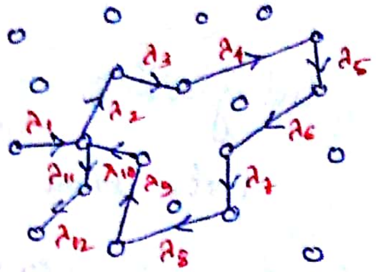
Mean free path

We calculated that K.T. gives $\sim 1\ Km/s$ velocity for molecular movement. But we see clouds suspended in air holds together for hours. So there must be some factors that prevent the free escape of atoms.

Clausius showed that such discrepancy goes away if we take small & finite volume for atoms & they change velocity & direction of motion in the process of collission, zigzag path (discrete)



In between two successive collission, the traversed path is free path $(\lambda_1, \lambda_2, \cdots, \lambda_n)$.

$$\text{Mean free path} = \frac{\lambda_1 + \lambda_2 + \lambda_3 + \cdots + \lambda_N}{\text{Number of collision}}$$

Collision probability

Suppose collision rate is P, average velocity of an atom is $\bar{c}$ & in time t, distance covered $= \bar{c}t$ & number of collisions suffered is Pt. then $\lambda_{\bar{c}} = \dfrac{\bar{c}t}{Pt} = \dfrac{\bar{c}}{P}$.

Before we calculate "λ", let's compute the distribution of λ, meaning probability of an atom moving a distance x without collision, say $f(x)$. This means that $f(x+dx)$ is the probability that atom traverses $x+dx$ length without collision.

If P is collission probability per unit time, then for N atoms number of collisions in time $t = \frac{1}{2}NPt$. ($\frac{1}{2}$ because each collission between 2 atoms is counted twice).

Probability that after traversing x, an atom will suffer a collission within dx in time dt $= Pdt = P\dfrac{dx}{c} = \dfrac{dx}{\lambda}$

where $\lambda = \dfrac{c}{P}$ is the free path for atoms with velocity c.

$\therefore$ As total probability $=1$, probability of no collision in distance dx $= \left(1 - \dfrac{dx}{\lambda}\right)$.

As successive collisions are independent therefore the joint probability of no collision at $x+dx$ is $f(x) \times (1-\frac{dx}{\lambda})$

$$\therefore \quad f(x+dx) = f(x)(1-\frac{dx}{\lambda}).$$

Expand LHS using Taylor's theorem.

$$f(x) + f'(x)\,dx + \cancel{\tfrac{1}{2} f''(x)(dx)^2} + \cdots = f(x)(1-\frac{dx}{\lambda}) \quad [\lim_{dx\to 0}]$$

$$\text{or} \quad f'(x) = -f(x)/\lambda . \quad \text{or} \quad \frac{f'(x)}{f(x)} = -\frac{1}{\lambda}.$$

Integrating, $\ln f(x) = -\frac{x}{\lambda} + \ln c \Rightarrow f(x) = c e^{-x/\lambda}$.

note that when $x=0$, $f(x)=1$. $\therefore c=1$.

$$\therefore f(x) = e^{-x/\lambda}. \Longrightarrow \text{law of distribution of free paths}$$

<u>Method 2</u> Let, out of N atoms, N' atoms cross x without collision, & after that in dx distance, dN' atoms are thrown out due to collision. Then $dN' \propto N'$ & dx or $dN' = -PN'dx$ (–ive for decrease)

$$\text{or} \quad \frac{dN'}{N'} = -P\,dx$$

Integrating $\ln N' = -Px + \ln c$

or $N' = c e^{-Px}$. Now put boundary condition at $x=0$, $N'=N$.

$\therefore c = N$. $\therefore N' = N e^{-Px}$

thrown out molecules are $dN' = +PNe^{-Px}dx$ (+ive number)

$$\lambda = \frac{x_1 dN_1' + x_2 dN_2' + \cdots}{N} = \frac{1}{N}\int_0^\infty x\,dN'$$

$$= \frac{1}{N}\int_0^\infty xPNe^{-Px}dx = P\int_0^\infty e^{-Px}x\,dx \qquad \text{put } Px = z, \; P\,dx = dz$$

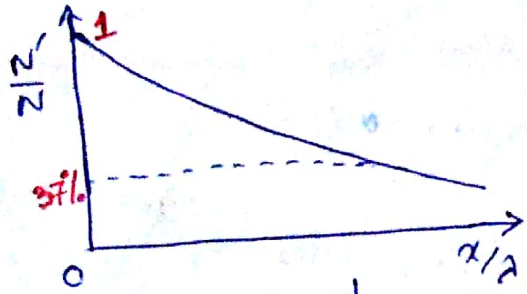
$$= P\frac{1}{P^2}\int_0^\infty e^{-z}z\,dz = \frac{1}{P}\Gamma(2) = \frac{1}{P}.$$

$$\therefore \boxed{N' = Ne^{-x/\lambda}} \quad \text{or} \quad f(x) = e^{-x/\lambda}$$

Scanned by CamScanner

This is the "survival equation".

$$dN' = \frac{N}{\lambda} e^{-x/\lambda} dx \quad \text{or} \quad \boxed{\frac{dN'}{dx} = \frac{N}{\lambda} e^{-x/\lambda}}$$



(a) $P \propto 1/\lambda \Rightarrow$ collision probability is reciprocal of free path.

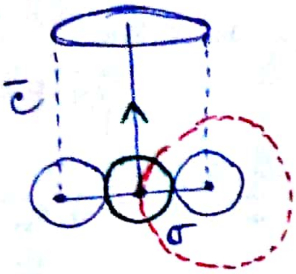
(b) Intensity of atomic beam $\propto$ number of atoms. $\therefore I' = I e^{-x/\lambda}$.

I' → final intensity. I → initial intensity.

Number $> \lambda$ is $e^{-1} \sim 37\%$

$< \lambda$ is $1 - 37\% = 63\%$

Calculation of λ



Sphere of influence

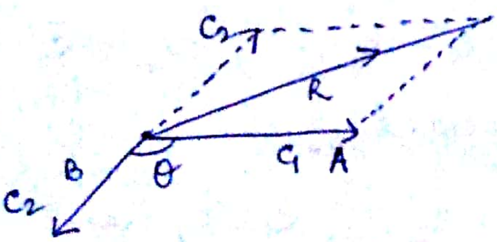
Suppose all atoms are rest but only one moves with velocity $\bar{c}$. Rigid spherical shape with diameter σ. It can only collide when they touch. & can reach distance $\bar{c}$, so it collides with $\pi\sigma^2\bar{c}n$ many atoms. This is also number of collisions per second.

$$\therefore \text{ Mean free path } \lambda = \frac{\bar{c}}{\pi\sigma^2\bar{c}n} = \frac{1}{n\pi\sigma^2}$$

This is approximate & Clausius did the first correction followed by Maxwell-Tait.

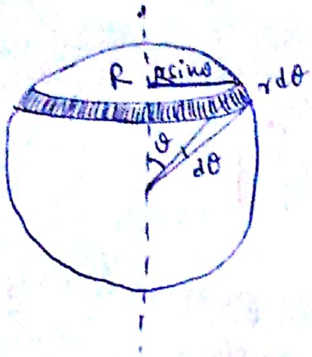
Clausius correction

Introduction of relative velocity. as all atoms are in motion.



Consider A & B atom moves with velocity c_1 & c_2 & angle θ. Making atom B observer (meaning applying equal & opposite velocity c_2 to B), B is in rest & relative to that A moves with relative velocity

$$R = \sqrt{c_1^2 + c_2^2 - 2c_1c_2\cos\theta}$$



Now we have to find mean relative velocity of atom A with respect to all others. If $dN_{\theta,\phi}$ is the number of atoms moving between θ & $\theta+d\theta$, ϕ & $\phi+d\phi$ then

$$dN_{\theta,\phi} = \frac{N}{4\pi R^2} R^2 \sin\theta \, d\theta \, d\phi = \frac{N \sin\theta \, d\theta \, d\phi}{4\pi}$$

and
$$\bar{R} = \frac{\int R \, dn_{\theta,\phi}}{\int dn_{\theta,\phi}} = \frac{\int_{\theta=0}^{\pi}\int_{\phi=0}^{2\pi} \sqrt{c_1^2+c_2^2-2c_1c_2\cos\theta}\,\frac{N\sin\theta\,d\theta\,d\phi}{4\pi}}{\int_{\theta=0}^{\pi}\int_{\phi=0}^{2\pi}\frac{N\sin\theta\,d\theta\,d\phi}{4\pi}}$$

$$= \cancel{\frac{N}{4\pi}}\cancel{2\pi}\int_{\theta=0}^{\pi}\sqrt{c_1^2+c_2^2-2c_1c_2\cos\theta}\,\sin\theta\,d\theta \Big/ \cancel{\frac{N}{4\pi}}\cancel{4\pi}^{\,2}$$

substitute $c_1^2+c_2^2-2c_1c_2\cos\theta = z$ or $2c_1c_2\sin\theta\,d\theta = dz$

$$\int_0^{\pi} z^{1/2}\frac{1}{2c_1c_2}dz = \frac{1}{2c_1c_2}\int_{(c_1-c_2)^2}^{(c_1+c_2)^2}\sqrt{z}\,dz = \frac{1}{2c_1c_2}\left[\frac{z^{3/2}}{3/2}\right]_{(c_1-c_2)^2}^{(c_1+c_2)^2}$$

$$= \frac{1}{3c_1c_2}\left[(c_1+c_2)^3-(c_1-c_2)^3\right]$$

$$\therefore \bar{R} = \frac{1}{6c_1c_2}\left[(c_1+c_2)^3-(c_1-c_2)^3\right].$$

According to Clausius's assumption $c_1 = c_2 = \bar{c}$

$\therefore \bar{R} = \frac{1}{6\bar{c}^2}8\bar{c}^3 = \frac{4}{3}\bar{c}$, meaning in traveling a distance $\bar{c}$, number of collision by molecule A with relative velocity $\bar{R}$ is $\pi\sigma^2\bar{R}n$ & therefore $\lambda_{cl} = \frac{\bar{c}}{\pi\sigma^2 n\bar{R}} = \frac{3}{4}\frac{1}{n\pi\sigma^2}$.

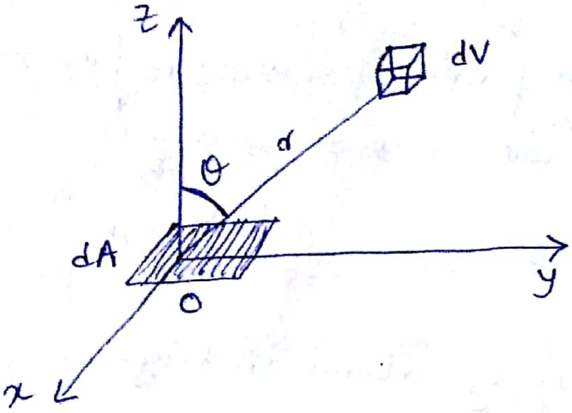
Maxwell's correction Clausius took $c_1 = c_2 = \dots = c_N = \bar{c}$ but they're Maxwellian distributed in reality!

Maxwell corrected by considering both $c_1 > c_2$ & $c_1 < c_2$ case with $dN_{c_2} = 4\pi N\left(\frac{m}{2\pi k_B T}\right)^{3/2} e^{-mc_2^2/2k_BT}c_2^2\,dc_2$

to obtain $\bar{R} = \sqrt{2}\,\bar{c}$ (see AB Gupta § 2.21.2 for derivation)

$$\therefore \lambda_{Maxwell} = \frac{\bar{c}}{\sqrt{2}\pi\sigma^2 n \bar{c}} = \frac{1}{\sqrt{2}\pi\sigma^2 n}$$

Pressure of a gas using mean free path



Once again, we want to compute atoms within volume dV at distance r with inclination θ to a surface dA at origin that reach dA after collision with other atoms, using survival equation.

Number of molecules between c & c+dc in volume dv is $dn_c dV$.

If λ is mean free path of the gas atoms then ~~no~~ number of collision suffered by one atom per unit time $= \frac{c}{\lambda}$.

As $1 \to 2$ & $2 \to 1$ collision is counted twice, so the number of collisions suffered by $dn_c dV$ number of atoms in unit time is $\frac{1}{2}\frac{c}{\lambda} dn_c dV$. But each collision results to two new paths along which atoms travel.

∴ The number of new paths or number of atoms emanating from dV per unit time $= \frac{1}{2}\frac{c}{\lambda} dn_c dV \times 2$ & fraction that are pointed towards the area dA is the solid angle subtended by dA at dV $= \frac{dA \cos\theta / r^2}{4\pi}$ (4π = all molecules contained)

∴ That exit from dV pointing to dA, that number is

$$N_0 = \frac{c}{\lambda} dn_c dV \frac{dA\cos\theta}{4\pi r^2} \quad \text{(per unit time)}.$$

In N_0, only those atoms with $\lambda \geq r$ can reach dA, which is

$$N = N_0 e^{-r/\lambda} = \frac{c}{\lambda} dn_c dV \frac{dA\cos\theta}{4\pi r^2} e^{-r/\lambda}$$

$$= \frac{c\, dn_c\, dA \cos\theta\, \cancel{r^2} \sin\theta\, d\theta\, d\phi\, dr\, e^{-r/\lambda}}{\lambda\, 4\pi \cancel{r^2}} \qquad (dV = r^2 \sin\theta\, d\theta\, d\phi\, dr)$$

$$= \frac{dA}{} \times \frac{c\, dn_c \sin\theta \cos\theta\, d\theta\, d\phi}{4\pi} \times \frac{e^{-r/\lambda}}{\lambda}\, dr$$

$\therefore$ No. of atoms striking dA is $= \frac{dA}{4\pi} \int_{c=0}^{\infty} c\, dn_c \int_{\theta=0}^{\pi/2} \sin\theta \cos\theta\, d\theta \int_{\phi=0}^{2\pi} d\phi \times \int_{r=0}^{\infty} e^{-r/\lambda} \frac{dr}{\lambda}$

$$= \frac{dA}{4\pi}\, n\bar{c}\, \frac{1}{2}\, 2\pi \times 1 = \frac{dA}{4}\, n\bar{c}$$

So per unit area per unit time, number of atoms striking is $\boxed{\frac{n\bar{c}}{4}}$.

Again, we know one colliding atom suffers momentum change $= 2mc\cos\theta$

So change of momentum for all atom are

$$\frac{dA}{4\pi} \int_{c=0}^{\infty} 2mc^2\, dn_c \int_{\theta=0}^{\pi/2} \sin\theta \cos^2\theta\, d\theta \int_{\phi=0}^{2\pi} d\phi \int_{r=0}^{\infty} e^{-r/\lambda}\, d(r/\lambda).$$

$$dF = \frac{m\, dA}{2\pi}\, n\bar{c}^2_{rms}\, \frac{1}{3}\, 2\pi = \frac{1}{3} m n \bar{c}^2_{rms}\, dA. \qquad \left[\bar{c}^2_{rms} = \frac{1}{n}\int_{c=0}^{\infty} c^2\, dn_c\right]$$

$$\therefore\ p = \frac{dF}{dA} = \boxed{\frac{1}{3} m n \bar{c}^2_{rms}}$$

Mean free path of a mixture of a gas

If we consider two different molecule with diameter σ_1, σ_2 then, σ_1 diameter molecule will collide with all molecule that are $\frac{\sigma_1+\sigma_2}{2}$ distance apart from σ_1 molecule. Hence λ will be $1/n\pi\sigma_a^2$ where $\sigma_a = \frac{\sigma_1+\sigma_2}{2}$ & $n =$ number of molecules per unit volume of σ_2 type. But σ_2 molecules are not in rest then if σ_1 type moves with $\bar{c}_1$ & σ_2 type moves with $\bar{c}_2$ & if the molecules of σ_2 move perpendicular to σ_1 then relative velocity $R = \sqrt{\bar{c}_1^2 + \bar{c}_2^2}$ & therefore $\frac{R}{\bar{c}_1} = \frac{\sqrt{\bar{c}_1^2+\bar{c}_2^2}}{\bar{c}_1}$

So λ_1 of σ_1 type of molecules within σ_2 type molecules are

$\lambda_1 = \frac{1}{n\pi\sigma_a^2 \frac{\sqrt{\bar{c}_1^2+\bar{c}_2^2}}{\bar{c}_1}}$. Similarly, λ_2 of σ_2 type of molecules within σ_1 type molecules are $\lambda_2 = \frac{1}{n\pi\sigma_a^2 \frac{\sqrt{\bar{c}_1^2+\bar{c}_2^2}}{\bar{c}_2}}$. The perpendicular directionality assumption gives Maxwell's distribution with relative velocity R, & if we had assumed $\bar{c}_1 = \bar{c}_2$ & then we could get back Maxwell's expression of free path.

If we now consider n_1 molecule of σ_1 type with $\bar{c}_1$ & n_2 molecule of σ_2 type with $\bar{c}_2$ avg. velocity then no. of impact/sec by σ_1 molecules

$$\Gamma_1 = \underbrace{\sqrt{2}\,\bar{c}_1 n_1 \pi \sigma_1^2 \left(= \frac{\bar{c}_1}{\lambda_{11}}\right)}_{\sigma_1 \text{ with } \sigma_1} + \underbrace{n_2 \pi \sigma_a^2 \cancel{\bar{c}_1} \frac{\sqrt{\bar{c}_1^2+\bar{c}_2^2}}{\cancel{\bar{c}_1}} \left(= \frac{\bar{c}_1}{\lambda_{12}}\right)}_{\sigma_1 \text{ with } \sigma_2}$$

∴ Mean free path of σ_1 type molecules in the gas mixture

$$\lambda_1 = \frac{\bar{c}_1}{\Gamma_1} = \frac{\bar{c}_1}{\sqrt{2}\pi n_1 \bar{c}_1 \sigma_1^2 + \pi\sigma_a^2 n_2 \sqrt{\bar{c}_1^2+\bar{c}_2^2}}$$ & Mean free path for the other

$$\lambda_2 = \frac{\bar{c}_2}{\Gamma_2} = \frac{\bar{c}_2}{\sqrt{2}\pi n_2 \bar{c}_2 \sigma_2^2 + \pi\sigma_a^2 n_1 \sqrt{\bar{c}_1^2+\bar{c}_2^2}}$$

<u>HW</u> 1. Estimate the size of a He atom, assuming its mean free path is 28.5×10^{-6} cm at N.T.P. & density is 0.178 gm/litre at N.T.P. & the mass of He atom is 6×10^{-24} gm.

2. The diameter of a gas molecule is 3×10^{-8} cm. Calculate the mean free path at N.T.P. Given $K_B = 1.38 \times 10^{-16}$ ergs/°c.

3. Find the diameter of a molecule of Benzene if its mean-free path is 2.2×10^{-8} m & the number of Benzene molecules/unit volume is 2.79×10^{25} molecules/m³.