9 The Kinetic Theory of Gases

1] Review

We have already seen that pressure exerted by an ideal gas is a consequence of multiple collisions by the molecules against the sides of the container.

For 1 molecule, contribution to pressure is

$$|P_1| = \frac{1}{A}\left[m\frac{|\Delta u_x|}{\Delta t}\right] = \frac{1}{A}m\frac{2u_x}{2L/u_x} = m\frac{u_x^2}{AL} = mu_x^2/V$$

For N molecules $\qquad \bar{P} = N m\overline{u_x^2}/V \qquad (*)$

Assuming motion is isotropic $\Rightarrow \overline{u_x^2} = \overline{u_y^2} = \overline{u_z^2} = \frac{1}{3}\overline{|\underline{u}|^2}$

Can rewrite $(*)$ in terms of the mean (translational) kinetic energy $\quad \overline{KE} = N\frac{1}{2}m\overline{|\underline{u}|^2} = N\frac{3}{2}m\overline{u_x^2} = \frac{3}{2}\bar{P}V$

But $\quad PV = nRT = NkT \qquad \left(\text{with } k = \frac{R}{N_A} = 1.381\times10^{-23}\,\text{J/K}\right)$

So the total kinetic energy of the system is

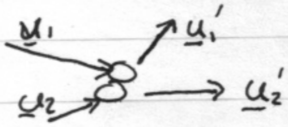
$$\overline{KE} = \frac{3}{2}NkT$$

This derivation only worked with mean-square velocities, not accounting for the expectation that the molecules will have a <u>distribution</u> of velocities, with some speeding up and some slowing down upon collisions.

Despite individual changes, in equilibrium the distribution should be the same.

2] THE MAXWELL-BOLTZMAN VELOCITY DISTRIBUTION

DENOTE THE VELOCITY DISTRIBUTION BY $F(\underline{u})$ (SO $F(\underline{u})d\underline{u}$ IS THE # PARTICLES OF HAVING VELOCITY BETWEEN $\underline{u}$ AND $\underline{u}+d\underline{u}$)



CONSIDER COLLISION BETWEEN TWO PARTICLES

IN TIME Δt, # COLLISIONS BETWEEN 2 PARTICLES WITH VELOCITIES $\underline{u}_1$ AND $\underline{u}_2$ IS $\propto F(\underline{u}_1)F(\underline{u}_2)$

IN REVERSE PROCESS HAVE COLLISION BETWEEN $\underline{u}_1'$ & $\underline{u}_2'$ OCCURRING $\propto F(\underline{u}_1')F(\underline{u}_2')$ TIMES

FOR EQUILIBRIUM, MUST HAVE $\boxed{F(\underline{u}_1)F(\underline{u}_2) = F(\underline{u}_1')F(\underline{u}_2')}$

BECAUSE COLLISIONS ARE ELASTIC $|\underline{u}_1|^2 + |\underline{u}_2|^2 = |\underline{u}_1'|^2 + |\underline{u}_2'|^2$

TO FIND F, SOLVE $\ln F(\underline{u}_1) + \ln F(\underline{u}_2) - \ln F(\underline{u}_1') - \ln F(\underline{u}_2') + \lambda(|\underline{u}_1|^2 + |\underline{u}_2|^2 - |\underline{u}_1'|^2 - |\underline{u}_2'|^2) = 0$

WHERE λ (CONSTANT)

CONSIDER u_{1x} DERIVATIVE:

$$\frac{d}{du_{1x}} \ln F(\underline{u}_1) + \lambda \frac{d}{du_{1x}} u_{1x}^2 = 0$$

$$\Rightarrow F(\underline{u}_1) = C(u_{1y}, u_{1z})\, e^{-\lambda u_{1x}^2}$$

LIKEWISE CONSIDERING u_{1y} AND u_{1z} DERIVATIVES, GET

$$F(\underline{u}_1) = \mathcal{C}\, e^{-\lambda|\underline{u}_1|^2} \quad , \mathcal{C}, \lambda \text{ CONSTANTS}$$

FIND $\mathcal{C}$ & λ USING MASS & ENERGY RELATIONS

1) TOTAL NUMBER OF PARTICLES IS

$$N = \iiint F(\underline{u})\,d\underline{u} = \int_0^\infty \int_0^{2\pi} \int_0^\pi F(\underline{u})\,(u\,d\theta)(u\sin\theta\,d\phi)\,du$$

ASSUME F IS ISOTROPIC IN $\underline{u}$. I.e. $F(\underline{u}) = F(u)$

$$\Rightarrow N = \int_0^\infty 4\pi u^2 F(u)\,du = 4\pi\mathcal{C}\int_0^\infty u^2 e^{-\lambda u^2}\,du$$

2) TOTAL KINETIC ENERGY IS $\frac{3}{2}NKT$

$$\Rightarrow \frac{3}{2}NKT = \int_0^\infty \int_0^{2\pi} \int_0^\pi \frac{1}{2}mu^2 F(\underline{u})\,(u\,d\theta)(u\sin\theta\,d\phi)\,du$$

$$= 2\pi m \int_0^\infty u^4 F(u)\,du = 2\pi m\mathcal{C}\int_0^\infty u^4 e^{-\lambda u^2}\,du$$

2] (CONT'D)

A SIDE NOTE ON INTEGRATING GAUSSIAN FUNCTIONS.

1) LET $I = \int_0^\infty e^{-x^2} dx$

$$\Rightarrow \quad I^2 = \left(\int_0^\infty e^{-x^2} dx\right)\left(\int_0^\infty e^{-y^2} dy\right)$$
$$= \int_0^\infty \int_0^\infty e^{-x^2-y^2} dx\, dy$$
$$= \int_0^\infty \int_0^{\pi/2} e^{-r^2} (r\, d\theta)\, dr$$
$$= \frac{\pi}{2} \int_0^\infty r e^{-r^2} dr = \frac{\pi}{4} \int_0^\infty e^{-(r^2)} d(r^2)$$
$$= \pi/4$$

So $I = \frac{1}{2}\sqrt{\pi}$

2) $$\int x^2 e^{-x^2} dx = \int x\,(x e^{-x^2})\, dx$$
$$= \int x\, d(-\tfrac{1}{2} e^{-x^2})$$
$$= x(-\tfrac{1}{2} e^{-x^2})\Big| - \int (-\tfrac{1}{2} e^{-x^2})\, dx$$

So $\int_0^\infty x^2 e^{-x^2} dx = \frac{1}{2}\int_0^\infty e^{-x^2} dx = \frac{1}{4}\sqrt{\pi}$

3) $$\int x^4 e^{-x^2} dx = \int x^3 (x e^{-x^2}) dx$$
$$= x^3(-\tfrac{1}{2} e^{-x^2}) - \int (-\tfrac{1}{2} e^{-x^2})\, d(x^3)$$
$$= \quad '' \quad + \frac{3}{2}\int x^2 e^{-x^2} dx$$

So $\int_0^\infty x^4 e^{-x^2} dx = \frac{3}{2}\left(\frac{1}{4}\sqrt{\pi}\right) = \frac{3}{8}\sqrt{\pi}$

GETTING BACK TO OUR FORMULAE:

1) $$N = 4\pi C \int_0^\infty u^2 e^{-\lambda u^2} du \overset{x=\sqrt{\lambda}u}{=} 4\pi C \lambda^{-3/2} \int_0^\infty x^2 e^{-x^2} dx$$
$$= 4\pi C \lambda^{-3/2}\left(\frac{1}{4}\sqrt{\pi}\right) = \pi^{3/2} C \lambda^{-3/2}$$

2) $$\frac{3}{2} NkT = 2\pi m C \int_0^\infty u^4 e^{-\lambda u^2} du = 2\pi m C \lambda^{-5/2}\, \frac{3}{8}\sqrt{\pi}$$
$$\Rightarrow \frac{3}{2}\left(\pi^{3/2} C \lambda^{-3/2}\right) kT = \frac{3}{4}\pi^{3/2} m C \lambda^{-5/2}$$
$$\Rightarrow \lambda = \frac{1}{2} m \frac{1}{kT}$$

HENCE $C = N \lambda^{3/2} \pi^{-3/2} = N\left(\frac{m}{2\pi kT}\right)^{3/2}$

So $F(\underline{u}) = N\left(\frac{m}{2\pi kT}\right)^{3/2} \mathrm{EXP}\left[-\frac{1}{2} m u^2/(kT)\right]$, WITH $u \equiv |\underline{u}|$

THIS IS THE MAXWELL-BOLTZMAN VELOCITY DISTRIBUTION

3] Boltzmann statistics

Because $F(\underline{u})$ is isotropic in $\underline{u}$ we found

$$\int \int_0^{2\pi} \int_0^{\pi} F(\underline{u})\, u^2\, d\theta\, d\phi\, du = \int 4\pi u^2 F(u)\, du$$

So it is convenient to define $\mathcal{N}(u) \equiv 4\pi u^2 F(u)$ as the "speed" distribution.

Explicitly $\mathcal{N}(u) = 4\pi u^2 N \left(\frac{m}{2\pi kT}\right)^{3/2} e^{-\frac{mu^2}{2kT}}$

(By construction $\int \mathcal{N}(u)\, du = N$. So probability distribution is $\frac{1}{N}\int \mathcal{N}(u) du$)

From this we get the following measures of average speed:

① Mean speed : $\bar{u}$

$$\bar{u} \equiv \frac{1}{N}\int_0^\infty u\, \mathcal{N}(u)\, du = 4\pi\left(\frac{m}{2\pi kT}\right)^{3/2}\int_0^\infty u^3 e^{-u^2/(2kT/m)}\, du$$
$$= \cdots = \left(8kT/\pi m\right)^{1/2} \simeq \underline{1.596\,(kT/m)^{1/2}}$$

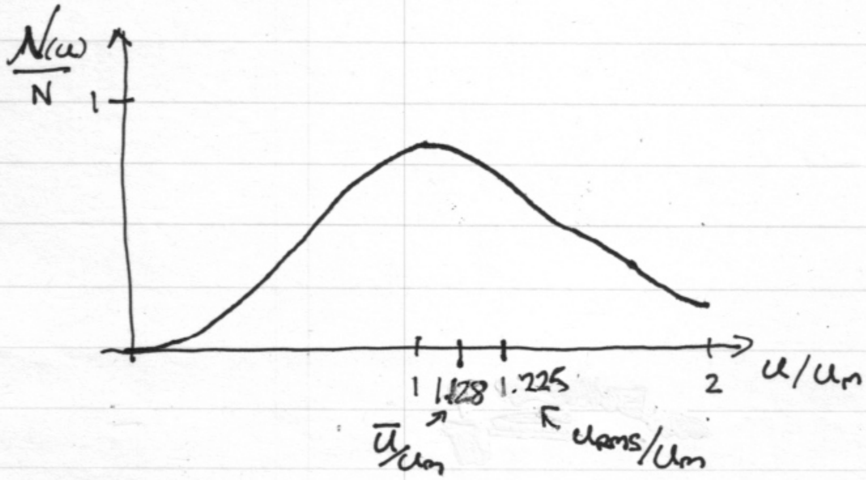
② Root-mean-square speed : u_{rms}

$$\overline{u^2} = \frac{1}{N}\int_0^\infty u^2\, \mathcal{N}(u)\, du = \cdots = \frac{3kT}{m}$$
$$\Rightarrow u_{rms} = (\overline{u^2})^{1/2} = \left(\frac{3kT}{m}\right)^{1/2} \simeq \underline{1.732\,(kT/m)^{1/2}}$$

(Same result as eqn ② on p. 10 of notes)

③ Most probable speed: u_m

$$\frac{d}{du}\mathcal{N}(u)\Big|_{u=u_m} = 0$$
$$\Rightarrow 0 = \frac{d}{du}\left(u^2 e^{-mu^2/2kT}\right)\Big|_{u=u_m}$$
$$= 2u_m e^{-mu_m^2/2kT} + u_m^2\left(-\frac{mu_m}{kT}\right)e^{-mu_m^2/2kT}$$
$$\Rightarrow u_m = (2kT/m)^{1/2} \simeq 1.414\,(kT/m)^{1/2}$$



Some values of $\bar{u}$ at 273K:

H_2	1690 m/s
He	1210 m/s
H_2O	570 m/s
N_2	450 m/s
O_2	420 m/s

4] ENERGETICS

TO DERIVE $F(\underline{u}) = N\left(\frac{m}{2\pi kT}\right)^{3/2} \mathrm{EXP}\left[-\frac{1}{2}m|\underline{u}|^2/kT\right]$

WE REQUIRED $N = \iiint F(\underline{u})\,|d\underline{u}|$

AND TOTAL KINETIC ENERGY $\frac{3}{2}NkT = \iiint \frac{1}{2}m|\underline{u}|^2 F(\underline{u})\,|d\underline{u}|$

IN WHICH $|d\underline{u}| = u^2 \sin\theta\, d\theta\, d\phi\, du$ IN SPHERICAL CO-ORDINATES

NOW CONSIDER BREAKDOWN IN X-Y-Z CO-ORDINATES.

EXPLOITING SYMMETRY, WRITE

$$\frac{1}{N}F(\underline{u}) = \left\{\left(\frac{m}{2\pi kT}\right)^{1/2} e^{-mu_x^2/2kT}\right\}\left\{\left(\frac{m}{2\pi kT}\right)^{1/2} e^{-mu_y^2/2kT}\right\}\left\{\left(\frac{m}{(2\pi kT)}\right)^{1/2} e^{-mu_z^2/2kT}\right\}$$

$$= \left(Ce^{-E_x/kT}\right)\left(Ce^{-E_y/kT}\right)\left(Ce^{-E_z/kT}\right), \text{ WITH } E_i = \tfrac{1}{2}mu_i^2,\ C = \left(\tfrac{m}{2\pi kT}\right)^{1/2}$$

SO, TO FIND MEAN VALUE OF $E_x = \frac{1}{2}mu_x^2$, COMPUTE

$$\overline{E_x} \equiv \frac{\iiint E_x F(\underline{u})\,|d\underline{u}|}{\iiint F(\underline{u})\,|d\underline{u}|} = \frac{\iiint \frac{1}{2}mu_x^2 \left(Ce^{-E_x/kT}\right)\left(Ce^{-E_y/kT}\right)\left(Ce^{-E_z/kT}\right)du_x du_y du_z}{\iiint \left(Ce^{-E_x/kT}\right)\left(Ce^{-E_y/kT}\right)\left(Ce^{-E_z/kT}\right)du_x du_y du_z}$$

$$= \frac{\left(\int \frac{1}{2}mu_x^2\left(Ce^{-E_x/kT}\right)du_x\right)\left(\int\left(Ce^{-E_y/kT}\right)du_y\right)\left(\int\left(Ce^{-E_z/kT}\right)du_z\right)}{\left(\int\left(Ce^{-E_x/kT}\right)du_x\right)\left(\int\left(Ce^{-E_y/kT}\right)du_y\right)\left(\int\left(Ce^{-E_z/kT}\right)du_z\right)}$$

$$= \frac{\int \frac{1}{2}mu_x^2\left(Ce^{-E_x/kT}\right)du_x}{\int\left(Ce^{-E_x/kT}\right)du_x} = \frac{\frac{1}{2}m\int_{-\infty}^{\infty} u_x^2 e^{-mu_x^2/2kT}\,du_x}{\int_{-\infty}^{\infty} e^{-mu_x^2/2kT}\,du_x}$$

$$= \frac{\frac{1}{2}m\left(\frac{m}{2kT}\right)^{-3/2}\left(\frac{1}{2}\sqrt{\pi}\right)}{\left(\frac{m}{2kT}\right)^{-1/2}\left(\sqrt{\pi}\right)} = \frac{1}{2}kT$$

LIKEWISE IN Y & Z FIND $\overline{E_y} = \frac{1}{2}kT$, $\overline{E_z} = \frac{1}{2}kT$

BY EXTENSION, WE CAN CONSIDER ENERGY ASSOCIATED WITH ROTATION OF MOLECULES $\mathcal{E}_i = \frac{1}{2}I_i\omega_i^2,\ i=1,2,3$, I_i IS MOMENT OF INERTIA

THEN MEAN ENERGY ASSOCIATED WITH ROTATION ABOUT $i=1$ AXIS IS

$$\overline{\mathcal{E}_1} = \frac{\int\cdots\int \mathcal{E}_1 C^3 e^{-(E_x+E_y+E_z)/kT}\, C^3 e^{-(\mathcal{E}_1+\mathcal{E}_2+\mathcal{E}_3)/kT}\,|d\underline{u}|\,|d\underline{\omega}|}{\int\cdots\int C^3 e^{-(E_x+E_y+E_z)/kT}\, C^3 e^{-(\mathcal{E}_1+\mathcal{E}_2+\mathcal{E}_3)/kT}\,|d\underline{u}|\,|d\underline{\omega}|}$$

$$= \frac{\int \frac{1}{2}I_1\omega_1^2 e^{-I_1\omega_1^2/2kT}\,d\omega_1}{\int e^{-I_1\omega_1^2/2kT}\,d\omega_1} = \frac{1}{2}kT$$

SO MEAN ENERGY OF ROTATION SAME AS MEAN ENERGY OF TRANSLATION

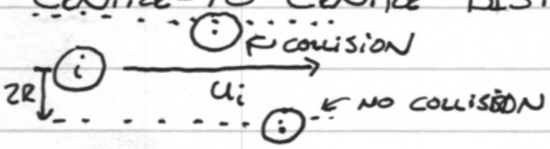
THUS WE ATTRIBUTE ENERGY $U = Nf\frac{1}{2}kT = \frac{1}{2}f(nR)T$ TO IDEAL GAS WITH f DEGREES OF FREEDOM. $f=3$ MONATOMIC, $f=5$ DIATOMIC

$\Rightarrow C_V = \frac{\partial U}{\partial T} = \frac{1}{2}fnR$, $C_P = C_V + nR = \left(\frac{1}{2}f+1\right)nR \Rightarrow \gamma = \frac{C_P}{C_V} = \frac{f+2}{f}$

5] MEAN FREE PATH

THIS IS THE AVERAGE DISTANCE TRAVELLED BY A MOLECULE BETWEEN COLLISIONS.

APPROXIMATE THE MOLECULES BY SPHERES OF RADIUS R. SO A COLLISION OCCURS IF ONE MOLECULE APPROACHES ANOTHER WITH CENTRE-TO-CENTRE DISTANCE $< 2R$



BETWEEN SUCCESSIVE COLLISIONS, MOLECULE i TRAVELS FREELY THROUGH DISTANCES $l_1, l_2, l_3, \ldots l_{n_c}$ (KNOWN AS FREE PATHS)

THE MEAN FREE PATH IS $l = \frac{1}{n_c} \sum_{i=1}^{n_c} l_i$

SUPPOSE n_c COLLISIONS OCCUR IN TIME t.

THEN $\sum l_i = \bar{u} t$ WHERE $\bar{u}$ IS MEAN SPEED

THE NUMBER OF COLLISIONS CAN BE ESTIMATED BY THE NUMBER OF MOLECULES WITHIN THE VOLUME SWEPT OUT BY MOLECULE i IN TIME t: $\bar{n}_c = \underbrace{\left[(\bar{u}t)\, \pi (2R)^2\right]}_{\text{SWEPT OUT VOLUME}} \times \frac{N}{V}$ ← TOTAL # MOLECULES / ← TOTAL VOLUME

$$\text{So} \quad \bar{l} \simeq \bar{u}t / \bar{n}_c$$
$$\simeq \bar{u}t / \left[(\bar{u}t)\, 4\pi R^2 \frac{N}{V}\right]$$
$$\Rightarrow \bar{l} = \left[4\pi R^2 \frac{N}{V}\right]^{-1}$$
$$pV = NkT \Rightarrow \boxed{\bar{l} = kT/(4\pi R^2 p)} \qquad (k = 1.381 \times 10^{-23}\ \text{J/K})$$

EXAMPLES: ① AIR AT SEA LEVEL: $p \sim 1.0 \times 10^5$ Pa, $T = 300$K

TAKE $R \sim 1.5 \times 10^{-10}$ m $\Rightarrow \bar{l} \simeq 1.5 \times 10^{-7}$ m. $\gg R$! WHEW

COMPARE WITH INTERMOLECULAR SPACING: $\left(\frac{V}{N}\right)^{1/3} = \left(\frac{kT}{p}\right)^{1/3} \simeq 3.5 \times 10^{-9}$ m

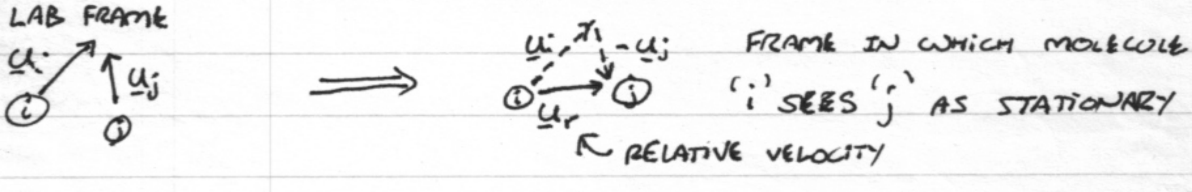
② IN THERMOSPHERE AT 200km: $p \sim 1.0 \times 10^{-6}$ Pa, $T \sim 1000$K

$\Rightarrow \bar{l} \simeq 50$ km WHEREAS $\left(\frac{V}{N}\right)^{1/3} \simeq 2 \times 10^{-5}$ m

5] (CONT'd)

IMPROVED CALCULATION OF MEAN FREE PATH

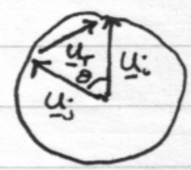
IN DERIVING FORMULA FOR # COLLISIONS, n_c, WE ASSUME THAT MOLECULE i MOVED INTO A FIELD OF OTHERWISE STATIONARY MOLECULES. HERE WE ACCOUNT FOR MOTION OF OTHER MOLECULES.

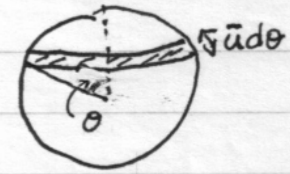


IN FRAME WITH 'j' STATIONARY, 'i' APPROACHES AT RELATIVE VELOCITY $\underline{u}_r = \underline{u}_i - \underline{u}_j$. WE WISH TO FIND THE MEAN $\overline{u}_r = \overline{|\underline{u}_r|}$.

FOR SIMPLICITY, SUPPOSE ALL MOLECULES HAVE SAME SPEED, $\overline{u}$. BUT THE ORIENTATION OF THE VELOCITY VECTORS CHANGE. FOR $\underline{u}_j$ AT ANGLE θ TO $\underline{u}_i$

$$|\underline{u}_r| = 2\overline{u}\sin(\theta/2)$$





THE FRACTION OF MOLECULES WITH $\underline{u}_j$ AT ANGLE BETWEEN θ & $\theta + d\theta$ IS $\frac{1}{4\pi\overline{u}^2}\left[2\pi(\overline{u}\sin\theta)\times u\,d\theta\right]$

$$= \frac{1}{2}\sin\theta\,d\theta$$

$$\text{So } \overline{u}_r = \int_0^{\pi} u_r\left(\tfrac{1}{2}\sin\theta\,d\theta\right) = \overline{u}\int_0^{\pi}\sin(\theta/2)\sin\theta\,d\theta$$

$$= \overline{u}\int_0^{\pi}\sin(\theta/2)\left(2\sin\theta/2\cos\theta/2\right)d\theta = \cdots = 4/3\,\overline{u}$$

So # COLLISIONS IN TIME t IS $n_c = \left[(\overline{u}_r t)\pi(2R)^2\right]\times\frac{N}{V}$

$$\Rightarrow \ell \simeq (\overline{u}t)/\left[(\overline{u}_r t)\cdot 4\pi R^2\frac{N}{V}\right] = \frac{3}{4}\left[4\pi R^2\frac{N}{V}\right]^{-1} = \frac{3}{4}\overline{\ell}$$

AN EVEN BETTER CALCULATION ASSUMES $\underline{u}_j$ HAS MAXWELL-BOLTZMAN DIST^{N}. INTEGRATING IN u AS WELL AS θ GIVES $\overline{u}_r = \sqrt{2}\,\overline{u}$

$$\Rightarrow \ell = \frac{1}{\sqrt{2}}\left[4\pi R^2\frac{N}{V}\right]^{-1} = \frac{1}{\sqrt{2}}\overline{\ell} \quad \text{(6\% DIFFERENT THAN } \tfrac{3}{4}\overline{\ell} \text{ ESTIMATE)}$$

6] COLLISION FREQUENCY

RETURNING TO OUR SIMPLE MODEL OF COLLISIONS, WE FOUND
$n_c = (\bar{u}t)\, 4\pi R^2 N/V$ IS # COLLISIONS IN TIME t.

THE COLLISION FREQUENCY IS # COLLISIONS PER UNIT TIME:

$$f_c = n_c/t = \bar{u}\, 4\pi R^2 N/V$$

$$\Rightarrow \boxed{f_c = \bar{u}/\bar{\ell}} \quad \text{WITH } \bar{\ell} = \left(4\pi R^2 \frac{N}{V}\right)^{-1} \text{ (SIMPLE ESTIMATE)}$$

WE CAN GO ON TO CALCULATE THE FREQUENCY OF COLLISIONS OF ALL MOLECULES WITHIN A UNIT VOLUME:

$$f_{c,\text{TOTAL}} = \frac{1}{2}\frac{N}{V}\bar{u}/\bar{\ell} = 2\pi R^2 \left(\frac{N}{V}\right)^2 \bar{u} = 4\pi R^2 \left(\frac{N}{V}\right)^2 \left(\frac{2kT}{\pi m}\right)^{1/2}$$

IN WHICH THE $\frac{1}{2}$ KEEPS US FROM COUNTING EACH COLLISION TWICE

EXAMPLE: FOR AIR AT SEA LEVEL, FOUND $\bar{\ell} \simeq 1.5 \times 10^{-7}\,m$
AND $\bar{u} \simeq 0.80\,\bar{u}_{N_2} + 0.20\,\bar{u}_{O_2} = 0.80\,(450\,m/s) + 0.20\,(420\,m/s)$
$\simeq 444\,m/s$

SO $f_c = (444\,m/s)/(1.5\times 10^{-7}\,m) \simeq 3.0 \times 10^9\ \underbrace{Hz}_{\text{COLLISIONS/SECOND}}$

(BILLIONS OF COLLISIONS OF ONE MOLECULE EACH SECOND)

TOTAL # COLLISIONS $/m^3/$SEC IS $f_{c,\text{TOTAL}} = \frac{1}{2}\frac{N}{V} f_c = \frac{1}{2}\left(\frac{P}{kT}\right) f_c$
$\simeq 1.2 \times 10^{25}\ \cancel{Hz}/m^3$

THIS LAST RESULT CAN BE USED TO ESTIMATE CHEMICAL REACTION RATES BETWEEN 2 SPECIES IN A GAS. LET N_A & N_B BE # MOLECULES OF SPECIES A & B IN A VOLUME V. THEN # COLLISIONS BETWEEN A & B / TIME IS $\simeq \pi(R_A+R_B)^2 \left(\frac{2kT}{\pi m}\right)^{1/2} \left(\frac{N_A}{V}\right)\left(\frac{N_B}{V}\right)$.

BUT REACTION TAKES PLACE ONLY IF COLLIDING ~~MOLECULE~~ HAS ENOUGH ENERGY TO BREAK BONDS, etc OF THE OTHER SPECIES. FRACTION OF MOLECULES WITH ENERGY $\gtrsim E_0$ IS $\approx \int_{E_0}^{\infty} \frac{1}{kT} e^{-E/kT}\, dE = e^{-E_0/kT} \Rightarrow$ REACTION RATE IS $\pi(R_A+R_B)^2 \left(\frac{2kT}{\pi m}\right)^{1/2} \left(\frac{N_A}{V}\right)\left(\frac{N_B}{V}\right) e^{-E_0/kT}$
$\propto T^{1/2} e^{-E_0/kT}$ AS TYPICALLY OBSERVED.

7] PROBABILITY OF TRAVELLING A DISTANCE X WITHOUT COLLISION

EXPECT PROBABILITY OF COLLISION TO OCCUR IN DISTANCE dx IS $\alpha\, dx$ ($\alpha > 0$, PROPORTIONALITY CONSTANT) (i.e. TRAVELLING TWICE THE DISTANCE, DOUBLES THE PROBABILITY OF COLLISION)

$$\text{So} \quad \underbrace{p(x+dx)}_{\text{PROB. NO COLLISION BEFORE } x+dx} = \underbrace{(1-\alpha\, dx)}_{\text{PROB NO COLLISION AFTER TRAVELLING } dx} \underbrace{p(x)}_{\text{PROB NO COLLISION BEFORE } x.}$$

$$\text{BUT} \quad P(x+dx) \sim P(x) + \frac{dP}{dx} dx$$

$$\Rightarrow p(x) + \frac{dP}{dx} dx = p(x) - \alpha\, dx\, p(x)$$

$$\Rightarrow \frac{dP}{dx} = -\alpha P$$

$$\Rightarrow p(x) = \mathcal{C} e^{-\alpha x}$$

SINCE X IS DISTANCE FROM LAST COLLISION, EXPECT, $P(0) = 1$.

$$\Rightarrow p(x) = e^{-\alpha x}$$

EXPECT α TO BE RELATED TO THE MEAN FREE PATH ℓ . ∞
DENOTE PROBABILITY DISTRIBUTION BY $f(x)$: $p(x) = \int_x f(x)\, dx$

$$\Rightarrow f(x) = \alpha e^{-\alpha x} \quad \text{(DEFINED TO BE POSITIVE FOR ALL } x)$$

$$\text{So} \quad \ell = \int_0^\infty x f(x)\, dx = \int_0^\infty \alpha x e^{-\alpha x}\, dx = \frac{1}{\alpha}.$$

$$\Rightarrow \boxed{P(x) = e^{-x/\ell}}$$

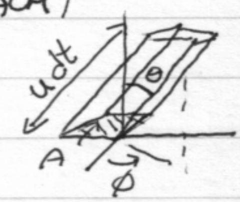
SO PROBABILITY OF TRAVELLING A DISTANCE X WITH NO COLLISION DECREASES EXPONENTIALLY. TO TRAVEL A DISTANCE $x = \ell$ WITHOUT COLLISION HAS PROBABILITY $1/e \approx 0.37$.

8] Collisions with a Solid Surface

Earlier we considered # particles colliding with a small area $\perp$ to x per unit time imagining the particles have uniform speed and focusing upon x-component of velocity.

Let's do this rigourously assuming we know the probability distribution of particle speeds $P(u) \equiv \frac{1}{N} N(u) = 4\pi \left(\frac{m}{2\pi kT}\right)^{3/2} u^2 e^{-\frac{mu^2}{2kT}}$ (see p. 69 of notes).

A) Ignore intermolecular collisions ("Prism" approach)



Consider a prism with base being the area A and sides tilted at angles θ & ϕ from $\perp$ to A and length $u\,dt$.

The volume of the prism is $A\,u\,dt\cos\theta$

So all atoms moving toward A with speed u and angles θ & ϕ that lie within the prism will strike A in time dt.

The number of such atoms within du, $d\theta$, & $d\phi$ of u, θ, ϕ is given by number density $n \equiv N/V$ and probability distribution

$$\Rightarrow \left(A\,u\,dt\cos\theta\right) \times \frac{n}{4\pi} P(u) \sin\theta\, d\theta\, d\phi\, du$$

So # collisions/area/time is

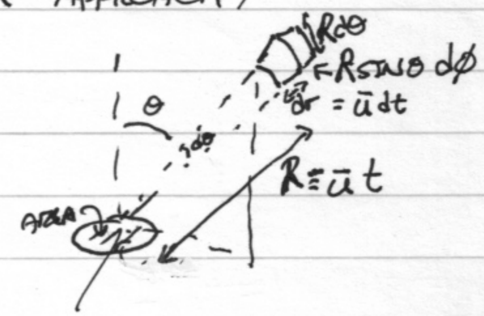
$$\Phi = \frac{1}{A\,dt} \int_0^\infty du \int_0^{\pi/2} d\theta \int_0^{2\pi} d\phi \left[A u\, dt\cos\theta \cdot \frac{n}{4\pi} P(u) \sin\theta \right]$$

$$= \frac{n}{4\pi} \underbrace{\left(\int_0^\infty u\, P(u)\, du\right)}_{\bar{u}} \underbrace{\left(\int_0^{\pi/2} \cos\theta \sin\theta\, d\theta\right)}_{1/2} \underbrace{\left(\int_0^{2\pi} d\phi\right)}_{2\pi}$$

$$\Rightarrow \boxed{\Phi = \frac{1}{4} n \bar{u}}$$

8] (CONT'd)

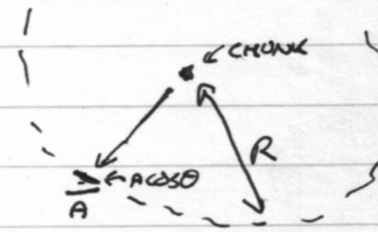
B) IGNORE INTERMOLECULAR COLLISIONS ("CHUNK" APPROACH)



CONSIDER PARTICLES WITH SPEED $\bar{u}$ AT A TIME t BEFORE THEY STRIKE THE AREA.

THE NUMBER OF PARTICLES IN THE CHUNK OF THE HEMISPHERICAL SHELL SPANNING $R = \bar{u}t \rightarrow \bar{u}(t+dt)$ IS $\quad n(\bar{u}\,dt)(R\,d\theta)(R\sin\theta\, d\phi)$

FROM THE CHUNK'S PERSPECTIVE, THE FRACTION OF PARTICLES REACHING A IS THE RATIO OF THE AREA AS 'SEEN' BY THE CHUNK, $A\cos\theta$, TO THE SURFACE AREA OF THE SPHERE OF RADIUS R: $4\pi R^2$.



SO THE # COLLISIONS / AREA / TIME IS

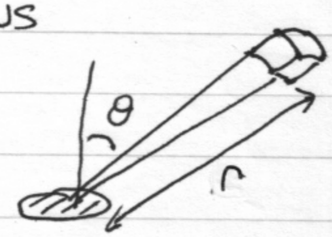
$$\Phi = \frac{1}{A\,dt} \int_0^{\pi/2} d\theta \int_0^{2\pi} d\phi \left[\left(A\cos\theta / 4\pi R^2\right) \cdot n(\bar{u}\,dt) R^2 \sin\theta \right]$$

$$= \frac{1}{4\pi} n\bar{u} \left(\int_0^{\pi/2} \cos\theta \sin\theta \, d\theta \right) \left(\int_0^{2\pi} d\phi \right)$$

$$\Rightarrow \boxed{\Phi = \frac{1}{4} n\bar{u}} \text{, AS BEFORE}$$

8] (CONT'd)

C) ACCOUNTING FOR INTERMOLECULAR COLLISIONS



BEGIN AS IN B), BY CONSIDERING A VOLUME ELEMENT A DISTANCE r FROM THE AREA : $dV = r^2 \sin\theta \, dr \, d\theta \, d\phi$.
NOW r IS AN ARBITRARY DISTANCE (NOT FIXED AS $\bar{u}\,dt$)

THE # COLLISIONS/TIME TAKING PLACE WITHIN THIS VOLUME IS $f_{c,\text{TOTAL}}\, dV = (\frac{1}{2} n \bar{u}/\ell)\, dV$. (SEE P. 73 OF NOTES)
EACH COLLISION INVOLVES 2 PARTICLES. SO # PARTICLES/TIME COMING FROM dV IMMEDIATELY AFTER A COLLISION IS

$$2 f_{c,\text{TOTAL}}\, dV = (n\bar{u}/\ell)\, dV$$

THE FRACTION OF THESE DIRECTED TOWARD AREA IS

$$(A\cos\theta/4\pi r^2) \times (n\bar{u}/\ell)\, dV \qquad \text{(AS IN B))}$$

BUT THESE ONLY REACH AREA IF THEY DON'T COLLIDE AGAIN. WE HAVE FOUND THAT THE PROBABILITY OF TRAVELLING A DISTANCE r WITH NO COLLISION IS $e^{-r/\ell}$ (SEE P. 74 OF NOTES)

SO # PARTICLES/TIME LEAVING dV TOWARD A WITHOUT COLLIDING AGAIN IS

$$e^{-r/\ell}\,(A\cos\theta/4\pi r^2) \times (n\bar{u}/\ell)\; r^2 \sin\theta \, dr\, d\theta\, d\phi$$

SO TOTAL # PARTICLES/AREA/TIME IS

$$\Phi = \frac{1}{A}\int_0^\infty dr \int_0^{\pi/2} d\theta \int_0^{2\pi} d\phi \left[e^{-r/\ell}\, \frac{A\cos\theta}{4\pi r^2} \cdot \frac{n\bar{u}}{\ell}\, r^2 \sin\theta \right]$$

$$= \frac{1}{4\pi}(n\bar{u}/\ell)\left(\int_0^\infty e^{-r/\ell}\, dr\right)\left(\int_0^{\pi/2} \cos\theta \sin\theta\, d\theta\right)\left(\int_0^{2\pi} d\phi\right)$$

$$\Rightarrow \boxed{\Phi = \frac{1}{4} n\bar{u}} \text{ , AS BEFORE!}$$

A & B WORKED SO WELL BECAUSE AS ONE PARTICLE IS DEFLECTED BY A COLLISION, ANOTHER MUST TAKE ITS PLACE

8] (CONT'D)

EXAMPLE: "MISSION TO MARS"

IN THE MOVIE MISSION TO MARS, THE SPACESHIP IS PUNCTURED BY A MICROMETEORITE. THE CREW THEN PANICS TO FIND THE HOLE BEFORE THEY LOSE ALL THEIR AIR. SHOULD THEY PANIC?

SUPPOSE THE PUNCTURED SPACE MEASURES 3m x 3m x 10m, CONTAINING AIR AT 20°C. THE HOLE HAS RADIUS 0.1 mm. HOW LONG BEFORE 1% OF THE AIR IS LOST?

SOL$^{\underline{N}}$:

THE # MOLECULES LEAVING THE HOLE/TIME IS

$$\frac{dN}{dt} = -A\Phi = -A\left(\frac{1}{4}n\bar{u}\right) = -A\left(\frac{1}{4}\frac{N}{V}\right)\left(\frac{8kT}{\pi m}\right)^{1/2}$$

$$\Rightarrow \frac{dN}{dt} = -\frac{1}{\tau}N \quad \text{WITH } \tau = \frac{4V}{A}\left(\frac{\pi m}{8kT}\right)^{1/2} \sim \text{CONSTANT}$$

SOLUTION: $N(t) = N_0 e^{-t/\tau}$ WHERE $N_0 \equiv N(t=0)$

WHEN 1% OF THE AIR IS LOST $0.99 = \frac{N}{N_0} = e^{-t/\tau}$

$$\Rightarrow t = -\tau \ln(0.99) \simeq 0.01\tau$$

IT REMAINS TO FIND τ!

$$\tau = \frac{4(3\times3\times10)}{\pi(10^{-4})^2}\left(\frac{\pi\times(28.97\times1.673\times10^{-27})}{8\times1.38\times10^{-23}\times293}\right)^{1/2}$$

$$\simeq 2.5\times10^7\,\text{s}$$

SO THE TIME TO LOSE 1% OF AIR IS

$$t \simeq 0.01\tau \simeq 2.5\times10^5\,\text{s} \simeq \boxed{2.9 \text{ DAYS}}$$