Kinetic Theory of Gases

Let's apply Boltzmann statistic ideas to gases + see where it leads.

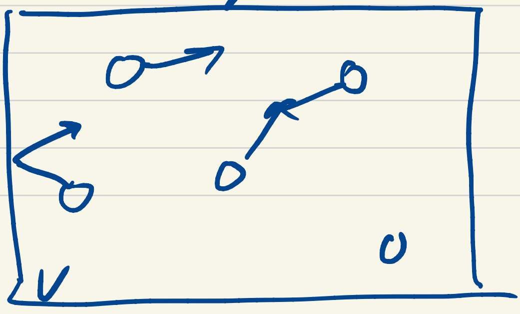
Postulates

1. gas consists of particles of mass m, diameter d

2. aggregate size of particles much less than container

$$N d^3 \ll V$$

3. molecules interact w/ each other and container only by perfectly elastic collisions



We know physics: $F = ma$, $p = mv$

$KE = \frac{1}{2}mv^2$

We know Boltzmann:

$$P(v_x) \propto e^{-\frac{1}{2}mv_x^2/k_BT}$$

What can we learn by combining, that a ChemE might care about?

thermo $\begin{cases} \text{EOS} \\ \text{heat capacity} \end{cases}$

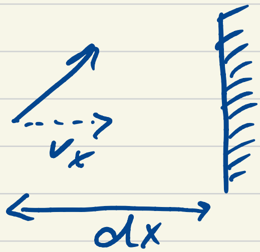
kinetics $\{$ collisions

How many are hitting a wall in unit time?

Particles with

$v_x dt > dx$

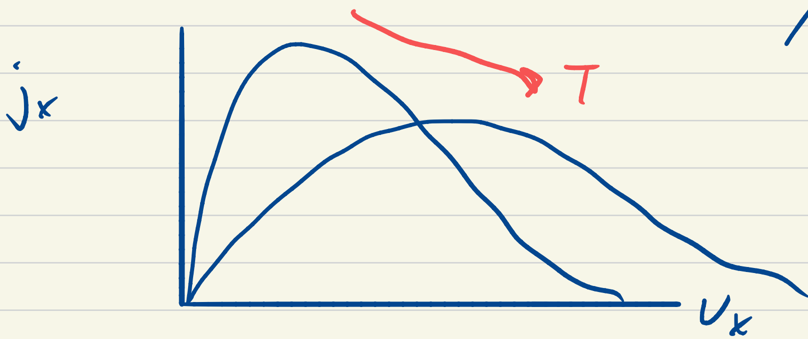
will hit the wall



velocity $\perp$ wall

Number to have v_x + be within striking distance?

$$j_x(v_x)\,dt = \underbrace{v_x P(v_x) \cdot \left(\cancelto{N/V}{\frac{N}{\text{area}\cdot\text{dist}}}\right)}_{\#/\text{area}\cdot\text{velocity}\cdot\text{time}} dt$$



$$J_w = \int_0^\infty v_x P(v_x)\left(\frac{N}{V}\right) dv_x$$

$$= \frac{N}{V}\frac{1}{\sqrt{2\pi}}\left(\frac{k_B T}{M}\right)^{1/2} = \frac{1}{4}\frac{N}{V}\langle v\rangle$$

wall collision frequency

ex N_2 @ 298 K $\quad 4\times10^{-5}$ mol/cm^3

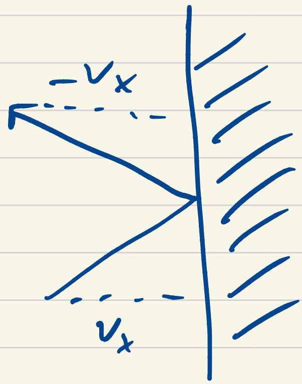
(typical of air)

$$\frac{\#\ \text{collisions}}{\text{area}\cdot\text{time}} = \frac{1}{4}\cdot(4\times10^{-5})\left(47500\ \frac{\text{cm}}{\text{s}}\right)$$

$$= 0.48\ \frac{\text{mol}}{\text{cm}^2\cdot\text{s}}\quad !!$$

$\Delta p = 2mv_x$

change in momentum



sum effect of all those changes

$\langle \Delta p\rangle$ / area · time

$$\int_0^\infty \Delta p(v_x)\, j_x(v_x)\, dv_x = 2m\int_0^\infty v_x\, j_x(v_x)\, dv_x$$

$$= 2m\left(\frac{N}{V}\right)\int_0^\infty v_x^2\, P(v_x)\, dv_x$$

$$= 2m\left(\frac{N}{V}\right)\langle v_x^2\rangle = 2m\left(\frac{N}{V}\right)\cdot\frac{1}{2}\frac{k_BT}{m}$$

$$\langle \Delta p\rangle = \frac{N}{V}\cdot k_BT$$

$$\frac{\langle \Delta p \rangle}{\text{area} \cdot \text{time}} = \text{Pressure} = \frac{N}{V} \cdot kT$$

$$PV = nRT$$

Ideal gas law consequence of model assumptions + Boltzmann

Consistent w/ observation

Physics works!

Might care about ... heat capacity

All internal energy is kinetic here

$$C_v = \left(\frac{\partial U}{\partial T}\right)_v \qquad U = \langle KE \rangle$$

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

$$= \frac{1}{2} m \left\{ \langle v_x^2 \rangle + \langle v_y^2 \rangle + \langle v_z^2 \rangle \right\}$$

$$= \frac{1}{2} m \cdot 3 \cdot \frac{k_B T}{m}$$

$$= \frac{3}{2} k_B T$$

$$C_v = \frac{3}{2} k_B = \frac{3}{2} R$$

Very good estimate for a gas that fits our model.

Have already shown velocity in any direction follows

$$P(v_x)\,dv_x = \left(\frac{m}{2\pi kT}\right)^{1/2} e^{-\frac{1}{2}m|v_x|^2/kT}\,dv_x$$

$$\sigma = \left(\frac{k_B T}{m}\right)^{1/2}$$

In 3-dimensions, would be

$$P(v_x, v_y, v_z) = P(v_x)P(v_y)P(v_z)$$

seperable

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

$$v^2 = v_x^2 + v_y^2 + v_z^2$$

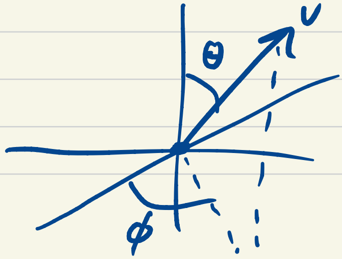
Translate to spherical coordinates:

$$(v_x, v_y, v_z) \longrightarrow (v, \theta, \phi)$$

$0 < v < \infty$

$0 < \theta < \pi$

$0 < \phi < 2\pi$



$$P(v,\theta,\phi) = (\quad)^{3/2} e^{-\frac{1}{2}mv^2/kT}$$

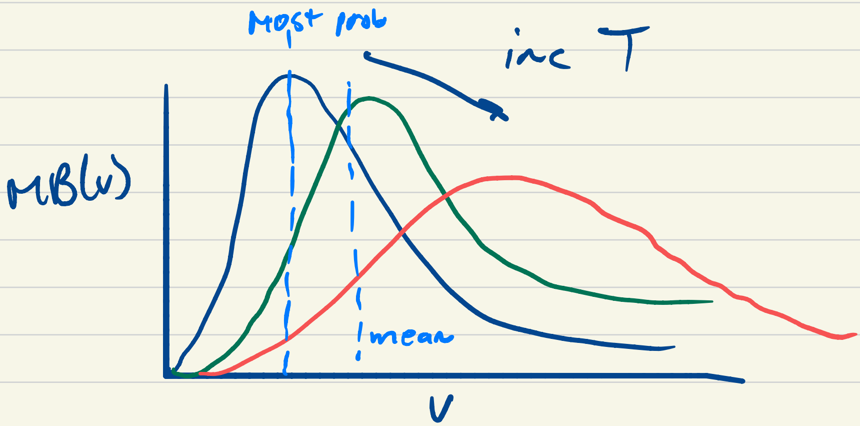
Integrate out angle parts:

$$P(v) = \int_0^{2\pi}\int_0^{\pi} P(v,\theta,\phi)\, v^2 \sin\theta \, d\theta \, d\phi$$

...

$$P_{MB}(v) = 4\pi v^2 \left(\frac{m}{2\pi kT}\right)^{3/2} e^{-\frac{1}{2}m|v|^2/kT}$$

Maxwell-Boltzmann speed distribution



$$v_{M\text{-}p} = \left(\frac{2k_BT}{m}\right)^{1/2} \quad \uparrow T^{1/2} \quad \downarrow m^{1/2}$$

$$\langle v\rangle = \int_0^{\infty} v\, P_{MB}(v)\, dv = \left(\frac{8kT}{m\pi}\right)^{1/2}$$

$$\langle v^2\rangle^{1/2} = v_{rms} = \quad = \left(\frac{3kT}{m}\right)^{1/2}$$

Can work backwards from this to Boltzmann convenient

ex N_2 @ 298 K $\qquad \frac{k_B T}{m} = \frac{RT}{MW}$

$m = 28 \times 10^{-3}$ kg

$v_{mp} = 420$ m/s $= 940$ mph!

$\langle v \rangle = 475$ m/s

$v_{rms} = 516$ m/s $= \langle v^2 \rangle^{1/2}$

How much translational kinetic energy in a gas?

$$\langle \varepsilon \rangle = \langle \tfrac{1}{2} m v^2 \rangle = \tfrac{1}{2} m \langle v^2 \rangle$$

$$= \tfrac{1}{2} m \cdot \left(\frac{3kT}{m} \right)$$

$$= \tfrac{3}{2} kT \text{ /molecules}$$

$$= \tfrac{3}{2} RT \text{ / mole}$$

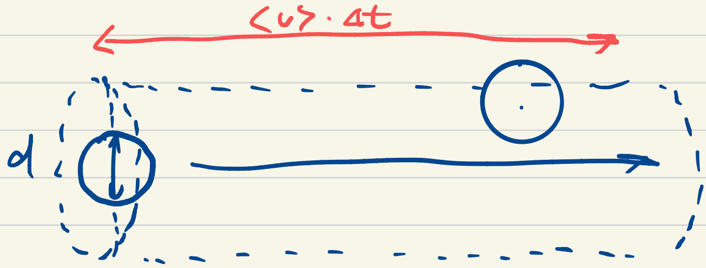
Internal energy under our model

$$U = \tfrac{3}{2} RT \qquad \left(\frac{\partial U}{\partial T} \right)_v = \tfrac{3}{2} R$$

very good estimate for monatomic gas

Kinetics

Collisions between molecules



$\sigma = \pi d^2$ "collision cross section"

Sweeps out cylinder of volume $V/t = \sigma \langle v\rangle$

$$Z = \frac{\#\ \text{collisions}}{\text{time}} = \frac{N}{V}\langle v\rangle \cdot \sigma \cdot \sqrt{2}$$

accounts for mutual motion

Ex How many collisions does an N_2 molecule make @ 298 K + 1 bar?

$\sigma_{N_2} \sim 0.43\ nm^2$

$$Z = \sqrt{2}\underbrace{\left(\frac{P}{RT}\right)}_{4\times10^{-5}\ mol/cm^3}\underbrace{\left(\frac{8kT}{\pi m}\right)^{1/2}}_{475\ m/s} \cdot \sigma = 7\times10^{9}/s$$

Ouch!

Total collisions / volume / time?

$$Z_{AA} = Z \cdot \left(\frac{N}{V}\right) \frac{1}{2}$$ ← to avoid double counts

$\frac{coll}{mol} \cdot \frac{mol}{vol}$

(origin of $\sqrt{2}$ above?)

N_2 again, 298 K, 1 bar

$$Z_{AA} = Z\left(\frac{p}{RT}\right) \cdot \frac{1}{2}$$

$$= 8 \times 10^{28} \text{ collisions}/\text{cm}^3 \cdot \text{s}$$

Wow! In principle an upper bound on how fast reactions can happen.

mean free path? – distance between collisions

$$\lambda = \frac{\langle v \rangle}{Z}$$

$\frac{dist/time}{coll/time}$

$$= \frac{1}{\sqrt{2}\sigma} \cdot \left(\frac{V}{N}\right) = \frac{1}{\sqrt{2}\sigma}\left(\frac{RT}{p}\right)$$

only depends on size + density

N_2, 298K, 1 bar $\lambda = 68 \text{ nm} = 680$ Å

$$d = \left(\frac{\sigma}{\pi}\right)^{1/2} = 0.37 \text{ nm}$$

$\lambda/d \sim 180$ molecular diameters between collisions