Lecture 3 - Gases, Diffusion

⇒ What is a neutral, dilute → Transport
gas?

- ensemble of weakly correlated neutral particles (molecules)

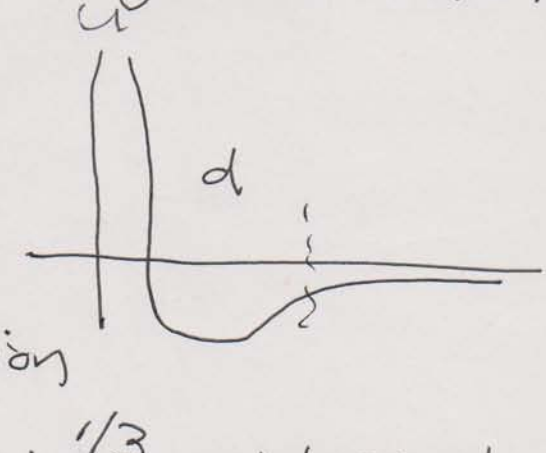
  which are thermally agitated interacting by 2 body collisions

- scales

  - d, range of intermolecular force

i.e.

$\sigma \sim \pi d^2$
↓
collisional
cross section



i.e.
Van-der-Waals
etc.

  - $1/\langle n \rangle^{1/3}$, intermolecular spacing

  - l_{mfp}, mean free path, i.e.

ime between collisions ⟺ length traversed between collisions.

— L macroscopic scale
i.e. box size, scale of gradients in thermodynamic quantities, etc.

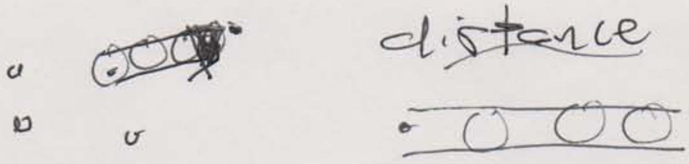
rdering:

$$\boxed{d < \langle n \rangle^{-1/3} < \ell_{mfp} \overset{\text{usually}}{<} L}$$

and $T/u(\bar{r}) >>$

i.e. dilute

Now, in



particle will have α collisions $\sim n\sigma L$ in this distance. Thus,

ean length between collisions is

$$L/\alpha \sim L/n\sigma L \sim 1/n\sigma$$

$$\Rightarrow \boxed{1/n\sigma = \ell_{mfp}}$$

$\nu_c \sim 1/\tau_c \sim v_{th}/l_{mfp} \sim (v_{th})(n\sigma)$

$\downarrow$ mean free time

$v_{Th} \sim (T/M)^{1/2}$

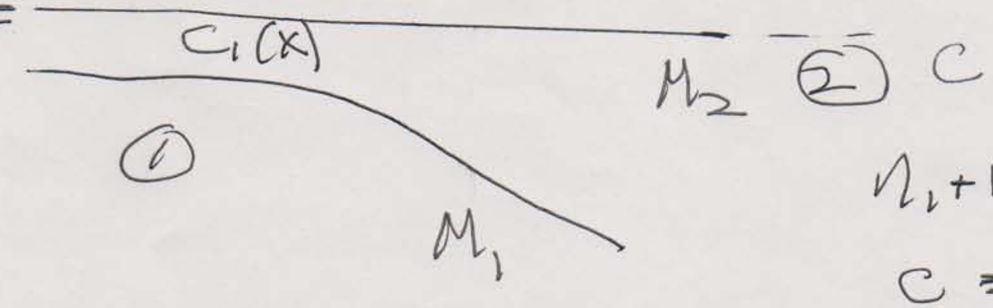
air, at room temperature: $v_{Th} \sim 300$ m/sec

Quantities of Interest:

- fluxes (heat, particles, concentration)
- transport coefficients (D, μ, ---) ⇒ {basic linear response "probe" of system
- transfer rates, etc.

n.b.:
- linear response
- define fluxes, entropy production

Ex. Flux ① into ②



$n_1 + n_2 \sim n_2$

$c = n_1/n$

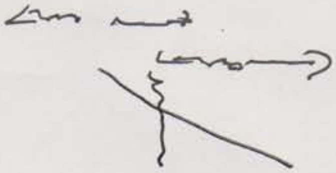
$c \ll 1$.

① diffuses into ②

T, P const.

→ dc/dx drives flux of particles.

then diffusive flux Γ:



$$\Gamma = \left[n_1(x-\ell) - n_1(x+\ell) \right] v_{Th}$$

$$= -\ell v_{Th} \frac{dn_1}{dx} \sim -\ell v_{Th} n \frac{dc}{dx}$$

equal prob. of jumping either way, but more on one side,

$$\Gamma \sim -\ell v_{Th} n \frac{dc}{dx} \equiv -D_c \frac{dc}{dx}$$

$$D_c = n D = n \ell v_{Th}.$$

in terms:

$$D \sim 1/n\sigma \sqrt{T/M_1}$$

$$\sim \frac{1}{P\sigma} \sqrt{T^3/M_1}$$

Some observations:

① $\Gamma \sim nV \sim -D\,\partial n_1/\partial x \sim -D n_1/L$

$\Downarrow$
flux

$\therefore$ mean $V_1 \sim \Gamma/n_1 \sim D/L$

velocity down gradient

② $\tau_D/\tau_c \sim \frac{L^2}{D}\frac{v_{th}}{l_{mfp}}$

D indep concen!

$\sim (L/l_{mfp})^2 \sim (Ln\sigma)^2$

Diffusion is slow

→ Now, how else drive flux ① into ②?

⇒ temperature gradient!

How? i.e. ∇T drives flux of particles

− $n_1 \ll n$ ⇒ T is supported by ②

so,

if no gradient in n_1

$$\Gamma'_T = \left[n_1(x-\ell)\, V_T(x-\ell) - n_1(x+\ell)\, V_T(x+\ell) \right]$$

$$\simeq n_1 (-\ell) \frac{dV_T}{dx}$$

$$\sim - n_1 \frac{v_{th}}{T} \ell \frac{dT}{dx}$$

$$\Gamma'_T \sim - n_1 \frac{v_{th}}{T} \ell \frac{dT}{dx} \Rightarrow$$ ∇T driven particle flux

so if:

$$\Gamma_T = - n \frac{D_{Td}}{T} \frac{dT}{dx}$$

then:

$$D_{Td} \sim c_1 \ell v_{th} \sim c_1 D$$

$$\sim \frac{c}{nT} \sqrt{T/M_1} \sim \frac{n_1}{n^2 T} \sqrt{T^5/M_1}$$

n.b. D_{Td} depends on concentration of lights!

$\Rightarrow$ How does "diffusion equilibrium" behave, for concentration of light particles in system with temp gradient of heavy particles.

↳ i.e. steady state source.

i.e. where do light particles concentrate.

Now, if at eqbrm:

$$\frac{d}{dx}(n_1 V) = 0$$

{ no change in local # density

$\Rightarrow$

$$\frac{d}{dx}\left(c n V\right) = \frac{d}{dx}\left(c(nT)\frac{V}{T}\right) = 0$$

$nT = P =$ const.

So $\frac{d}{dx}\left(c\frac{v}{T}\right)=0$

$\Rightarrow \quad c(x) \sim T(x)/v(x) \sim \sqrt{T(x)}$

i.e. **lighter gas concentrates in region of high temperature.**

Now, ... consider transport of heavy into light ...

$c_H \ll c_L$

→ much like drag problem of body in fluid, light particles will exert frictional force by momentum exchange with heavier

→ From $F_D \sim \rho_0 R^2 V^2$, one

might expect:

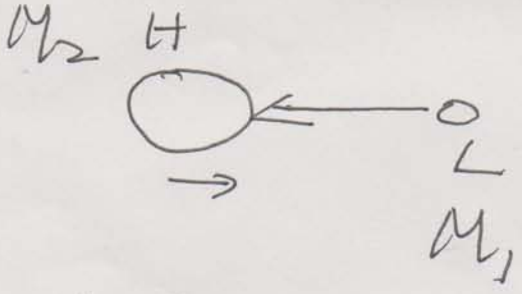
$$F_D \sim \rho_L \sigma v_{th} V$$

i.e
$v_{tot} = v_{th} + V$
$v_{th} >> V$

$$\Rightarrow \boxed{V = \mu F}$$

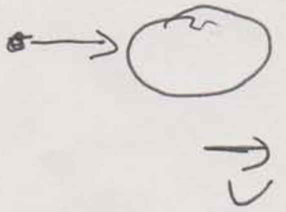
mobility, where $\mu = 1/\rho_L \sigma v_{th}$

Now, to show:



Lights give momentum to heavy.

in head-on, $M_1(V_{Th} + V)$ transfered to heavy.



in over-taking, $M_1(v_{th} - V)$ is transfered to heavy.

<u>so</u>

$$\Delta P_{heavy} \sim M_l (V_{Th} + V) - M_l (V_{Th} - V)$$

$$\sim M_l V$$

Rate of momentum transfer / change

$$\frac{\Delta P}{\Delta t} \sim \underset{\text{rate collns.}}{\nu_c} \left(\overset{\substack{\text{change/colln} \\ \downarrow}}{\Delta P}\right)$$

$$\sim (M_l V) \frac{v_{Th}}{l_{mfp}} \sim \frac{\overset{\substack{\text{momentum} \\ \downarrow}}{P_L} V}{l_{mfp}}$$

$P_L = M v_{Th} \sim$ light's momentum

<u>so</u>

$$F = \mu^{-1} V \Rightarrow \mu^{-1} \sim P_L / l_{mfp}$$

$$\boxed{\mu \sim l_{mfp} / P_L} \sim \frac{1}{n \sigma M_l v_{Th}} \sim \frac{1}{\rho_L \sigma v_{Th}}$$

$$\boxed{\mu \sim 1 / \rho_L \sigma v_{Th}}$$

<u>mobility</u>

⇒ One might also ask diffusivity of heavier ?

$$\Gamma_H = -D_H \frac{dn_2}{dx} \quad , \text{ by defn.}$$

t also know:

$$V = \mu F$$

$$n_2 V = \underset{\substack{\uparrow \\ \text{net flux}}}{\Gamma_H} = n_2 \mu F$$

ow, what is F, here ?

have, from Boltzmann statistics

$$n_2(x) \sim \exp\left[-\overset{\substack{\text{potential} \\ \downarrow}}{U}(x)/T\right]$$

$$\frac{1}{n_2}\frac{dn_2}{dx} \sim -\frac{1}{T}\frac{dU}{dx} \sim \frac{F}{T}$$

$F = -dU/dx$

so $n_2 F/T \sim dn_2/dx$

$$D_H \cancel{dn_2/dx} \sim n_2 \mu F \sim \cancel{n_2} \mu \frac{T}{\cancel{n_2}} \cancel{\frac{dn_2}{dx}}$$

$$\boxed{D_H \sim \mu T}$$ → Einstein Relation

⇒ relation between mobility of heavy in light gas, and diffusivity.

$$\boxed{D_H \sim T/\rho_L \sigma v_{Th_L}}$$

$$\sim \frac{1}{\rho\sigma}\sqrt{\frac{T^3}{M_1}}$$

→ Can also calculate heat / momentum transport coefficients.

i.e. thermal $\begin{cases}\text{diffusivity}\\ \text{conductivity}\end{cases}$

∇T drives flux

$q = -\chi\, dT/dx$

↳ thermal conductivity

heat flux

Now, heat flux q

$$q = E(T)\, n v$$

$\downarrow$
thermal energy / particle

if dT/dx,

$$q = E(T(x-\ell))\, n v - E(T(x+\ell))\, n v$$

$$= -\frac{dE}{dT}\, \ell \frac{dT}{dx}\, n v$$

$$\sim -(n v_{th})\, \ell \frac{dE}{dT} \frac{dT}{dx} \sim -C(v_{th} \ell) \frac{dT}{dx}$$

$C \equiv n\, dE/dT \equiv$ heat capacity per volume, of gas.

$$\lambda = C D \sim C v_{th} \ell$$

Now $C \sim n\, dE/dT$

$dE/dT \sim O(1)$

$\lambda \sim \cancel{n} \sqrt{T/M}\, 1/\cancel{n}\sigma$

$\sim \sqrt{T/M}/\sigma$

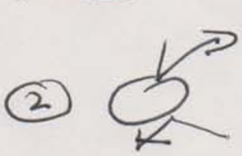
Can also compute viscosity, etc.

Examples:

- total particle flux of lights ?
- total heat flux ?
- ∇V driven concentration flux ?

⇒ Now, how do energy and momentum change in slow processes, i.e. processes where there is a weak deflection of quantity in each collision. ⇒ slow process.

Now, consider a trace heavy particle gas in a gas of lights.



⇒

by momentum conservation

$$\Delta p_2 \sim \Delta p_1$$

So $\langle(\Delta P_2)^2\rangle \sim P_1^2$ as random. i.e. start from rest.

Now [redacted] $\frac{d\langle(\Delta P_2)^2\rangle}{d\ell} \sim (n\sigma)\, P_1^2$

⇒

$$\frac{d}{dt}\langle(\Delta P_2)^2\rangle \sim v_{Th}\, n\sigma\, P_1^2$$

and $\langle(\Delta P_2)^2\rangle \sim v_{Th}\, n\sigma\, t\, P_1^2$

$$\Rightarrow \boxed{\langle(\Delta P_2)^3\rangle \sim v_{Th}\, n\sigma\, P_1^2\, t}$$

mean square momentum change.

Now, for deflection angle evolution:

$\Delta P_2 \sim P_2\, \Delta\Theta$

$$\Rightarrow \langle(\Delta\Theta)^2\rangle \sim v_{Th}\, n\sigma\, P_1^2/P_2^2\, t$$

$$\overset{\infty}{\equiv} \langle(\Delta\theta)^2\rangle \sim n\sigma \sqrt{T}\frac{\sqrt{M_1}}{M_2}$$

$$\sim n\sigma t \frac{\sqrt{TM_1}}{M_2}$$

→ higher temp randomizes faster!

→ $t_{randm} \sim M_2 / \sqrt{TM_1}\, n\sigma$

→ compare $\tau_c / \tau_{randm} \sim \frac{l_{mfp}}{v_{Th}} \frac{\sqrt{TM_1}\, n\sigma}{M_2}$

$$\sim \frac{1}{\cancel{n\sigma}} \sqrt{\frac{M_1}{T}} \frac{\sqrt{TM_1}\, \cancel{n\sigma}}{M_2}$$

$$\sim M_1 / M_2$$

$$\boxed{\tau_c / \tau_{randm} \sim M_1/M_2}$$

⇒ randomization of
heavy particle momentum / motion / direction
occurs after M_2/M collisions.

What about energy ?

(i → e
equilibration

$$\Delta E_2 \sim \Delta\left(P_2^2/M_2\right) \sim \frac{P_2 \Delta P_2}{M_2}$$

$$\Delta P_2 \sim P_1$$

$$\Delta E_2 \sim P_2 P_1 / M_2 \sim \sqrt{M_1/M_2}\, T \ll E_2 \sim T$$

$$\langle(\Delta E_2)^2\rangle \sim \langle(\Delta E_2)^2\rangle_{\text{colln}}\, n\sigma v_1 t$$

$$\sim \frac{M_1}{M_2} T^2 (n\sigma t) \sqrt{T/M_1}$$

$$\sim \frac{\sqrt{M_1 T \sigma}}{M_2}$$

Complete randomization:

$$\langle(\Delta E_2)^2\rangle \sim E_2^2 \sim T^2$$

$$\Rightarrow \tau^{e}_{\text{random}} \sim M_2 / \sqrt{M_1 T}\, n\sigma$$

$\tau_{rndm} / \tau_c \sim M_2 / M_1$, as <u>before</u>.

Diffusion, more deeply ....

— a diffusion process is one example of a Markov / Fokker - Planck process.