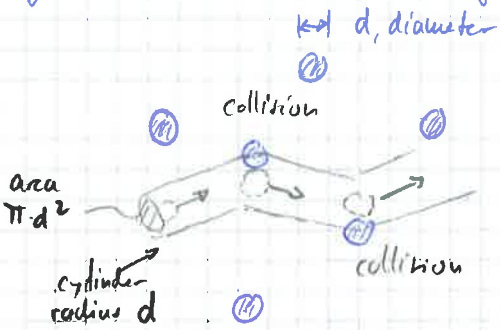
mean free path λ , $[\lambda] = m$

λ : avg. distance between two collisions for a molecule

Consider 1 moving molecule (others at rest) during time t ;



slide drawing

if center of incoming molecule ○ is ~~in the cylinder~~ closer or equal than d to other molecule : collision

in time t, moving molecule (speed v) will collide with all molecules within cylinder with volume $\pi \cdot d^2 \cdot \underbrace{v \cdot t}_{\text{length of cylinder}}$

nb collisions $= n_v \cdot \pi d^2 \cdot v \cdot t$, where $n_v = \dfrac{N}{V}$, nb molecules per unit volume

$$\| \ \text{mean free path (mfp)} = \frac{\text{total path}}{\text{nb collisions}} = \frac{v \cdot t}{n_v \cdot \pi \cdot d^2 \cdot v \cdot t} = \frac{1}{n_v \cdot \pi \cdot d^2} = \lambda$$

taking into account correction due to motion of other molecules (need to know speed distribution function of later)

$$\| \ \lambda = \frac{1}{\sqrt{2}} \cdot \frac{1}{n_v \cdot \pi \cdot d^2} \underset{*}{=} \frac{1}{\sqrt{2}} \cdot \frac{k_B \cdot T}{P \cdot \pi \cdot d^2}$$

example ↳ %

collision time τ (avg time between collisions) : $\tau = \dfrac{\lambda}{v_{avg}}$

$*$ $P \cdot V = n R \cdot T = \underbrace{n \cdot N_A}_{} \cdot k_B \cdot T$, hence $\dfrac{N}{V} = \dfrac{P}{k_B T}$

N, nb molecules

n: nb moles

$N_A := 6.022 \ 10^{23}$ "$\dfrac{\text{molecules}}{\text{mole}}$"

example λ

for molecules with $d = 0.3\ \text{nm}$ at $T = 300\text{K}$ & $P = 100\ \text{kPa}$

(26.85°C) (1 bar)

$\lambda \simeq 10^{-7}\ \text{m}$

$= 0.1\ \mu\text{m} = \underline{100\ \text{nm}}$, ~345× molecule diameter

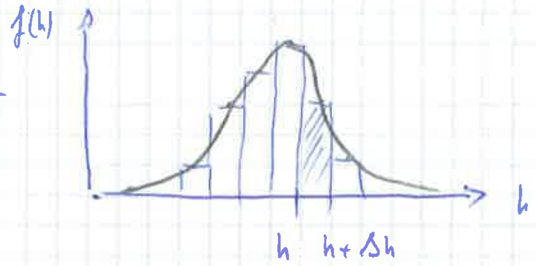
avg dist. between molecules $\simeq 3.5\ \text{nm}$

slide mfp for ideal gas

distribution function of gas velocities (Maxwell-Boltzmann)

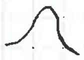
(see Tipler ch 17-4, p 575 for example)

math: distrib. function, e.g. f(h) : nb of persons with height h



a) histogram : count persons within [h and h+Δh[

b) function f(h)



For N people, N·f(h)·Δh is the nb of people whose height is between h and h+Δh

↑ continuous function

Similarly, Maxwell-Boltzmann speed distribution function (distrib can be measured cf Tipler ch 17-4)

$dN = N \cdot f(v) \cdot dv$ N gas molecules

dN : nb gas molecules with speed between v and v+dv

Result from stat mech:

$$f(v) = \frac{4}{\sqrt{\pi}} \cdot \left(\frac{m}{2k_BT}\right)^{3/2} \cdot v^2 \cdot \underbrace{e^{-mv^2/(2k_BT)}}_{\text{Boltzmann factor}}$$

, $e^{-\text{energy}/k_BT}$ ↑ relevant to problem here : kin energy molecule

slide Maxw. Boltz. distrib. function

- most probable speed v_{max} for f(v) max

$$v_{max} = \sqrt{\frac{2k_BT}{m}} = \sqrt{\frac{2RT}{M}}$$

↳ molar mass $M = m \cdot N_A$

- root mean square speed (see before) $v_{rms} = \sqrt{\frac{3RT}{M}}$

Specific heat of gases

- reminder : $\Delta Q = C . \Delta T$ capital c

  C: heat capacity $[C] = \frac{J}{K}$
  energy (heat) needed to warm a substance by 1 degree

  $\Delta Q = \underset{\substack{\uparrow \\ \text{small c}}}{c} . m . \Delta T$, $c = \frac{C}{m}$

  c: specific heat (capacity)
  $[c] = \frac{J}{kg . K}$, depend. on substance

- we have seen that the internal energy of a gas (monoatomic) consists of translational kinetic energy

$$K_{tran.} = N . \left(\frac{1}{2} m v^2\right)_{avg} = \overset{\substack{\text{3 deg. of freedom} \\ \swarrow}}{\frac{3}{2}} . \underset{\substack{\uparrow \\ \text{nb molecule}}}{N} . k_B . T = \frac{3}{2} . \underset{\substack{\uparrow \\ \text{nb. mole}}}{n} . R . T = E_{int}$$

increasing T is equivalent to increase E_{int}, hence the heat capacity can be written ($\Delta T \to dT$)

$$C_V = \frac{dQ}{dT} = \frac{dE_{int}}{dT} = \frac{3}{2} n R$$

$$\| \; \underset{\uparrow}{C_V} = \frac{3}{2} n R$$ ~~molar~~ ~~specific~~ heat capacity

(subscript "V" means at constant volume)

NB: why at const volume ?

V = const : all energy goes only to increasing the internal energy $\left(\frac{1}{2} m v^2\right)_{avg}$
if V = const ($p \nearrow$), no work done

V ≠ const : expansion (assume p = const), hence the heat dQ added to gas has to also produce work

$$dW = F . ds = P . A . ds = P . dV$$

only if $dV = 0$, is $dW = 0$.

$[P.V] = \frac{N}{m^2} . m^3 = \frac{N . m}{m^3} . m^3 = N m = J$ energy, work

and $C_p . dT - C_V . dT = p . dV$

Using the state eq. $PV = nRT$, $P dV = n R . dT$

we get

$$\| \; C_p - C_V = n . R$$

$$\| \; C_p = C_V + nR = \frac{5}{2} n R \quad , \quad C_V = \frac{3}{2} n R$$

for an ideal, monoatomic gas

def. molar (specific) heat c'

$$C' = \frac{C}{n} = \frac{mc}{n} = M\cdot c$$

C: heat capacity
n: nb moles
m: mass of sample (substance)
M: molar mass $[M] = \frac{kg}{mol}$

and $C_V' = \frac{3}{2}R$

- We only accounted for translational modes here; ok for monoatomic gas

Rem. equipartition theorem: if N nb atoms > 1 (a molecule), rot + vibration
total 3N modes (deg. freedom)

(slides) 1) equip theorem

2) C_V' for various molecules
compare measured value to ideal gas

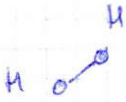
remember vibration modes
contribute to kin and pot energy (cf p 10 last lecture)

$$E_{int} = \sum_i E_{kin}^{transl} + \sum_i E_{kin}^{rot} + \underbrace{\left(\sum_i \underset{\frac{1}{2}mv^2}{E_{kin}^{vibr}} + \sum_i \underset{\frac{1}{2}kx^2}{E_{pot}^{vibr}}\right)}_{\text{" weight 2 "}}$$

for He, monoatomic 3 deg. freedom (trans)

$$C_V' = 3\cdot\frac{1}{2}R = \frac{3}{2}R$$

for N_2, diatomic 3 trans, 2 rot, 1 vibr $(= 6 = 3\times \underset{\overset{\uparrow}{\text{atoms}}}{2}.)$



$$C_V' = (\overset{transl}{3} + \overset{rot}{2} + \overset{vibr}{\overbrace{\underset{\overset{\uparrow}{kin}}{1} + \underset{\overset{\uparrow}{pot}}{1}}})\cdot\frac{1}{2}R = \frac{7}{2}R$$

for CO_2 ; 3 trans, 2 rot, 4 vibr $(= 9 = 3\times 3)$

$$C_V' = (3+2+4+4)\,\frac{1}{2}\cdot R = \frac{13}{2}R$$

(slide) · C_V' for H_2 vs T : excitation of rotation modes and vibration modes as T ↗
note : molecule start dissociating above 700K

L24 \ 3

heat capacity / specific heat of solid

following previous reasonning : no translation of atoms ; no transl. of wholebody
no rotation of atoms / molecule ; no rot. " "
→ vibrations (kin + pot.)

slide model of solid

total internal energy of solid

$$E_{int} = \underset{\substack{\uparrow \\ \text{vibration, kin}}}{\frac{1}{2} m v_x^2} + \frac{1}{2} m v_y^2 + \frac{1}{2} m v_z^2 + \underset{\substack{\uparrow \\ \text{vibration, pot.}}}{\frac{1}{2} k_{eff} \cdot x^2} + \frac{1}{2} k_{eff} \cdot y^2 + \frac{1}{2} \cdot k_{eff} \cdot z^2$$

k_{eff} : effective force constant of (hypothetical) springs between atoms

that is : 6 deg. of freedom

⇒ $E_{int} = 6 \cdot \frac{1}{2} R \cdot T = 3 R \cdot T$ for 1 mole

and || $C_V' = 3R$ heat capacity

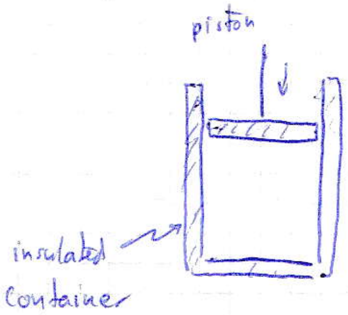
Dulong - Petit law , ok for alot of solids
at not too low temperature
(fails at low T ; due to energy quantization)

adiabatic process

process in which no heat transfers in or out of a system $\underset{(Q)}{}$

0/6

(e.g. very well insulated system)



· ~~slow~~ [illegible]) compression of gas,
(insulated container, $\Delta Q = 0$)

→ Eq. of state (ideal gas) : $P.V = n.R.T$

→ first law thermo : $dE_{int} = \underbrace{dQ_{in}}_{=0\text{, adiabatic process}} + dW_{on}$

slide
adiabatic process, pV diagram

seen previously: (L20 - L21)

$$dE_{int} = C_v . dT$$

↑ heat capacity at const V.

$$dW_{on} = -\underbrace{P.dV}_{\text{work done on gas}}$$

thus

$$C_v . dT = \overset{dQ=0\text{, adiabatic process}}{\overset{\downarrow}{0}} - P.dV$$

$(P.V = nRT, \quad P = \frac{nRT}{V})$

$$C_v dT + \frac{n.R.T}{V} . dV = 0$$

$$\frac{dT}{T} + \frac{n.R}{C_v} . \frac{dV}{V} = 0$$

integrate

$$\ln T + \underbrace{\frac{n.R}{C_v} . \ln V}_{\ln V^{nR/C_v}} = \text{const}$$

and

$$\ln \left(T . V^{nR/C_v} \right) = \text{const}$$

thus

$$T . V^{nR/C_v} = \text{const}$$

Using $\gamma = \frac{C_p}{C_v}$ and $C_p - C_v = nR$ (monoatomic gas, cf L20, L21)

C_p: specific heat at const P.

$$\frac{nR}{C_v} = \frac{C_p}{C_v} - 1 = \gamma - 1$$

L24 5

We have $\| \; T \cdot V^{\gamma-1} = \text{const}$

Using $PV = nRT$, $T = \frac{P \cdot V}{nR}$

$$\frac{P \cdot V}{nR} \cdot V^{\gamma-1} = \frac{P \cdot V^{\gamma}}{nR} = \text{const}$$

and ~~finally~~ also $\| \; P \cdot V^{\gamma} = \text{const}$ (at $n = \text{const}$) ; $\gamma = \frac{C_P}{C_V}$

adiabatic process (quasi-static)

exp adiabatic

gas mixtures (ideal gases)

e.g. air ~21% oxygen, 75% nitrogen

diving: oxygen-enriched air (nitrox) → longer dives

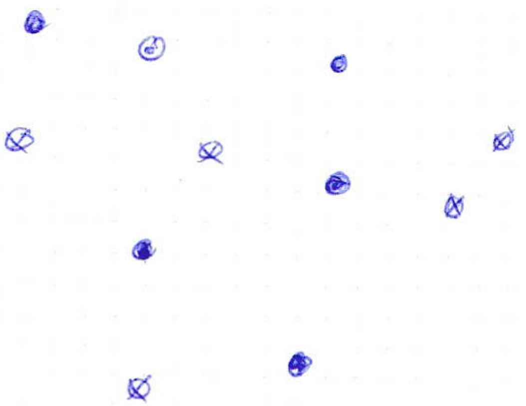
deep diving: oxygen + helium (heliox) –
(avoid nitrogen narcosis)

if mixture sufficiently dilute (in confined volume V), each gas occupies the whole volume V
(Vol. of gas molecules negligible as compared to V)

then $P_{\text{mixture}} = \sum_i P_i$, sum of individual pressures or partial pressures

$$= \frac{1}{V} \cdot \sum_i n_i \, R \cdot T$$

↑ nb of mole individual gases



brownian motion : random movement of microscopic particles suspended in a liquid or a gas

(Robert Brown 1827)
botanist

(explanation: Einstein, 1905 / Jean Perrin: quantitative observation 1905-1911, Nobel 1926; ended skeptism about atoms/molecules
(↳ discontinuous structure of matter)

exp Rauchkammer - smoke particle in air
~ 10nm - 1μm

origin of brownian motion : ‖ jittering of particle in a gas/liquid due to repeated collisions with molecules of gas

→ hypothesis/explanation Einstein : brownian motion as evidence for the existence of atoms (molecules)

(NB: 1st observation of atoms: 1980's STM, AFM.
1st " of electrons ~2010)

diffusion of particle, D: diffusion constant, $[D] = \frac{m^2}{s}$

avg particle motion : $\langle r^2 \rangle_{avg} \sim \underset{\text{diffusion constant}}{\underset{\uparrow}{D}} \cdot \underset{\text{time}}{\underset{\uparrow}{t}}$

Einstein
(Sutherland - Einstein)
of A.Pais, Subtle is the Lord

$$D = \frac{k_B \cdot T}{f} = \frac{k_B T}{6\pi\eta R}$$

$f = 6\pi \underset{\text{viscosity of liquid}}{\underset{\uparrow}{\eta}} R$, Stokes friction coefficient
particle radius R
%

$$\langle r^2 \rangle_{avg}^{1/2} \sim \sqrt{\frac{k_B T \cdot t}{6\pi\eta \cdot R}}$$

relationship between a macroscopic diffusion constant and the atomic nature/properties of matter
(like considering the motion of an iceberg due to penguins jumping on it)

and $\left(\frac{1}{2} \underset{\text{mass of atom}}{\underset{\uparrow}{m}} \underset{\text{avg speed of atom}}{\underset{\uparrow}{v}}^2\right)_{avg} = \frac{3}{2} k_B T$

slides - macromechanics
- nanomechanics

example: Brownian motion

gas, normal / Standard condition

$$n = \frac{N_A}{V} = \frac{6.02 \cdot 10^{23}}{0.022.4} \frac{\text{particle}}{m^3}$$

ρ

density ρ gas molecule

for 1 mol in std conditions

$P = 100 kA$, $T = 273.15 K$, $V = 22.4\ l$

typ. mean free path for gas molecule

$$\lambda = \frac{1}{\sqrt{2}} \cdot \frac{1}{n_v \pi \cdot d^2},$$

assume

$d = 1 \mathring{A} = 10^{-10} m$ (~ atom size)

$$\approx 8.4\ 10^{-7} m = 0.84 \mu m$$

assuming $\langle v^2 \rangle_{avg}^{1/2} = 10^3 m/s$ (Hydrogen estimate ~480 m/s)

$$\lambda = (v^2)_{avg}^{1/2} \cdot \tilde{\tau} \Rightarrow \tau \cong 8.4\ 10^{-10} s,$$ time between collision

hence $\underline{\underline{\frac{1}{\tau}}} \sim 10^9 s^{-1}$: nb collisions per second

L24 §8

real gas law - van der Waals equation of state

- at high pressure P or low temperature T : breakdown of ideal gas law

and $P \cdot V = n \cdot R \cdot T$ requires corrections:

$$\left\| \; \left(P + \frac{a \cdot n^2}{V^2}\right) \cdot \left(V - b \cdot n\right) = n \cdot R \cdot T \right.$$

n moles of gas

Van der Waals eq. of state

Corrections because 1) molecules have a finite (non zero) volume b for one mole of gas

2) force F between gas molecules:

- F attracts gas molecule approaching wall container (→ remember how we calculated P)
  $F \propto \frac{n}{V}$ density of molecules pulling back
- nb of molecules hitting container wall per unit time $\propto \frac{n}{V}$

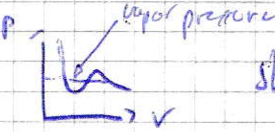
hence correction to pressure $P \propto \left(\frac{n}{V}\right)^2$

constant a: small for inert gases (Ar, N_2) (low reactivity)

($\frac{an^2}{V^2}$, $b \cdot n$ small for large V
→ ideal gas law)

slide

phase diag.

- isotherms 

shape! → ∃ critical point T_c

- v.d Waals eq. describes isotherms outside shaded region where liquid & vapor coexist → 2 different states gas liquid

⇒ gas can condensate when P & V $\searrow$

- phase diag. PV, PT, PVT
- condensation cloud behind aircraft

exp %