Lecture 2

Tuesday, September 12, 2023 11:30

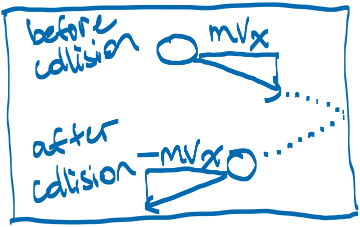
Topic 1B The Kinetic Model

- kinetic theory of gases or kinetic-molecular theory (KMT)

Three assumptions:

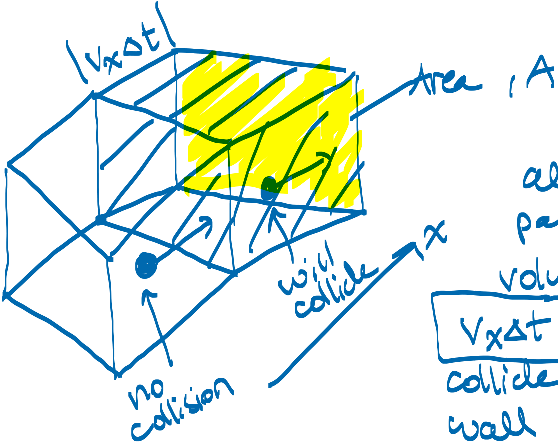
1. The gas consists of molecules of mass m in random motion; obey the laws of classical mechanics
2. The size of the molecules is negligible, i.e. diameter is much smaller than the average distance travelled between collisions; "point-like"
3. The molecules interact only through brief elastic collisions (i.e. the total translational kinetic energy is conserved)

- derive an expression that relates p, V to the mean speed.



total momentum change: $\boxed{2mv_x}$

y- and z- components are unchanged



all the particles in volume $\boxed{v_x \Delta t \cdot A}$ will collide with the wall (if they are travelling toward it)

$\mathcal{N}$: number density

number of molecules that are in this volume: $\boxed{\mathcal{N} v_x \Delta t \cdot A}$

$\mathcal{N} = \frac{n N_A}{V}$, n : total amount of molecules in volume

V

N_A : Avogadro's constant

$$\boxed{\frac{nN_A}{V} v_x \Delta t \cdot A}$$

number of molecules in volume V

↓ consider direction

average number of collisions

$$\frac{1}{2}\frac{nN_A}{V} v_x \Delta t \cdot A$$

Total change in momentum:

$$\frac{nN_A A v_x \Delta t}{2V} \cdot 2mv_x$$

$$= \frac{n\overbrace{mN_A}^{M} A v_x^2 \Delta t}{V}$$

$$= \boxed{\frac{nMAv_x^2 \Delta t}{V}}$$

total change in momentum for particles in volume V

$$\vec{F} = \frac{d\vec{p}}{dt}$$

Calculate the force (rate of change of momentum):

$$\frac{nMAv_x^2\,\Delta t}{V} \cdot \frac{1}{\Delta t} = \overset{\vec{F}}{\boxed{\frac{nMAv_x^2}{V}}}$$

Calculate the pressure (force over area):

$$\frac{nMAv_x^2}{V} \cdot \frac{1}{A} = \boxed{\frac{nMv_x^2}{V} = p}$$

$$\boxed{p = \frac{nM\langle v_x^2\rangle}{V}}$$ ← average or expected value of v_x^2

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

in a symmetric system, $\langle v_x^2 \rangle =$

$$\langle v_y^2\rangle = \langle v_z^2\rangle$$

$$\therefore \langle v_x^2\rangle = \frac{1}{3}\langle v^2\rangle$$

root-mean-square speed, v_{rms}

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

$$\boxed{pV = \frac{1}{3} n M v_{rms}^2}$$

relation between pressure and volume (KMT)

$$pV = nRT$$

The Maxwell-Boltzmann Distribution

$f(v)$: distribution of speeds

Boltzmann distribution:

$$f(v) = K e^{-\varepsilon/k_BT}$$

ε : kinetic energy

$$\varepsilon = \boxed{\frac{1}{2} m v_x^2 + \frac{1}{2} m v_y^2 + \frac{1}{2} m v_z^2}$$

$$a^{x+y+z} = a^x a^y a^z$$

$$f(v) = K e^{-(m v_x^2 + m v_y^2 + m v_z^2)/2k_B T}$$

$$= K e^{-m v_x^2/2k_B T} e^{-m v_y^2/2k_B T} e^{-m v_z^2/2k_B T}$$

$$f(v) = K_x e^{-m v_x^2/2k_B T} \leftarrow f(v_x)$$

$$\cdot K_y e^{-m v_y^2/2k_B T} \leftarrow f(v_y)$$

$$\cdot K_z e^{-m v_z^2/2k_B T} \leftarrow f(v_z)$$

$$f(v) = f(v_x) f(v_y) f(v_z)$$

$$K = K_x K_y K_z$$

$$\boxed{f(v_x) = K_x e^{-m v_x^2/2k_B T}}$$

distribution of speeds along the x direction

first, evaluate K_x

$$\int_{-\infty}^{\infty} f(v_x)\, dv_x = 1$$

$$1 = K_x \int_{-\infty}^{\infty} \overbrace{e^{-mv_x^2/2k_BT}}^{\text{Gaussian function}} dv_x$$

$$1 = K_x \left(\frac{2\pi k_BT}{m}\right)^{\frac{1}{2}}$$

$$K_x = \left(\frac{m}{2\pi k_BT}\right)^{\frac{1}{2}}$$

$$f(v_x) = \left(\frac{m}{2\pi k_BT}\right)^{\frac{1}{2}} \boxed{e^{-mv_x^2/2k_BT}}$$

Combine $f(v_x)$, $f(v_y)$, $f(v_z)$:

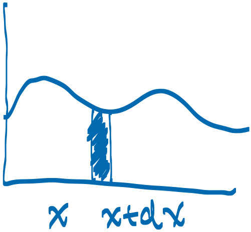
$f(v_x)\, f(v_y)\, f(v_z)\, dv_x\, dv_y\, dv_z$

v_x to $v_x + dv_x$

v_y to $v_y + dv_y$

v_z to $v_z + dv_z$

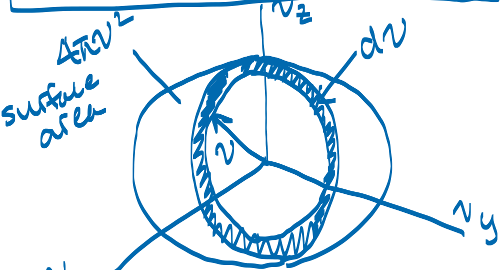
(probability that a molecule has a velocity in this range)



$$\left(\frac{m}{2\pi k_B T}\right)^{3/2} e^{-mv_x^2/2k_BT}\, e^{-mv_y^2/2k_BT}\, e^{-mv_z^2/2k_BT}$$

$$= \left(\frac{m}{2\pi k_B T}\right)^{3/2} e^{-m(v_x^2+v_y^2+v_z^2)/2k_BT}$$

$$= \boxed{\left(\frac{m}{2\pi k_B T}\right)^{3/2} e^{-mv^2/2k_BT}}\, dv_x\, dv_y\, dv_z$$



v_x

shell of radius $v = (v_x^2 + v_y^2 + v_z^2)^{\frac{1}{2}}$ and thickness dv

$$4\pi v^2 \, dv$$

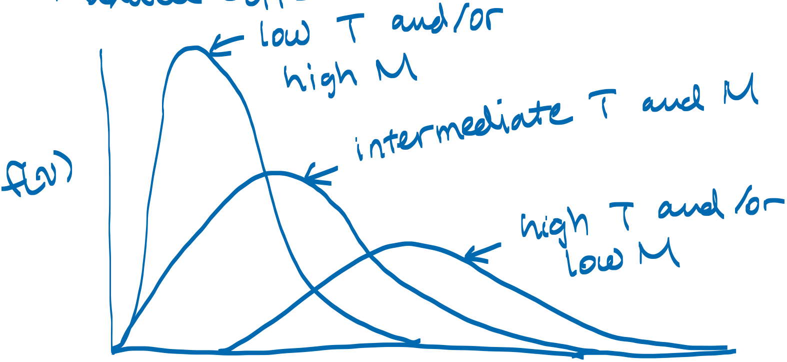
$$f(v)\,dv = \left(\frac{m}{2\pi k_B T}\right)^{3/2} e^{-mv^2/2k_BT} \, 4\pi v^2 dv$$

$$f(v) = 4\pi \left(\frac{m}{2\pi k_B T}\right)^{3/2} v^2 e^{-mv^2/2k_BT}$$

$$R = N_A k_B$$

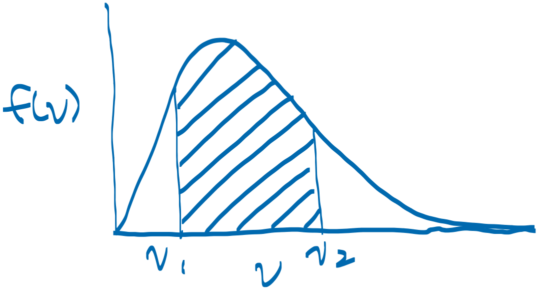
$$\boxed{f(v) = 4\pi \left(\frac{M}{2\pi RT}\right)^{3/2} \enclose{circle}{v^2} \, e^{-Mv^2/2RT}}$$

Maxwell-Boltzmann distribution (KMT)

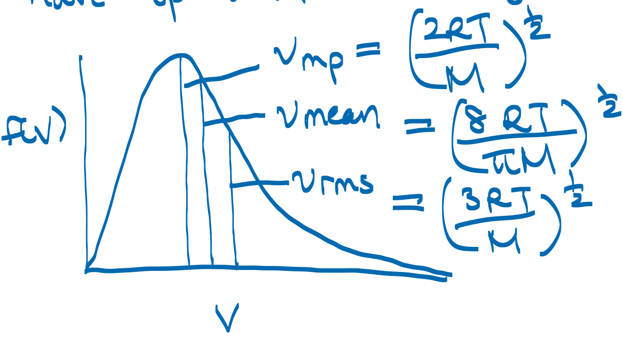


v

- factor v^2: goes to 0 as v goes to 0; fraction of molecules with very low speeds will be very small, regardless of their mass



area: probability that a molecule will have speed in the range v_1 to v_2



$$v_{mp} = \left(\frac{2RT}{M}\right)^{\frac{1}{2}}$$

$$v_{mean} = \left(\frac{8RT}{\pi M}\right)^{\frac{1}{2}}$$

$$v_{rms} = \left(\frac{3RT}{M}\right)^{\frac{1}{2}}$$

$$v_{mean} = \left(\frac{8RT}{\pi M}\right)^{\frac{1}{2}} = \left(\frac{8}{3\pi}\right)^{\frac{1}{2}} v_{rms}$$