Lecture 3 - Gases, Diffusion

- What is a neutral, dilute gas?

- Ensemble of weakly correlated neutral particles (molecules) which are thermally agitated interacting by 2-body collisions.

- Scale:
  - $d$, range of intermolecular force
    - $d = \frac{1}{n^{1/3}}$, intermolecular spacing
    - $\ell_{\text{mfp}}$, mean free path, i.e.

- Collision cross section

- $\sigma$
time between collisions $\leftrightarrow$ length
traversed between collisions.

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

ordering:

| $d$ | $\langle n \rangle^{1/3}$ | $\ell_{mp}$ | $L$ |

usually

and

$\frac{T}{\alpha(z)} \ll$

we dilute

Now, in a dilute distance $L$

particle will have $N$ collisions

$\sim N \ell L$ in this distance. Thus

mean length between collisions is

$L/2 \sim L/\alpha(z) \sim \sqrt{L}$

$\Rightarrow \frac{1}{\alpha(z)} = \ell_{mp}$
\[ \chi \sim \frac{1}{\rho} \sim \frac{v_{th}}{\text{mean free time}} \sim \frac{v_{th}}{(T/M)^{1/2}} \]

In air, at room temperature: \( v_{th} \sim 30 \text{ m/sec} \)

**Quantities of Interest:**

- **fluxes** (heat, particles, concentration)
- **transport coefficients** \( D, \mu, \cdots \)
- **transfer rates**
- **etc.**

**Diagram:**

- Flux \( \text{from } M_1 \text{ into } M_2 \)
- \( C_i(x) \)
- \( M_2 \)
- \( C \)
- \( n_1 + n_2 \sim n_2 \)
- \( c = n_1 / n \)
- \( c \ll 1 \)
- \( T, P \text{ constant} \)

**Note:**
- Linear response
- Define fluxes, entropy production
\[ \frac{dc}{dx} \text{ drives flux of particles.} \]

Then diffusive flux \( \Gamma \):

\[ \Gamma = \left[ n_1(x-e) - n_1(x+e) \right] v_{th} \]

\[ = -e \mu m n_1 \frac{dc}{dx} = -e \mu m n \frac{dc}{dx} \]

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

\[ \Gamma = -e \mu m n \frac{dc}{dx} = -D \frac{dc}{dx} \]

\[ D_0 = n D = n e \mu m. \]

In terms:

\[ D \sim \sqrt{n} \mu m \sqrt{t/M}, \]

\[ \sim \frac{1}{\sqrt{T}} \sqrt{t^3/M}. \]
Some observations:

1. $\Phi \sim n \nu \sim -D \frac{dn}{dx} \sim -\frac{Dn}{L}$

2. Flux:
   - Mean $v_i \sim \frac{L}{L} \sim \frac{D}{L}$
   - Down gradient

3. $\frac{\sigma_0}{\sigma_0} \sim L^2 \frac{V_i}{D}$

   Diffusion is slow.

Now, how else can flux occur?

- i.e. $D T$ drives flux of particles

\[ n \ll N \Rightarrow D T \text{ is supported by } 2 \]
if no gradient in \( n_i \)

\[
\Gamma_i^T = \left[ n_i(x-e) V_i(x-e) - n_i(x+e) V_i(x+e) \right]
\]

\[
\approx n_i(x) \frac{dV_i}{dx}
\]

\[
\approx -n_i \frac{V_i}{T} \frac{dT}{dx}
\]

\[
\Gamma_i^T = -n_i \frac{V_i}{T} \frac{dT}{dx} + DT \text{ driven particle flux}
\]

so if:

\[
\Gamma_i^T = -n_i \frac{V_i}{T} \frac{dT}{dx}
\]

then:

\[
Q_{\text{rad}} \sim c_i u_n \sim c_i D
\]

\[
\sim \frac{c_i}{\sqrt{\gamma M}} \sqrt{\frac{\gamma - 1}{\gamma}} \sqrt{\gamma M}
\]
n.b. $Q_{th}$ depends on concentration of light

How does "diffusion equilibrium" behave, for concentration of light particles in system with temp gradient of heavy particles, i.e. where do light particles concentrate.

New, if at eqn.:

$$\frac{d}{dx} (n_i v) = 0$$

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

$\n \n T = P = \text{const.}$
\[
\frac{d}{dx} \left( \frac{c}{v} \right) = 0
\]

\[c(x) \sim \frac{T(x)}{v(x)} \sim \sqrt{T(x)}
\]

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

Now, consider transport of heavy into light... 

\[\text{much like drag problem of body in fluid, light particles will exert frictional force by momentum exchange with heavier...}
\]

\[c_H \ll c_L
\]

\[F_d \sim \rho R^2 v^2
\]
might expect:

\[ F_0 \sim \sigma_0 \sigma_0 n \nu \]

\[ \nu = \frac{m}{q} \]

\[ \text{mobility, where } \mu = \frac{1}{e} \sigma_0 n \nu \]

Now, to show:

Lights onto momentum to heavy.

in head-on, \( M_1 (\nu + \nabla) \) transferred to heavy.

in overtaking, \( M_1 (\nu - \nabla) \) is transferred to heavy.
\[
\Delta P_{\text{heavy}} \sim M, (V_{\text{th}}+V) - M, (V_{\text{th}}-V) \\
\sim M, V \\
\]

Rate of momentum transfer/change

\[
\frac{\Delta P}{\Delta t} \sim \gamma (\Delta P) \\
\sim (M, V) \frac{V_{\text{th}}}{\text{temp}} \sim \frac{P_L}{\text{temp}} \\
P_L = M V_{\text{th}} \sim \text{light's momentum} \\
\]

\[
F = \mu_i V \\
\mu_i \sim \frac{P_L}{\text{temp}} \\
\mu \sim \frac{1}{\text{mfr}}/P_L \\
\mu \sim \frac{1}{\text{mfr}} \frac{M, V_{\text{th}}}{20 V_{\text{th}}} \\
\text{mobility} \\
\]
One might also ask diffusivity of heavier?

\[ \Gamma^H = -N^H \frac{d N^2}{dx}, \quad \text{by defn.} \]

We also know:

\[ V = u F \]

\[ N^2 V = \Gamma^H = n^2 u F \]

net flux

Now what is \( F \), here \( \Phi \)

have from Boltzmann statistics

\[ n^2(x) \sim \exp \left[ -u(x)/T \right] \]

\[ \frac{1}{N^2} \frac{dN^2}{dx} \sim \frac{-1}{T} \frac{du}{dx} - \frac{F}{T} \]

\[ F = -\frac{du}{dx} \]
\[ \nabla \cdot \mathbf{F} / T \sim d^2 n / dx \]

\[ \frac{d n}{d x} \sim n_2 M F \sim \frac{n_2 M}{n_2} \frac{T}{n_2} \]

\[ D_\# \sim n_2 T \]

\[ D_\# \sim T / \sqrt{T} \sim \sqrt{\frac{T}{M_\#}} \]

\[ \sim \frac{1}{\sqrt{\rho}} \left( \frac{T^3}{M_\#} \right) \]

\[ \Rightarrow \text{Can also calculate heat momentun transport coefficients} \]

\[ \text{or thermal diffusivity, conductivity} \]

\[ z = - \chi \frac{d T}{d x} \Rightarrow \text{thermal conductivity} \]

\[ \text{heat flux} \]

\[ \text{Einstein Relation} \]

\[ \Rightarrow \text{relation between mobility of heavy in light gas and diffusivity} \]

\[ \text{OT driven} \]

\[ \text{flux} \]
Now, heat flux $Q$

$$Q = E(T) n V$$

thermal energy/particle

if $dt/dx$, then

$$Q = E(T(x-e)) n V - E(T(x+e)) n V$$

$$= - \frac{dE}{dT} \frac{dT}{dx} n V$$

$$\sim - (\frac{1}{2} \mu m_l) T \frac{dE}{dT} \frac{dT}{dx} - C(\mu m_l) \frac{dT}{dx}$$

$$C = \frac{\partial E}{\partial T} \equiv \text{heat capacity per volume of gas}$$

$$\chi = C_D - C \mu m_l$$

Now $C = \frac{\partial E}{\partial T}$

$$\frac{dE}{dT} \sim o(1)$$

$$\sim \chi \sqrt{\frac{m}{kT}}$$
Can also compute viscosity, etc.

Examples:
- Total particle flux of lights?
- Total heat flux?
- UV 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 heavy particle in a gas of lights.

1. 
2. 

\[ \Delta P_2 \approx \Delta P_1 \]
\[ \langle (\Delta z)^2 \rangle \sim \rho_1^2 \]

e.g. random, i.e. start from rest.

Now

\[ \frac{d}{d\epsilon} \langle (\Delta z)^2 \rangle \sim (\nu \epsilon) \rho_1^2 \]

\[ \langle (\Delta z)^2 \rangle \sim \nu \epsilon \epsilon_1 \rho_1^2 \]

\[ \langle (\Delta z)^2 \rangle \sim \nu_1 \rho_1 \epsilon_1 + \rho_1^2 \]

Now, for deflection angle evolution:

\[ \Delta z \sim \rho_2 A \theta \]

\[ \langle (A \theta)^2 \rangle \sim \nu_1 \rho_1 \epsilon_1 \rho_1^2 + \epsilon_2 \]
\( \langle (\Delta \Omega)^2 \rangle \sim n \tau \sqrt{\frac{\mu M_1}{M_2}} \)

\( \sim n \tau \frac{\sqrt{\mu M_1}}{M_2} \)

- higher team randomizes faster!

\[ \tau_{\text{track}} \sim \frac{M_2}{\sqrt{\mu M_1} n \tau} \]

\[ \frac{\tau_{\text{track}}}{\tau_{\text{random}}} \sim \exp \left( \frac{\sqrt{\mu M_1} n \tau}{M_2} \right) \]

\[ \frac{T_0}{T_{\text{track}}} \sim \frac{M_1}{M_2} \]

\[ \sim \frac{M_1}{M_2} \frac{1}{\sqrt{\mu M_1} n \tau} \]

\( \tau_{\text{random}} \) is randomization of heavy particle momentum/motion/direction occurs after \( M_2/M_2 \) collisions.
What about energy $\Delta$?

$$\Delta E_2 \sim t \left( \frac{t}{M_2} \right) \sim \frac{t}{M_2}$$

$$\Delta E_2 \sim \frac{t}{M_2}$$

$$\langle (\Delta E_2)^2 \rangle \sim t^2 \frac{M_1 T}{M_2} \cos \theta$$

$$\sim \frac{M_1 T^2}{M_2}$$

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

Complete randomization:

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

$$\Rightarrow \text{tran} \sim M_2 / \sqrt{M_1 T}$$
Find \( \Delta x \sim M_2/M_1 \), as before.

Diffusing more deeply...

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