Topics for today's lecture:

equipartition with several applications

comparison of equipartition with experiment
- heat capacity as function of temp for H_2 gas
- heat capacity vs. T for metals

Sections 1.4, 1.5:

Heat and work

compression work of an ideal gas

Heat capacities

Dates of next two quizzes: Quiz 2: Feb 8

Quiz 3: Feb 22

Midterm: Mar 3

Demo of dye in Caro syrup

small diffusion constant because of big polymers

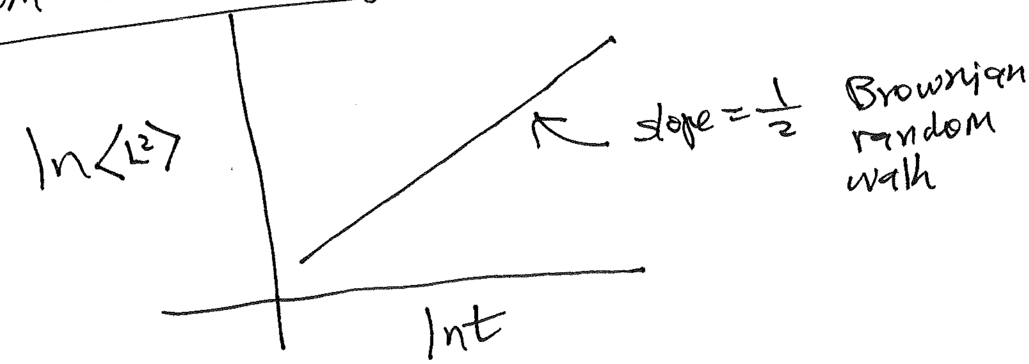
not in equilibrium, system depends on history

makes a nice magic trick

Tumbling of Bacteria
Levy Flights of Bacteria and Sharks

See movie by Emonet's group at Yale

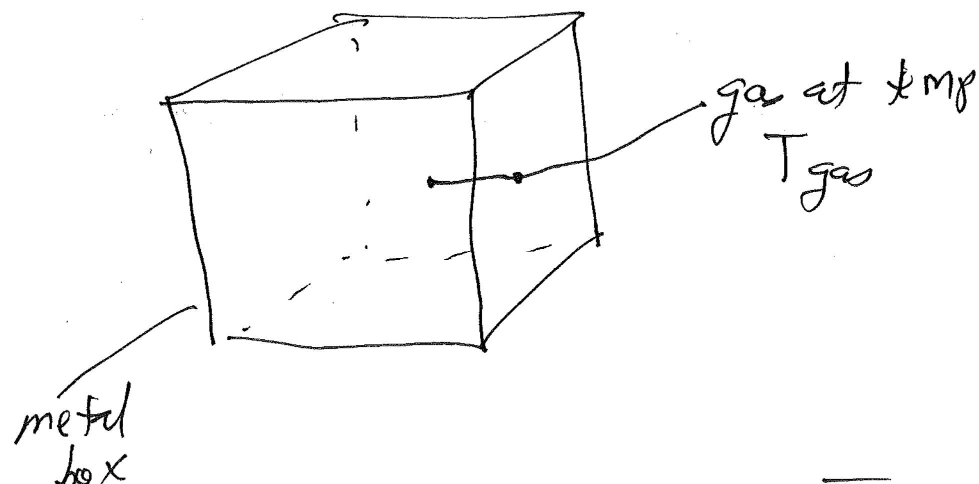
random walk as way to explore environment)



slope $> \frac{1}{2}$ superdiffusion
$< \frac{1}{2}$ subdiffusion

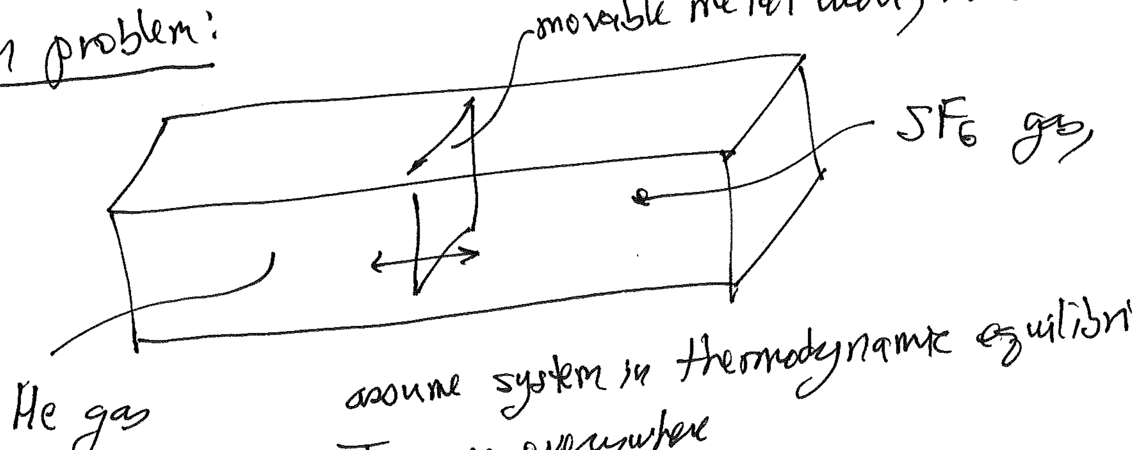
PRS question

effect of temperature change of wall on gas pressure on walls



jump wall temp from T_{gas} to $T_{new} > T_{gas}$
any change in pressure on wall?

<u>Harder problem:</u>



assume system in thermodynamic equilibrium
T same everywhere
P same
now jump temperature of movable metal wall
up: does it move? If so, which way?

Implications of

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

(1) can estimate rms molecular speed in terms of T:

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

read off mass of one mole from periodic table but convert grams to kilograms

7 N
nitrogen
14.00

M = molar mass in gm

$R \simeq 8 \frac{J}{mole\,K}$

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

$$M_{N_2} = 2M_N = 28g = 28 \cdot 10^{-3} kg$$

$$V_{rms} = \left[\frac{3 \cdot 8 \cdot 300}{30 \cdot 10^{-3} kg} \right]^{1/2} \simeq 500 \frac{m}{s}$$

$\langle V \rangle \simeq 0.9 V_{rms}$ so either useful for estimate of molecular speeds

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

(2) $\frac{1}{2} m v_{rms}^2$ same for all moleculs in a gas

$$\left\langle \frac{1}{2} m_{He} v_{He}^2 \right\rangle = \left\langle \frac{1}{2} m_{N_2} v_{N_2}^2 \right\rangle = \cdots$$

implies more massive molecule move more slowly <u>on average</u>

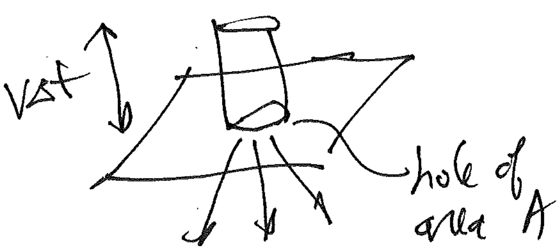
for equilibrium gas at temp T

$$\frac{v_1}{v_2} = \sqrt{\frac{m_2}{m_1}}$$

consider <u>effusion</u> through small hole whose diameter is comparable to (with factor of 10) of mean free path

$$\Delta N = (v \Delta t) A \cdot \frac{N}{V} \cdot \frac{1}{6}$$

anisotropic kinetic model



$\Rightarrow$ particle flux

$$\Phi = \frac{1}{A}\frac{dN}{dt} = \frac{1}{6} v \left(\frac{N}{V}\right)$$

v = average speed (not rms)

conclude: lighter mass moleculs leak out more rapidly

$$\Phi_1 / \Phi_2 = \sqrt{\frac{m_2}{m_1}}$$

Effusion and Isotope Purification

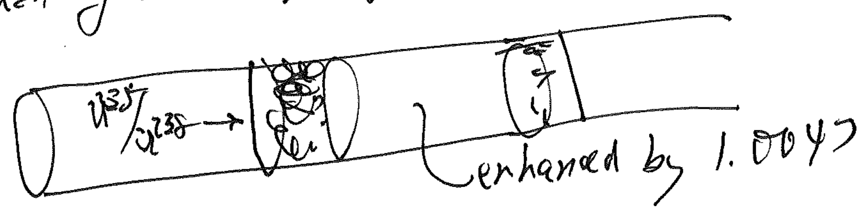
show slide of Iranian ~~prin~~ president Ahmadinejad

$U^{235}F_6 \cdot m = 349$ $\qquad \dfrac{\Phi^{235}}{\Phi^{238}} = \left[\dfrac{352}{349}\right]^{1/2} = 1.0043$

$U^{238}F_6 : m = 352$

can slowly enhance concentration of U^{235} by using many successive effusers

alternately, push gas through porous plug



or use centrifuges, we will analyze this case later, get same small ratio 1.0043 of enhancement but net flux greater

other applications: isotopic walls for fusion reactors, reduce neutron damage

$\left\langle \frac{1}{2}mv^2 \right\rangle = \frac{3}{2}kT$: Planetary Atmospheres

consider planets: Mercury, Venus, Earth, Mars
no H, no He in atmospheres

Jupiter, Saturn, ⋯ : lots of H, He, Titan

solar system started with primordial mix
75% H, 25% He

show slide: Mercury vs Titan

answer: $\boxed{V_{thermal} = \sqrt{\frac{3kT}{m}} \gtrsim \frac{1}{5} V_{escape} = \frac{1}{5}\sqrt{\frac{2GM}{R}}}$

recall $\underbrace{\frac{GmM}{R}}_{\substack{\text{potential energy} \\ \text{of mass } m \text{ brought} \\ \text{from } \infty \text{ to surface} \\ \text{of moon of radius } R, \\ \text{mass } M}} = \underbrace{\frac{1}{2}mv^2}_{\substack{\text{energy needed} \\ \text{to escape}}} \Rightarrow V_{esc} = \sqrt{\frac{2GM}{R}}$

surface temp of sunny side of moon

$V_{esc}[\text{moon}] = 2.4 \frac{km}{s}$ $\quad V_H(400K) \simeq 2.6 \frac{km}{s} \Rightarrow$ no H

$V_{N_2}(400) \simeq 0.5 \frac{km}{s}$

$V_{esc}[\text{earth}] = 11 \frac{km}{s}$ $\quad V_H(300K) \simeq$

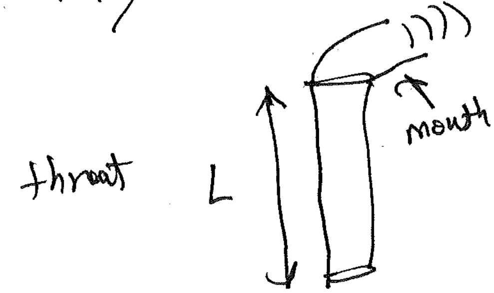
$\langle \frac{1}{2} m v^2 \rangle = \frac{3}{2} kT$: <u>speed of sound</u>

we will see later that V_{rms} close to speed of sound in ideal gas

more massive molecules $\Rightarrow$ slower sound speed

show video of Adam Savage of Mythbusters

vocalizing with He vs vocalizing with SF_6



$$c_s = \lambda f$$

$$\lambda = \frac{L}{n}$$

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

thought question:

if you replace air in symphonic music hall with He gas, which instruments will sound out of tune?

Equipartition Theorem
~1876

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

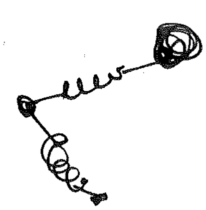
leads to guess where 3 comes from: # of spatial dimension

$$\left\langle \frac{1}{2}mv^2 \right\rangle = \frac{1}{2}m\left[\left\langle v_x^2 + v_y^2 + v_z^2 \right\rangle\right]$$
$$= \frac{1}{2}m\langle v_x^2\rangle + \frac{1}{2}m\langle v_y^2\rangle + \frac{1}{2}m\langle v_z^2\rangle$$
$$= \cancel{\frac{3}{2}}\ 3 \times \frac{1}{2}m\langle v_x\rangle^2$$

sine by symmetry $\langle v_x^2\rangle = \langle v_y^2\rangle = \langle v_z^2\rangle$

so guess $\frac{1}{2}kT$ basic unit of "thermal energy"

confirmed by deeper analysis we will carry out later in course (§6.3 of Schroeder, pages 238–241)



write energy of molecule (classical molecule)

$$E = \frac{1}{2}mv_x^2 + \frac{1}{2}mv_y^2 + \frac{1}{2}mv_z^2 + \frac{I_x}{2}\omega_x^2$$
$$+ \frac{1}{2}I_y\omega_y^2 + \frac{1}{2}I_z\omega_z^2$$
$$+ \frac{1}{2}k_x(x-x_0)^2 + \frac{1}{2}k_y(y-y_0)^2 + \cdots$$

Each quadratic term is called a "degree of freedom", call # f

for gas in equilibrium with N moleculs, each with f degrees of freedom:

$$\boxed{U_{thermal} = N \cdot f \cdot \frac{kT}{2}}$$

equipartition theorem

for atom, consider point particle (?!), $f=3$

diatomic molecule, $f=7$

atoms in crystal $f=6$

rough idea is that random endless collisions pump energy into each mode or remove energy until everything is balanced <u>on average</u>

Example: <u>interstellar ice grain</u> (macroscopic)

sphere $R = 10^{-7}\,m = 0.1\,\mu m$ tiny

$\rho = 10^{3}\,\frac{kg}{m^3}$ ice

interacts with gas $T \sim 100\,K$

moves with speed $\frac{1}{2}(V\rho)\langle v^2\rangle = \frac{3}{2}kT$

$v_{grain} \simeq 3\,\frac{cm}{s}$ not so fast

but also <u>rotates</u>

$$\frac{1}{2}I\langle\omega_x^2\rangle \simeq \frac{1}{2}kT$$

$I_{sphere} = \frac{2}{3}MR^2 \Rightarrow \omega_{x,rms} \simeq 10^5\,\frac{rad}{s}$

fast!

Broad Implications of kT

For systems in equilibrium with temp T, every small feature tends to wobble, vibrate, spin, move with average energy kT

engineers: need to beat kT for stable design
minimal energy to store, retrieve memory needs to exceed $\approx kT$
current device $\approx 10^5 kT$, lots of room for improvem

$\frac{1}{2}CV^2$, $\frac{1}{2}LI^2$: noise in electrical devices
drop temp is one way to reduce noise

biology: reliable information processing $\gtrsim kT$
neurons, heart cells $\quad eV \approx kT$

$$V \sim \frac{kT}{e} = \frac{k(300)}{(1.6 \cdot 10^{-19} C)} \approx 30 \text{ mV}!!!$$

evolution operates right at limits set by equipartition

1/27/14

How To Count Degrees of Freedom

assume atoms are point particles so can't rotate

only kinetic motion so $\boxed{f = 3 \text{ for atom}}$

assume molecule, not collinear, with K point atoms

total degrees of freedom $= 3K$

3 associated with center of mass

3 associated with rotation about center of mass

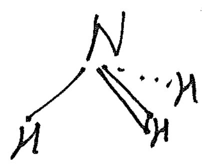
remaining degrees of freedom $3K-6$ are internal vibrational modes.

each vibrational mode contributes two degrees of freedom

$\frac{1}{2}mv^2$ kinetic + $\frac{1}{2}kx^2$ spring potent

so $$\boxed{f = 3 + 3 + 2(3K-6) = 6(K-1)}$$ non-colinear molecule

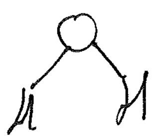
example: ammonia



$K=4$

$f = 6(4-1) = 18$

water



$K=3$

$f = 6(3-1) = 12$

Degrees of Freedom Cont'd

What about collinear molecule? $H-C\equiv C-H$ acetylene

assume K point atoms

3 center-of-mass kinetic energy,

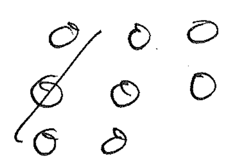
2 rotation: one less because rotation about axis can't happen for point atom

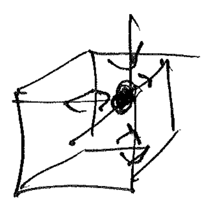
$$f = 3 + 2 + 2(3K-5) = 6K-5$$

examples: $H-C\equiv C-H$ $K=4$, $f=19$

$$\boxed{N\equiv N \quad K=2 \quad f=7}$$ ⟸ most common case, diatomic molecules

One last case: cubic crystal





3 vibrational modes so

$$\boxed{f=6}$$

no trans, no ~~rei~~ rotation

Test of Equipartition

Recall heat capacity of object is

$$C = \frac{Q}{\Delta T}$$

add heat (numerator), measure change in temperature ΔT

for constant volume of substance, $Q \stackrel{\Delta}{=} U_{therm}$

$$\underbrace{C_V}_{\substack{\text{constant volume} \\ \text{heat capacity}}} = \frac{\Delta U_{thermal}}{\Delta T} \simeq \frac{dU_{thermal}}{dT}$$

But $\quad U_{therm} = N \cdot f \cdot \frac{kT}{2}$

$$\Rightarrow \boxed{C_V = \frac{dU_{therm}}{dT} = N f \frac{k}{2}}$$

Predictions: C_V independent of temperature

for atomic gas, one mole $\quad C_V = \frac{3}{2}R$

for diatomic gas one mole $\quad C_V = \frac{7}{2}R$

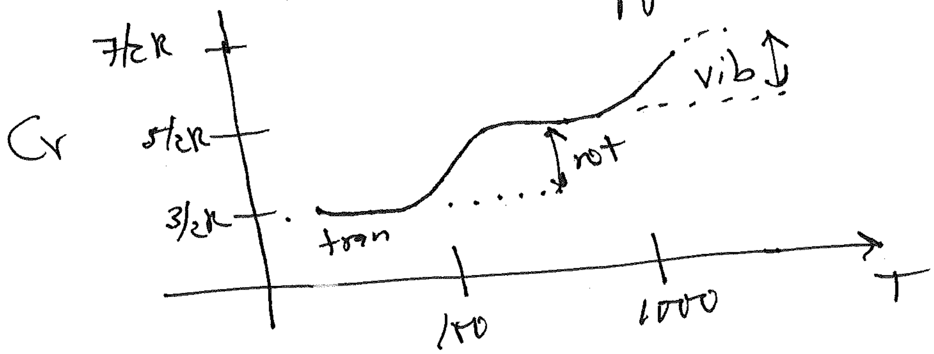
for crystalline solid one mole $\quad C_V = 3R$ } rule of Dulong and Petit

Look At Data

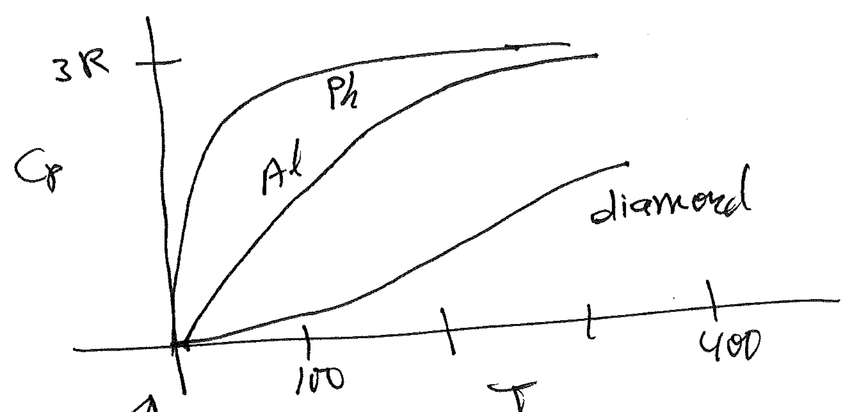
Show slides H_2 heat capacity C_V

metals $\qquad$ $C_P \leftarrow$ close to C_V, for ~~...~~ solids

extremely important plots, memorize, appreciate!



H_2



$C_P \to 0$!
general result we will derive, explain why one can't get to absolute zero

we will derive mathematical theories for all details of these plots, great triump of statistical physics and QM