Gas Kinetics

Some fundamental numbers to know are:

$A \Rightarrow$ Avogadro's # $\left[\frac{\#\,molecules}{kmol}\right] = 6.022 \times 10^{26}$

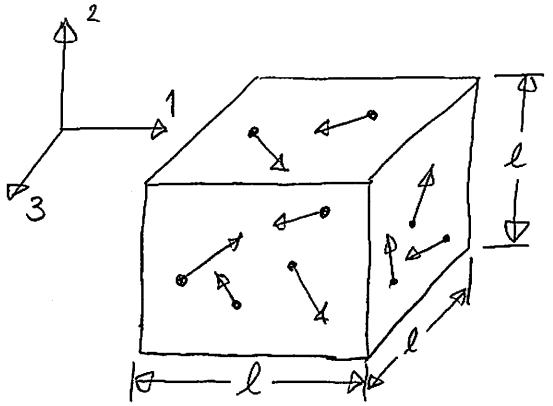
$R \Rightarrow$ Universal gas constant $\left[\frac{J}{kmol \cdot K}\right] = 8314.3$

$k_B \Rightarrow$ Boltzmann constant $\left[\frac{J}{molecule \cdot K}\right] = 1.38 \times 10^{-23}$ $\Rightarrow$ Relates individual molecule energy to temperature

$M \Rightarrow$ Molecular weight $\left[\frac{kg}{kmol}\right]$

$$k_B = \frac{R}{A}$$

We can now develop a model to give meaning for pressure in a rarified gas (non-interacting gas molecules)



$\forall = \ell^3$

N molecules in our volume

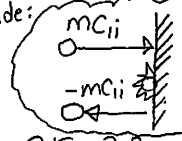
$\ell < \lambda$ (Rarified gas)

m $\Rightarrow$ mass per particle

We have a particle traveling at C_{1i} ← i'th particle with velocity component in 1 direction

The change in momentum from a collision with the wall normal to 1 is $2mC_{1i} = \Delta p$

Aside:



$\Delta p = p_i - p_f = [C_{1i} - (-C_{1i})]m = 2mC_{1i}$

Relating this to force: $F = \frac{\Delta p}{\Delta t}$, or as you know it $F = \frac{dp}{dt}$

Δt can be related to the frequency of particle collisions, f, with the wall.

$$f = \frac{C_{1i}}{2\ell} \Rightarrow \Delta t = \frac{1}{f} = \frac{2\ell}{C_{1i}}$$

$$F_i = \frac{2mc_{1i}}{\frac{2\ell}{c_{1i}}} = \frac{mc_{1i}^2}{\ell}$$

$$F_1 = \sum F_i = \frac{m}{\ell}\sum_{i=1}^{N} c_{1i}^2$$

$$P_1 = \frac{F_1}{\ell^2} = \frac{m}{\ell^3}\sum_{i=1}^{N} c_{1i}^2$$

(Pressure)

So for our three surfaces:

$$P_1 = \frac{m}{\ell^3}\sum_{i=1}^{N} c_{1i}^2 \; ; \quad P_2 = \frac{m}{\ell^3}\sum_{i=1}^{N} c_{2i}^2 \; ; \quad P_3 = \frac{m}{\ell^3}\sum_{i=1}^{N} c_{3i}^2$$

The total pressure in our chamber can be found by taking the average of our 3 directional pressures.

$$P = \frac{P_1 + P_2 + P_3}{3} = \frac{m}{\ell^3}\frac{1}{3}\cdot\sum_{i=1}^{N}\underbrace{c_{1i}^2 + c_{2i}^2 + c_{3i}^2}_{c_i^2}$$

$$P = \frac{m}{\ell^3}\frac{1}{3}\sum_{i=1}^{N} c_i^2$$

From statistical thermodynamics, we know that:

$$\underbrace{\frac{1}{2}m\overline{c^2}}_{\text{average molecule KE.}} = \underbrace{\frac{3}{2}k_B T}_{\frac{1}{2}k_B T \text{ for every translational degree of freedom}}$$

We also know that: $m = \frac{M}{A}$ $\left[\frac{kg}{molecule}\right]$

$$\frac{1}{2}m\overline{c^2} = \frac{3}{2}k_B T = \frac{1}{2}\frac{M}{A}\overline{c^2}$$

$$M\overline{c^2} = 3k_B A T \Rightarrow \text{we know that } k_B A = R$$

$$\boxed{M\overline{c^2} = 3RT} \quad (1)$$

Another more rigorous way to prove:

$$F_1 = \frac{m}{\ell}\sum_{i=1}^{N} c_{1i}^2$$

$$= \frac{M}{A\ell}\sum_{i=1}^{N} c_{1i}^2$$

$$= \frac{MN_{mol}}{\ell}\underbrace{\frac{\sum_{i=1}^{N} c_{1i}^2}{N}}_{\overline{c_1^2}}$$

$F_1 = \frac{MN_{mol}}{\ell}\overline{c_1^2}$, we know that

Due to random motion: $\overline{c_1^2} = \frac{1}{3}\overline{c^2}$

Looking back at our pressure term

$$P = \frac{m}{\ell^3} \cdot \frac{\sum c_i^2}{3}$$

$$= \frac{M}{A\ell^3} \cdot \frac{\sum c_i^2}{3} \Rightarrow A = \frac{N}{N_{mol}} \left[\frac{\#\,molecules}{\#\,kmol}\right]$$

$$= \frac{N_{mol} M}{N\ell^3} \frac{\sum c_i^2}{3} \Rightarrow \text{Since } \frac{\sum c_i^2}{N} = \overline{c^2} \text{ (average molecule speed)}$$

$$= \underbrace{\frac{N_{mol} M}{\ell^3}}_{\rho} \cdot \frac{1}{3}\overline{c^2} = \frac{1}{3}\rho\overline{c^2}$$

$$\Rightarrow \boxed{P = \frac{1}{3}\rho\overline{c^2}} \quad (2)$$

Now we can equate (1) and (2) & isolate for $\overline{c^2}$

$$\overline{c^2} = \frac{3P}{\rho} = \frac{3RT}{M}$$

$$P = \frac{\rho}{M} RT \text{, note } \rho \Rightarrow \left[\frac{kg}{m^3}\right]; \; M \Rightarrow \left[\frac{kg}{kmol}\right]$$

$\boxed{P = \rho_m RT}$ $\Rightarrow$ Ideal Gas Law $\Rightarrow$ ρ_m = molecular density $\left[\frac{kmol}{m^3}\right]$

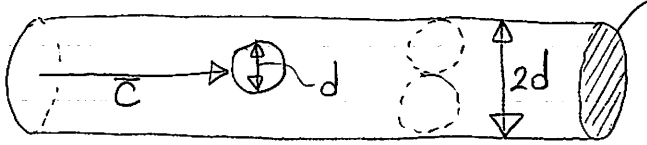
R = universal gas const.

P = pressure.

or

$\boxed{PV = N_{mol} RT}$

Now if we look at the microscopic picture of the molecule



2d is chosen due to the size of the molecule and the fact that it can interact with other molecules nearby.

We could have chosen 3d, however there is a chance that the molecule doesn't interact at all then with molecules within the swept path.

$$\frac{\text{Swept Volume}}{\text{time}} = \pi d^2 \cdot c$$

$$\frac{\#\text{collisions}}{\text{time}} = \pi d^2 n \cdot c \quad , \quad n \Rightarrow \left[\frac{\#\text{molecules}}{\text{volume}}\right]$$

$$\lambda = \text{mean free path} = \frac{\text{distance traveled/time}}{\#\text{collisions/time}}$$

$$\lambda = \frac{\ell}{\pi d^2 n \ell} = \frac{1}{\pi d^2 n}$$

$$\boxed{\lambda = \frac{1}{\pi d^2 n}} \Rightarrow \text{Mean free path}$$

We can work with this a bit further to get it into a more usefull form: (using our ideal gas law)

$$PV = N_{mol} RT \Rightarrow A = \frac{N}{N_{mol}} \Rightarrow N_{mol} = \frac{N}{A}$$

$$PV = \frac{N}{A} RT = \underbrace{\left(\frac{R}{A}\right)}_{k_B} NT$$

$$PV = k_B N T$$

$$\frac{N}{V} = n = \frac{P}{k_B T} \Rightarrow \text{Back substituting}$$

$$\boxed{\lambda = \frac{k_B T}{\pi d^2 P}}$$

If we look at our overall statistical distribution

$$\boxed{\lambda = \frac{k_B T}{\sqrt{2}\pi d^2 P}} \Rightarrow \text{As } T \uparrow, \lambda \uparrow$$
$$P \downarrow, \lambda \uparrow$$

$\sqrt{2}$ comes from molecules having a velocity relative to one another.

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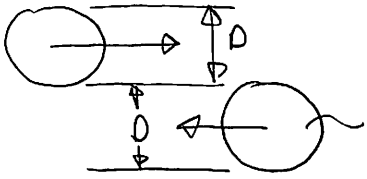
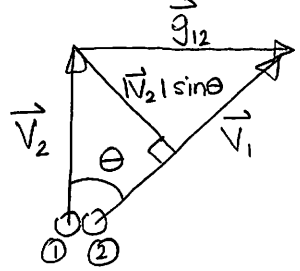
Extra Derivation (Where the $\sqrt{2}$ in λ comes from)



This molecule is not stationary, it will have a speed as well.

We need to know the mean relative speed between molecules: (consider two arbitrary molecules)



$$|g_{12}| = \left[|V_2|^2 \sin^2\theta + \left(|V_1| - |V_2|\cos\theta\right)^2\right]^{1/2}$$

Rearranging, we obtain

$$|g_{12}|^2 = |V_2|^2 + |V_1|^2 - 2|V_1||V_2|\cos\theta$$

Taking $\bar{g}$ to be the root mean square value of $|g_{12}|$, we have

$$\bar{g} = \langle |g_{12}|^2 \rangle^{1/2} = \langle |V_2|^2 + |V_1|^2 - 2|V_1||V_2|\cos\theta \rangle^{1/2}$$

In our model, we assumed $|V_1| = |V_2| = c$

$$\bar{g} = \langle |g_{12}|^2 \rangle^{1/2} = \langle c^2 + c^2 - 2c^2\cos\theta \rangle^{1/2} = 2c^2\left(1 - \langle\cos\theta\rangle\right)^{1/2}$$

If we average from $\theta = 0$ to $\theta = 2\pi$ $\Rightarrow$ $\langle\cos\theta\rangle = \frac{1}{2\pi}\int_0^{2\pi}\cos\theta\, d\theta$

$= \frac{1}{2\pi}\sin\theta\Big|_0^{2\pi} = 0$

$$\therefore \boxed{\bar{g} = \left(2c^2\right)^{1/2} = \sqrt{2}\,c} \Rightarrow \text{Use this in \# of collisions/time equation.}$$

FIVE STAR ★★★★★

Example #1 If we look at air at 273K

$M = 28.9\ kg/kmol$
$\rho_{air} = 1.288\ kg/m^3$
$\rho_{liquid,air} = 0.86 \times 10^3\ kg/m^3$
$A = 6.022 \times 10^{26}\ molecules/kmol$
$R = 8314.3\ J/kmol \cdot K$
$k_B = 1.38 \times 10^{-23}\ J/K$

First we can calculate the mass per molecule (m)

$$m = \frac{M}{A} = 4.8 \times 10^{-26}\ kg/molecule$$

$$n = \frac{\rho}{m} = 2.684 \times 10^{25}\ molecules/m^3$$

$$P = 1.01325 \times 10^5\ N/m^2 \Rightarrow$$

Aside:

$$\overline{c^2} = \frac{3P}{\rho} = \frac{3(101325\ Pa)}{(1.288\ kg/m^3)}$$

$$\overline{c} \approx \sqrt{\overline{c^2}} \doteq 486\ m/s$$

$$\approx 1750\ km/hr$$

⇓

2.5x faster than a commercial jet plane.

How do we feel this: With static pressure

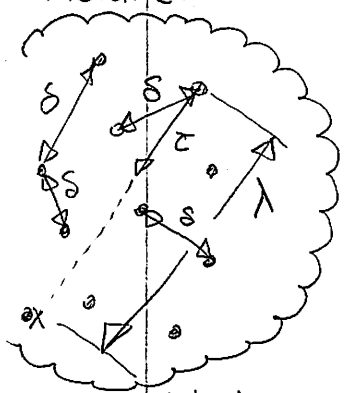
$P_s = \frac{1}{2}\rho_{Air}\overline{c^2} \approx 100\ kPa$ Works!

Assuming that the volume of the air molecule can be approximated as d^3

$$\frac{1}{d^3} = n_{liq} = \frac{\rho_{liq}}{m}$$

$$d = \left(\frac{m}{\rho_{liq}}\right)^{1/3} = 3.83 \times 10^{-10}\ m$$

Picture:



$$\lambda = \frac{1}{\sqrt{2}\,\pi d^2 n} = 5.717 \times 10^{-8}\ m = \boxed{57.2\ nm = \lambda}$$

Distance between collision

$$\delta = \frac{1}{n^{1/3}} = 3.35 \times 10^{-9}\ m = \boxed{3.35\ nm}$$ (molecular spacing) Not same as λ.

Note, we showed earlier that $T = \frac{M\overline{c}^2}{3k_B A}$, so why doesn't your temperature increase when youre flying in a plane?

Aside: Comes from the classic Boltzmann dist.

$f(E) = \frac{1}{Ae^{E/k_BT}}$ = prob. that a particle has energy E.

↳ Constant

$S = k_B \ln W$

Maxwellian Velocity Distribution

$$\phi(c_i) = \frac{1}{\sqrt{\pi}} \left(\frac{m}{2k_BT}\right)^{1/2} e^{-\left(\frac{mc_i^2}{2k_BT}\right)}$$

$0 < \phi(c_i) < 1$

↳ probability of a particle or molecule having a velocity c going in the i'th direction. (1D)

Like any other distribution:

$$\int_{-\infty}^{\infty} \phi(c_1)\,dc_1 = \int_{-\infty}^{\infty} \phi(c_2)\,dc_2 = \int_{-\infty}^{\infty} \phi(c_3)\,dc_3 = 1$$

We know that:

$$\frac{2}{\sqrt{\pi}} \int_0^x e^{-x^2} dx = erf(x), \quad erf(\infty) = 1, \quad erf(0) = 0$$

$$\int_0^{\infty} e^{-c^2} dc = \frac{\sqrt{\pi}}{2}$$

Now let's take a closer look:

$$\frac{1}{\sqrt{\pi}} \int_{-\infty}^{\infty} \left(\frac{m}{2k_BT}\right)^{1/2} e^{-\left(\frac{mc_1^2}{2k_BT}\right)} dc_1 \Rightarrow$$

Let $c\left(\frac{m}{2k_BT}\right)^{1/2} = \hat{c}$

$dc = \frac{1}{\left(\frac{m}{2k_BT}\right)^{1/2}} d\hat{c}$

$$\frac{1}{\sqrt{\pi}} \int_{-\infty}^{\infty} e^{-\hat{c}_1^2} d\hat{c}_1 = \frac{2}{\sqrt{\pi}} \int_0^{\infty} e^{-\hat{c}_1^2} d\hat{c}_1 = 1$$

$\int_0^{\infty} e^{-\hat{c}_1^2} d\hat{c}_1 = \frac{\sqrt{\pi}}{2}$

↳ Multiplied by 2 changed lower bound to 0 since distribution is symmetric and centered about 0.

$= I_0$

Now if we look at higher power integrals:

$$I_m = \int_0^{\infty} c^n e^{-c^2} dc = \int_0^{\infty} \underbrace{c^{n-1}}_{u} \cdot \underbrace{c e^{-c^2} dc}_{dv}$$

Using integration by parts $\int u\,dv = uv - \int v\,du$

$$\int dV = \int c e^{-c^2} dc \Rightarrow \text{Let } u = c^2 \Rightarrow du = 2c\,dc \Rightarrow \int \not{c} e^{-u} \frac{du}{2\not{c}} = \frac{1}{2}\int e^{-u} du$$

$$\therefore V = -\frac{1}{2} e^{-c^2}$$

$$\frac{dV}{dc} = -\frac{1}{2}(-2c) e^{-c^2} = c e^{-c^2} \Rightarrow dV = c e^{-c^2} dc \Rightarrow \text{WORKS!}$$

$$u = c^{n-1}$$

$$du = (n-1) c^{n-2} dc$$

Back substituting

$$\int u\,dv = uv - \int v\,du = (c^{n-1})\left(-\frac{1}{2} e^{-c^2}\right)\Big|_0^\infty - \int_0^\infty -\frac{1}{2} e^{-c^2} (n-1) c^{n-2} dc$$

$$I_m = -\frac{c^{n-1}}{2} e^{-c^2}\Big|_0^\infty + \frac{(n-1)}{2}\int_0^\infty c^{n-2} e^{-c^2} dc$$

Need to use l'Hopital's rule $(\infty)\cdot(0)$

Can prove to yourself that $\to 0$

$$\boxed{I_m = \frac{n-1}{2}\int_0^\infty c^{n-2} e^{-c^2} dc = \frac{n-1}{2} I_{n-2}}$$

↳ Recursive Solution

Example: $I_2 = \frac{2-1}{2} I_{2-2} = \frac{1}{2} I_0$

$= \frac{1}{2}\frac{\sqrt{\pi}}{2} = \frac{\sqrt{\pi}}{4}$

Now we can have some fun:

$I_0 = \frac{\sqrt{\pi}}{2}$ $\quad I_1 = \frac{1}{2}$

$I_2 = \frac{\sqrt{\pi}}{4}$ $\quad I_3 = \frac{1}{2}$

$I_4 = \frac{3}{8}\sqrt{\pi}$ $\quad I_5 = 1$

$I_6 = \frac{15}{16}\sqrt{\pi}$ $\quad \ldots$

Note, we haven't solved for I_1, however need to solve it to get I_3, I_5, I_7, etc... To solve for I_1, let $u = c^2$ & integrate. Try it

END ~~OF~~ LECTURE 2

Now we can look at each directional component of velocity

$$\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \phi(c_1)\,\phi(c_2)\,\phi(c_3)\,dc_1\,dc_2\,dc_3 = 1$$

This is true since the probability for three independent events is the product of the three individual probabilities.