write $\langle v_r \rangle \approx \sqrt{\langle v_r^2 \rangle}$ with a very small error if the molecules follow Maxwell-Boltzmann distribution. For example,

$$\frac{\langle v \rangle}{\sqrt{\langle v^2 \rangle}} = \sqrt{\frac{8}{3\pi}} = 0.92 \text{ and so, the error is less than } 10\%.$$

$$\therefore \langle v_r \rangle \approx \sqrt{\langle v_r^2 \rangle} \approx \sqrt{2} \langle v \rangle$$

$$\therefore \lambda \approx \frac{\langle v \rangle}{\sqrt{2} n \sigma \langle v \rangle}$$

$$\boxed{\therefore \lambda = \frac{1}{\sqrt{2} n \sigma}}$$

Substituting $P = n k_B T \Rightarrow n = \frac{P}{k_B T}$ we get,

$$\cancel{\lambda} \quad \boxed{\lambda = \frac{k_B T}{\sqrt{2} P \sigma}}$$

Also,

$$\boxed{\lambda = \frac{1}{n \sigma \sqrt{2} v}}$$