Today's topics:

- elementary kinetic theory of gases

  derive connection between temp. T of ideal gas law $PV = NkT$ and average kinetic energy of molecules in gas, $\langle \frac{1}{2} m v^2 \rangle$

- apply kinetic theory to effusion

- equipartition theorem and experiments

Reading: finish Chapter 1
only read pages 1–33
skip enthalpy
skip §1.7

1/25/11 (2)

Section 1.2 of Schroeder

Use ideal gas law to understand meaning of T: average kinetic energy of molecules

empirical discovery spanning 18^{th} + 19^{th} centuries

$PV = NkT$ (k: Boltzmann constant; N: # molecules) or $PV = nRT$ (n: # moles; R: gas constant $\approx 8.3 \frac{J}{mole \cdot K}$)

P = pressure pascals or $\frac{N}{m^2}$ — 1 atm $\approx 10^5$ pascals

V = volume of gas m^3 — 1 liter $= 10^{-3} m^3$

N = # molecules

k = Boltzmann constant $\approx 1.4 \cdot 10^{-23} \frac{J}{K}$] memorize!

note: power of ten easy to remember, reciprocal of Avogadro's constant

T = temp in kelvin

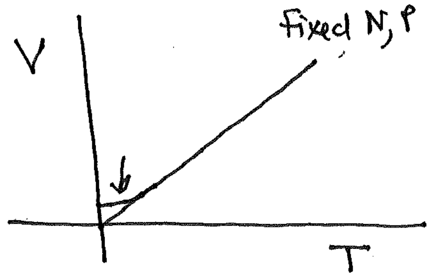
at STP: $N \sim 6 \cdot 10^{23}$ molecules $T \approx 300\,K$ (273 + 20)

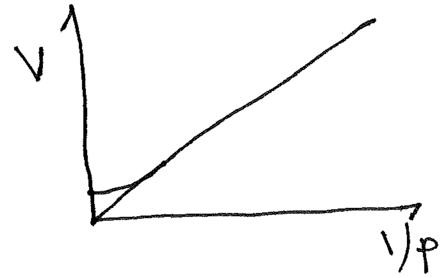
$V \sim 20$ liters $= 2 \cdot 10^{-2} m^3$

≈ 1 cubic foot

Quick class discussion:

examples of when $PV = NkT$ is wrong?





one criterion for ideal behavior:

$$\lambda_{\text{de Broglie}} \ll \left(\frac{V}{N}\right)^{1/3}$$

$$\frac{h}{\sqrt{2\pi m kT}} \ll \left(\frac{V}{N}\right)^{1/3} = \left(\frac{kT}{P}\right)^{1/3}$$

always satisfied for: high T, ~~big N~~, big V

no phase transitions with $PV = NkT$!

Simple Kinetic Theory

Given: $PV = NkT$

what does T mean?

Use Daniel Bernoulli's insight and calculation of 1738 (!)

assume gas made of particles in constant motion

collisions with wall cause pressure

what is pressure? $P = \frac{F}{A}$ $\quad \frac{N}{m^2}$

what is force?

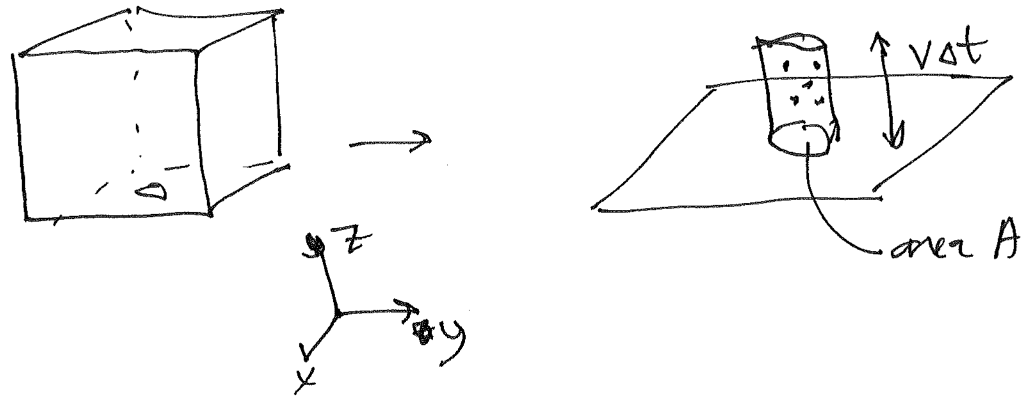
$$F = ma = m\frac{dv}{dt} = \frac{d(mv)}{dt} = \frac{dp}{dt}$$

$$\simeq \frac{\Delta p}{\Delta t} = \frac{\text{total change in momentum}}{\text{short change in time}}$$

strategy: count how many particles collide with small area on wall in short time Δt

multiply that number by change in momentum per particle

Anisotropic Kinetic Theory
Simplest version



assumptions:

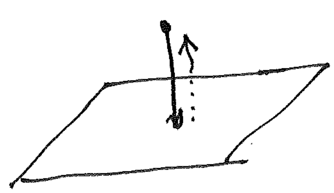
(1) all particles identical with mass m

(2) all particles move with same speed v

(3) 1/6 of particles move along coordinate axis direction $\pm x, \pm y, \pm z$

this is why motion is anisotropic, some directions are special

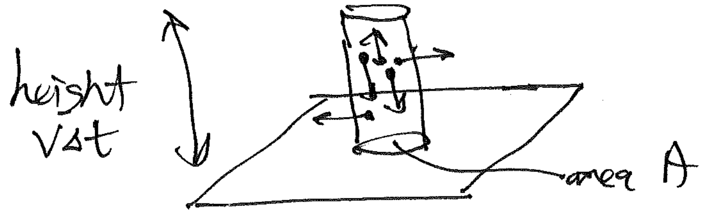
(4) assume particles "reflect" off walls by perfectly elastic collisions, walls perfectly smooth



$$\Delta p = mv - (-mv)$$
$$= 2mv$$

per particle

Anisotropic Kinetic Theory Cont'd



Give different argument than Schroeder on pages 10–12

my approach has several advantages:

- don't need to know size or shape of container
- can generalize to isotropic velocities
- clarifies role of mean free path

assume short time Δt. will discuss that "short" means

$$\Delta t \lesssim \frac{\bar{\ell}}{v}$$

$\bar{\ell}$ = mean free path

$d_{N_2} \simeq 0.4\,\text{nm} < \underbrace{\left(\frac{V}{N}\right)^{1/3}}_{\sim 4\,\text{nm}} < \overbrace{\bar{\ell}}^{\simeq 300\,\text{nm}} < \underbrace{V^{1/3}}_{\simeq 1\,\text{m}}$

how many molecules will hit area A on wall in this time?

only particles closer than $v\Delta t$ to wall

$$\Delta N = \text{"volume of cylinder"} \times \left(\frac{\text{number of molecules}}{\text{volume}}\right) \times \text{fraction moving toward wall}$$

$$= \underbrace{(v\Delta t)\,A}_{\Delta V} \times \frac{N}{V} \times \frac{1}{6}$$

Each of ΔN molecules transfer same amount of momentum to wall: $2mv$

total change in momentum in time Δt is then

$$\Delta P_{total} = \Delta N \cdot 2mv$$

$$= \underbrace{[(v\Delta t)A] \cdot \frac{N}{V} \cdot \frac{1}{6}}_{\Delta N} \cdot \underbrace{2mv}_{\text{momentum transfer to wall per particle}}$$

pressure due to collisions is therefore

$$\boxed{P = \frac{F}{A} \cong \frac{1}{A} \frac{\Delta P_{total}}{\Delta t} = \frac{1}{3} mv^2 \cdot \frac{N}{V}}$$

But $PV = NkT$. Conclude

$$\frac{1}{3} mv^2 = kT$$

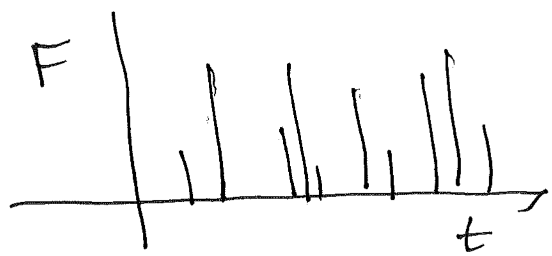
or $$\boxed{\frac{1}{2} mv^2 = \frac{3}{2} kT}$$

we assumed all molecules move at same speed, real gases have spread of speeds. guess that

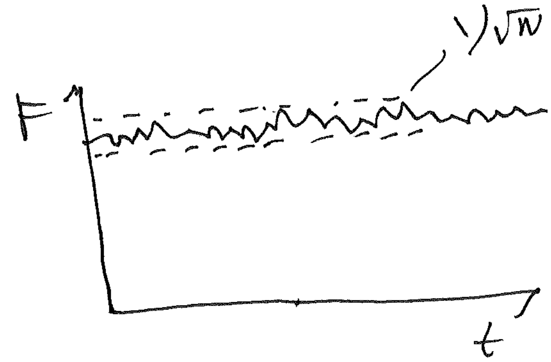
$$\left\langle \frac{1}{2} mv^2 \right\rangle = \frac{1}{2} m \langle v^2 \rangle = \frac{3}{2} kT$$

Gas must be macroscopic

pressure P doesn't make sense unless there are many particles colliding



force on area A as f^n of time, few molecules



many particles

random walk argument of earlier lecture can be used to show that

$$\frac{\Delta P}{P} = \frac{\text{standard dev of } P}{P} \propto \frac{1}{\sqrt{N}}$$

where $N = \#$ molecules. For $N \sim 10^{23}$, $\frac{1}{\sqrt{N}} \approx 10^{-10}$

P pressure seems perfectly constant and precise.

biophysics comment: <u>mammalian eardrum</u> has evolved to max. sensitivity allowed by laws of physics, extra factor of 10, your hearing would be drowned out by molecular collisions [Bialek + others]

Isotropic Constant Speed Kinetic Theory

Before discussing implications of $\langle \frac{1}{2} m v^2 \rangle = \frac{3}{2} kT$,

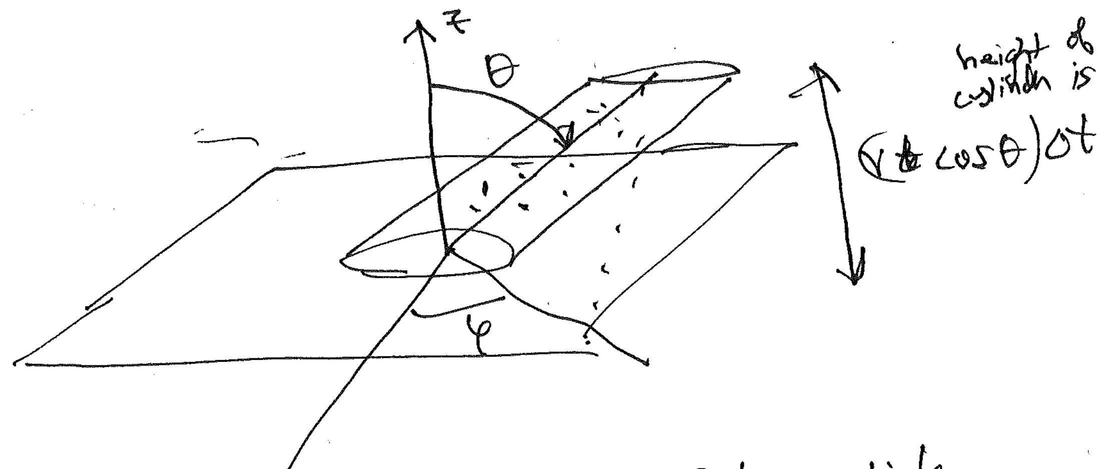
give refined discussion

(1) assume all molecules move with same speed v

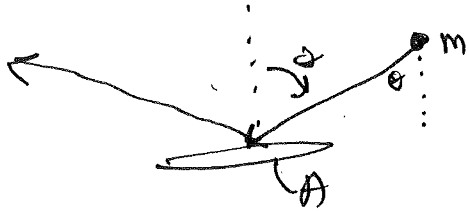
(2) but now ~~??~~ velocities are isotropic, all possible directions are equally likely.

Trick is to introduce spherical coordinates centered on area A, consider particles arriving from direction θ, φ

for
$$0 \leq \theta \leq \pi/2$$
$$0 \leq \varphi \leq 2\pi$$



consider tilted cylinder with base A, Only particles closer to wall than $(v\cos\theta)\Delta t$ will strike in time Δt



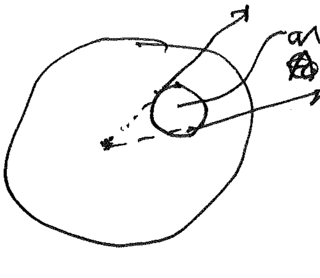
$P_z = m(v\cos\theta)$

change in momentum per particle different since comes in at angle

$$\Delta p = 2mv\cos\theta$$

hard part: what fraction of particles in cylinder of volume height × area $= [v\cos\theta/\Delta t]A$ are moving in direction θ,φ toward plate?

use concept of solid angle Ω, extension of ~~angle~~ angle in radians to surfaces



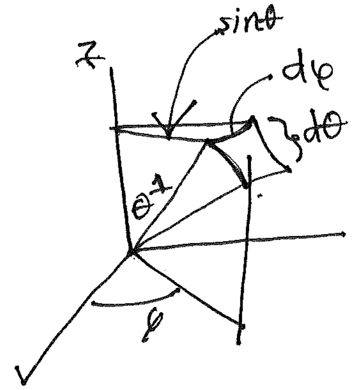
$$\Omega = \frac{\text{area on sphere}}{\text{radius}^2}$$

extremely important when collecting data from detector

$$0 \leq \Omega \leq 4\pi$$

units of solid angle called steradian like radian

in spherical coordinates



$$d\Omega(\theta,\varphi) = \sin\theta\, d\theta\, d\varphi$$
$$= (\sin\theta\, d\varphi) \times d\theta$$

$$\text{fraction} = \frac{d\Omega}{4\pi} = \frac{\sin\theta\, d\theta\, d\varphi}{4\pi}$$

Isotropic Kinetics Cont'd

What is total change in momentum in time Δt?

$$\Delta p(\theta,\varphi) = \underbrace{\left[\underbrace{(v\cos\theta)\,\Delta t}_{\text{height}}\right] A}_{\text{small volume}} \times \frac{N}{V} \times \underbrace{\frac{\sin\theta\, d\theta\, d\varphi}{4\pi}}_{\substack{\text{fraction moving}\\ \text{along } \theta,\varphi \\ \text{toward } A}} \times \underbrace{2mv\cos\theta}_{\substack{\text{change in}\\ \text{momentum}\\ \text{per particle}}}$$

$$\Delta P_{total} = \underbrace{\int_0^{\pi/2}}_{\theta} \underbrace{\int_0^{2\pi}}_{\varphi} \Delta p(\theta,\varphi)$$

$$= \int_0^{\pi/2} d\theta \int_0^{2\pi} d\varphi \; \frac{1}{2\pi} \cdot mv^2 \cdot \Delta t \cdot A \cdot \sin\theta\cos^2\theta \cdot \frac{N}{V}$$

$$du = -\sin\theta\, d\theta \qquad u = \cos\theta$$

$$= mv^2 \cdot \Delta t \cdot A \frac{N}{V} \cdot \int_0^{\pi/2} \cos^2\theta \sin\theta\, d\theta = \int_1^0 (-u^2)\,du = \frac{1}{3}$$

$$= \frac{1}{3} mv^2 \Delta t\, A \cdot$$

so $$\boxed{P = \frac{\Delta P_{total}/\Delta t}{A} = \frac{1}{3} mv^2 \cdot \frac{N}{V}}$$ just as before

Surprisingly, more careful isotropic model gives same result. Conclusion: always try simplest case first.

Effusion:

Same argument can be used to calculate arrival of other quantities:

$$dN(\theta,\varphi) = (v\cos\theta)\Delta t \cdot A \cdot \frac{N}{V} \cdot \frac{\sin\theta\, d\theta\, d\varphi}{4\pi} \times \begin{cases} 1 & \text{particle } \# \\ \frac{1}{2}mv^2 & \text{energy} \\ 2mv\cos\theta & \text{moment} \\ Q & \text{charge} \end{cases}$$

For example, let's replace area A by hole of area A and ask: how many particles leave hole in time Δt, i.e. what is flux of particles through small hole?

$2mv\cos\theta \rightarrow 1$ to count particles arriving in time Δt at A

Note: $\sqrt{A} \lesssim \bar{l}$ hole must be of order mean free path or smaller for this argument to work

$$\boxed{\Phi = \frac{1}{A}\frac{dN}{dt} \approx \frac{1}{A}\frac{\Delta N}{\Delta t} = \frac{1}{4}\bar{v}\left(\frac{N}{V}\right)}$$

Flux proportional to speed ($\bar{v}$ not v_{rms} as we will see later)

Example of effusion

astronaut on moon has 1mm micrometeorite puncture hole in suit. How long for gas to leak out?

$$\frac{1}{A}\frac{dN}{dt} = -\frac{1}{4} v \frac{N}{V}$$

or $$\frac{dN}{dt} = -\frac{N}{\left[\frac{V}{4vA}\right]} = -\frac{1}{\tau} N$$

characteristic time

$$\tau = \frac{V}{4vA}$$

$V \simeq 5\,l$

$v \simeq 500\ \frac{m}{s}$

$A = 1mm^2 \simeq (10^{-3} m)^2$

$$\tau \simeq \frac{5 \cdot 10^{-3} m^3}{4 \cdot 500 \frac{m}{s} \cdot 10^{-6} m^2} \simeq \frac{1}{4} \cdot 10^{-3+6-2}$$

$\simeq$ 1–10 s

1/25/14

Implication of $\boxed{\frac{1}{2} m\langle v^2\rangle = \frac{3}{2}kT}$

(1) can calculate root-mean-square speed of equilibrium gas in terms of T

$$V_{rms} = \sqrt{\langle v^2\rangle} = \sqrt{\frac{3kT}{m}} = \sqrt{\frac{3RT}{M}}$$

mass of one mole

example: N_2 at $T = 300\,K$

$$m_{N_2} = 2m_N = \frac{2\left[\frac{14\,g}{mole} \times \frac{10^{-3}\,kg}{g}\right]}{6.0 \cdot 10^{23}\,\frac{molecules}{mole}}$$

$V_{rms} \simeq 520\,\frac{m}{s}$ note: V_{rms} within 8% of $\langle v\rangle$ so good estimate

(2) $V_{rms} = \sqrt{\frac{3kT}{m}} \Rightarrow$ smaller mass $\Rightarrow$ higher speeds

He atom mixed with air will move faster so

$$\frac{1}{2} m_{He}\langle V_{He}^2\rangle = \frac{1}{2} m_{N_2}\langle V_{N_2}^2\rangle$$

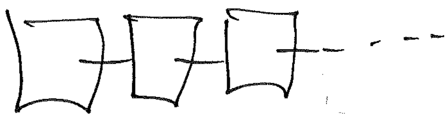
now $\Phi = \frac{1}{4} v\left(\frac{N}{V}\right)$ so lighter molecules effuse out of tiny hole in greater amount

Examples Cont'd

show slide of centrifuges and Ahmadinejad

$U^{235}F_6 \quad m = 349$ $\qquad \dfrac{\Phi^{235}}{\Phi^{238}} \approx \sqrt{\dfrac{352}{349}} = 1.0043$

$U^{238}F_6 \quad m = 352$

create many banks 

inefficient but current technology uses this idea

Speed of sound $\qquad c_s \propto V_{rms} \propto m^{-1/2}$

sulfur hexafluoride vs He in lungs

$f = \dfrac{c_s}{2L} \propto m^{-1/2}$

show YouTube mythbusters demo

---

atmospheres of moons and planets: why no H, He around
Mercury, Venus, Earth, Mars?

primordial universe $\qquad$ 75% H 25% He

escape speed of mass m $\qquad \dfrac{GmM}{R^2} = \dfrac{1}{2}mv^2 \Rightarrow V_{esc} = \sqrt{\dfrac{2GM}{R}}$

$V_{thermal} = \sqrt{\dfrac{3kT}{m}} \gtrsim 0.2\sqrt{\dfrac{2GM}{R}}$ lose gas!!

V_{esc} moon $= 2.4 \frac{km}{s}$ $\qquad V_H(400K) \approx 2.6 \frac{km}{s}$