Transport I

"Stuff"

- gases — colliding particles (dilute) — molecules
- plasmas — charged particles — ions, electrons
  partially ionized gases
- dielectrics — lattices, phonons
- conductors — free electrons, quantum effects
- liquids — colliding particles, (not dilute)

How probe the nature of "stuff"

⇒ Transport

$\boxed{\text{see: Krainov}}$

Key idea: Flux — Force relation.

how flux responds to force.

$$\underbrace{\Gamma}_{\substack{\text{flux} \\ \text{(macro)}}} = - \overbrace{D}^{\substack{\text{transport coefficient} \\ \text{(micro)}}} \underbrace{\nabla n}_{\substack{\text{gradient — thermodynamic force} \\ \text{(macro)}}}$$

i.e. transport ⇔ probe ⇔ response.

Basic Ideas of Transport, Relaxation — Gases

starts from:

⇒ Boltzmann Eqn. and H-Thm

Consider gas, evolving by binary collisions:

then: $$\boxed{\frac{\partial f}{\partial t} + \underline{v} \cdot \underline{\nabla} f = C(f)}$$ → Boltzmann Eqn.

$f = f(q, p, t)$

micro transition probability ~ T

$$C(f) = \int dp_2 \int dp_3 \int dp_4 \; W(p_1, p_2; p_3, p_4) * \left[f(p_1) f(\underline{p}_2) - f(\underline{p}_3) f(\underline{p}_4) \right]$$

↓ collision integral

Collision conserves energy and momentum (i.e. particle dynamics are Hamiltonian)

$\underline{p}_1 + \underline{p}_2 = \underline{p}_3 + \underline{p}_4$; $\epsilon_1 + \epsilon_2 = \epsilon_3 + \epsilon_4$

H-Thm:

$$H = \int d\Gamma \, f \ln f$$ tends increase

↓ entropy

i.e. $\boxed{dH/dt \ge 0}$ $\left\{ \frac{dH}{dt} = 0 \text{ for uniform Maxwellian} \right.$

Proof:

- energy, momentum conservation in single collision
- $f(1,2) = f(1) f(2)$ "Principle of Molecular Chaos"

– $C(f) = 0 \Rightarrow f = f_{Max.}$

i.e. local Maxwellian annihilates the collision integral.

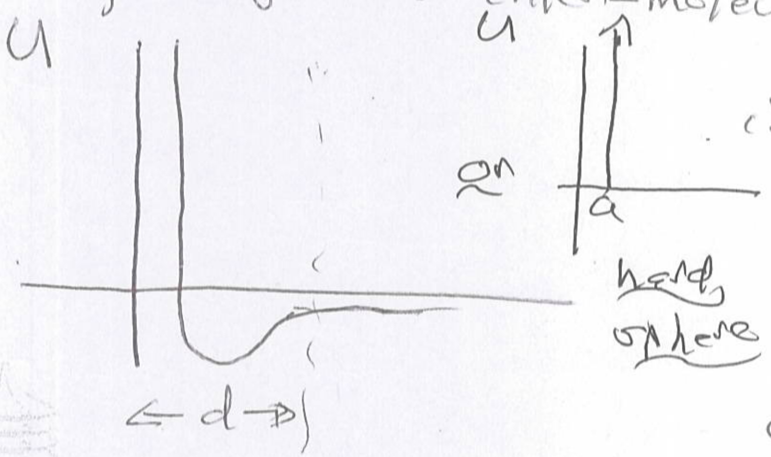
$\Rightarrow$ Regime of Short Mean Free Path or Hydrodynamics

i.e. prototype: neutral, dilute gas

– ensemble of weakly correlated neutral particles (molecules), thermally agitated, interacting by 2 body collisions

– scales:

– d, range of inter-molecular force



i.e. Van-der-Waals

hard sphere $\sigma \sim \pi d^2$

$\Downarrow$

collisional cross section

$d \sim 10\,\text{Å}$

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

- l_{mfp}, mean free path-length traversed between collisions

- L macroscopic system size i.e. box scale, scale of gradients in thermo quantities

so

$$\boxed{d < \langle n \rangle^{-1/3} < l_{mfp} < L}$$

and

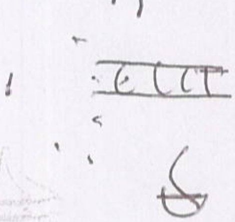
$$\boxed{T/\langle u \rangle >> 1}$$

thermal agitation energy >> interaction energy

are dilute gas, short mfp orderings.

For l_{mfp}:

n



interaction cylinder

Volume $\sim \sigma L$

so # collisions in L

$\alpha = n(\sigma L)$

so $\Rightarrow$ mean length between collisions

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

so $\boxed{l_{mfp} \sim 1/n\sigma}$

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

and collision frequency

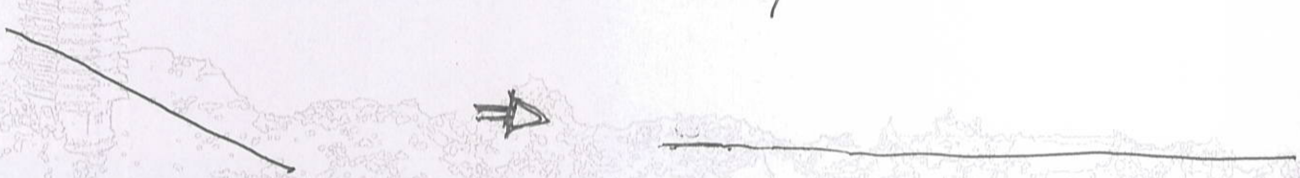
$$v_{Th}/l_{mfp} \sim v_{Th}\, n\sigma \sim \nu_c$$

n.b. $v_{Th} \sim 300$ m/sec. for air, room temp.

Now, in short mean free path regime, describe by moments $\int d^3v\, \underline{v}^n f$, where l.o. are $n(\underline{x})$, $V(\underline{x})$, $T(\underline{x})$ and parametrize Maxwellian locally.

i.e.
$$\langle f \rangle \sim \frac{n(\underline{x})}{(v_{Th}(x))^3} \exp\left[-(\underline{v} - \underline{V}(x))^2 / v_{Th}^2(x)\right]$$

Now, spatial inhomogeneities will relax toward uniformity



$t \to \infty$

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This occurs by diffusive flux, relaxing inhomogeneity of local Maxwellian.

i.e. $\Gamma = -D \underline{\nabla} n$ → linear response

How? → realize inhomogeneity, local Maxwellian does not solve B.E. Correction exists.

→ use correction to calculate flux

Details not required: Chapman-Enskog Expansion

$$\frac{\partial f}{\partial t} + \underline{v} \cdot \underline{\nabla} f = C(f)$$

then st. st. ⇒

$$\underline{v \cdot \nabla} f = C(f)$$

recall: $d < \langle n \rangle^{-1/3} < l_{mfp} < L$

$$C(f) \sim \nu_c f \sim (v_{th}/l_c) f$$

$$\underline{v} \cdot \nabla f \sim v_{th}/L \; f$$

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so

$$f = f_0 + \delta f$$

deviation due inhomog.

expect local Maxwellian.

$$C(f) = 0$$
$$\Rightarrow f = f_{max}$$

relaxn., Krook model

i.e. $$\underline{V}\cdot\underline{\nabla}(f_0 + \delta f) = -\nu[f - f_0]$$

0-O: $$0 = -\nu[f - f_0]$$

$$f = f_0$$

effectively linear response theory

1^{st} O: $$\underline{V}\cdot\underline{\nabla}(f_0) = -\nu\,\delta f$$

linear response

$$\delta f = -\frac{1}{\nu}\,\underline{V}\cdot\underline{\nabla} f_0 \sim \nabla T$$

Then, say, for heat flux due ∇T:

$$\underline{Q} = \int d^3\underline{V}\;\underline{V}\left(\frac{1}{2}mV^2 f\right)$$

total dist.

$$= \int d^3V\;\underline{V}\left(\frac{1}{2}mV^2\left(f_0 - \frac{1}{\nu}\underline{V}\cdot\underline{\nabla} f_0\right)\right)$$

① ②

Now:

① → odd in $\underline{v}$

② → even in $\underline{v}$

$$Q = -\int d^3\underline{v}\ \underline{v}\ \frac{1}{2}mv^2\ \frac{\underline{v}\cdot\nabla f_0}{\nu}$$

$$\cong -\underbrace{K}_{\text{thermal conductivity}}\ \nabla T$$

thermal conductivity (λ used in Krainov)

$\Rightarrow K \simeq C D$

$D \sim v_{th}\, l_{mfp}$

$C = n\, dE/dT$

↓

heat capacity/volume

Note:

- Fluxes follow Fick's Law $\quad Q \sim -D\,\nabla T$

- all particles undergo random walk, due thermal motion

step size $\sim l_{mfp}$

step time $\sim (v_{th}/l_{mfp})^{-1}$ $\qquad D \sim l_{mfp}^2/\tau_c$

Then, entropy production must occur during relaxation, so argue rate by analogy:

$S \to$ energy

(T norm)

$dS/dt \to$ power

$$\text{Power} \simeq \underbrace{\underline{F}}_{\text{force}} \cdot \underbrace{\underline{V}}_{\text{Flux}}$$

$$\to -\underline{\nabla}T \cdot \underline{q}$$

so ⇒

$$\boxed{\frac{dS}{dt} \sim \text{[redacted]} \int \frac{D(\nabla T)^2}{T^2}}$$

entropy production rate during collisional relaxation of spatial inhomogeneity.

⇒ this defines a time scale for relaxation:

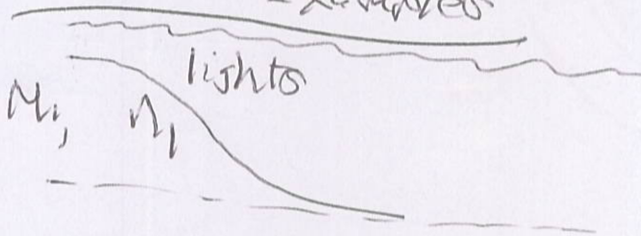
$$1/\tau_D \sim D\left(\frac{\nabla T}{T}\right)^2 \sim \frac{D}{L^2} \sim \left(\frac{l_{mfp}}{L}\right)^2 \nu_c$$

Thus, $\tau_D / \tau_c \sim (L/l_{mfp})^2 \gg 1$.

→ Relaxation to maximum energy state is two step process:

- fast relaxn to local Maxwellian, on 1 collision time
- slow relaxn to uniform Maxwellian, on $(L/l_{mfp})^2$ collision times.

Specific Examples



heavier m_2, n_2

T, P const.

$m_1 < m_2$

$n_1 + n_2 \sim n_2$

i.e. $n_1 \ll n_2$

$c = n_1/n_2 \ll 1$.

what happens:

- dc/dx driven flux of n_1 particles (lighter)
- so c diffuses (agitation + gradient)

$\Gamma_1 = [n_1(x-l) - n_1(x+l)] V_{T_1} \ldots \equiv \ldots$

so

$$\Gamma \cong -l v_{Th_L} \frac{dn_1}{dx} \cong -l v_{Th_L} n \frac{dc}{dx}$$

$n \simeq n_2$

i.e. equal probability jumping either way, but more on LHS.

$l = l_{mfp}$ with σ_{LH} (light-heavy)

so $\boxed{\Gamma \sim -D_c\, dc/dx}$

$\boxed{D_c \cong n D \cong n l v_{Th_L}}$ → concentration diffusivity.

D indep. concen.

In pragmatic terms:

$D_c \sim n D,$

$$D \sim \frac{1}{n_2 \sigma} \sqrt{T/M_1}$$

$$\sim \frac{1}{p \sigma_{LH}} \left(T_L^3 / M_1 \right)^{1/2}$$

$v_{Th} \sim 800$ m/sec

$\sigma \sim \pi d^2$

$d \sim 10 Å$

$10^{25}\ m^{-3} = n$, air.

[co]mpute D.

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Some observations

– $\underbrace{\Gamma}_{\text{flux}} \sim nV \sim -D\frac{\partial n_1}{\partial x} \sim -Dn/L$

Mean flow $V \sim \Gamma/n_1 \sim D/L \sim v_{Th}\, l_{mfp}/L$
down gradient

– $\tau_D/\tau_c \sim (L n \sigma)^2$
slow!

More questions:

– how else drive flux of lights ① into heavies ②? ($\nabla n_1 = 0$)

– where do light particles concentrate in system with inhomogeneous temperature?

① – Temperature gradient!

$n_1 \ll n \Rightarrow T$ supported by $n_2 \sim n$.

$\nabla n_1 = 0$

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so

$$\Gamma_i = \left[n_i \left(x - \tfrac{\ell}{2}\right) v_{th}(x - \ell/2) - n_i \left(x + \tfrac{\ell}{2}\right) v_{th}\left(x + \tfrac{\ell}{2}\right) \right]$$

homog.

$$\cong + n_i (-\ell) \frac{d v_{th}}{dx}$$

$$\sim n_i \frac{v_{th} \ell}{T} dT/dx$$

$$\boxed{\Gamma_T \sim - n_i \frac{v_{th} \ell}{T} \frac{dT}{dx}}$$

$\Rightarrow$ ∇T driven particle flux

so if:

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

$$\boxed{\begin{aligned} D_{T,d} &= C_1 \ell v_{th} \\ &= c_1 D \end{aligned}}$$

$$\boxed{D_{T,d} \sim \frac{c}{n \sigma_{LH}} \sqrt{T/M_i} \sim \frac{n_i}{\rho^2 \sigma_T} \left(T^5/M_i\right)^{1/2}}$$

n.b. $D_{T,d}$ demands/requires concentration of lights.

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- where do lights go?

⇒ asks what is equilibrium?

⇒ zero flux ⇒ $n_l(x-\ell)\, v_T(x-\ell) = n_l(x+\ell)\, v_{th}(x+\ell)$

$\therefore \; d/dx(n\, v_{th}) = 0$

but for lights: $\frac{d}{dx}\left(c n\, v_{th}\right) = \frac{d}{dx}\left(c n T \frac{v_{th}}{T}\right)$

but $p \sim$ const.

$$\Rightarrow \boxed{\frac{d}{dx}\left(c p \frac{v_{th}}{T}\right) = 0}$$

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

lights concentrate in region of high temperature!

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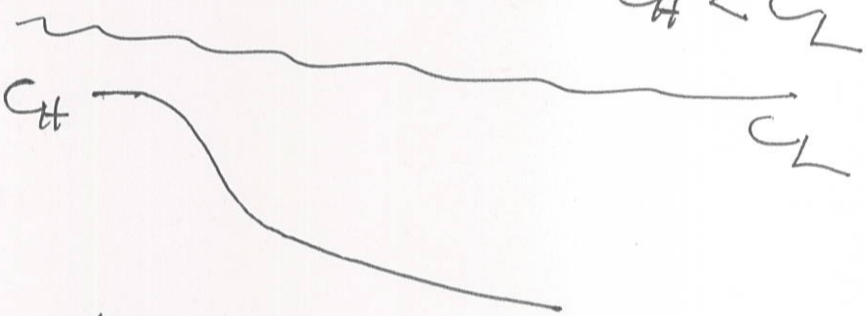
→ Transport of Heavies onto Lights.

i.e. consider case $C_H < C_L$



— akin sphere-in-fluid problem.

So, — if force acts on heavies, expect drag, and steady frictional velocity

— should be consistent with linear response theory.

i.e.

$$\underline{F}_d \simeq \alpha_{drag} \underline{V}$$

or

$$\underline{V} = \mu \underline{F}$$

mobility → velocity measure.

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Now, one might view light gas as fluid

so $F_D \sim \rho_L R^2 V^2$

$R^2 \to \sigma$

$V^2 \to (V_{th} \pm V)$

big

tends cancel

so might expect:

$$\underline{F}_D \sim \rho_L \sigma_{LH} V_{th} \underline{V}$$

so $$\boxed{\mu \simeq 1/\rho_L \sigma_{LH} V_{th_L}}$$

$V_{th_L} \sim (T_L/M_L)^{1/2}$

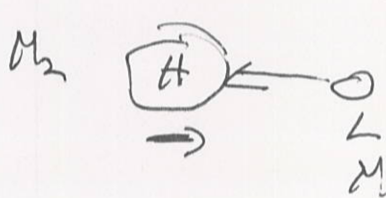
mobility of heavy particle

Now, to show:

Lights bounce off heavies

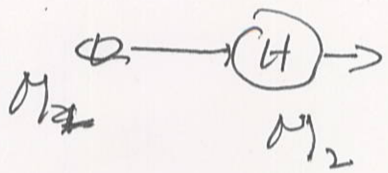
consider difference of:

head on collision



$\Rightarrow M_1(\underline{V} + V_{th})$ transferred to heavy

overtaking collision



$\Rightarrow M_1(V_{th} - \underline{V})$ transferred to heavy

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so

$$\Delta P_H \sim M_1 (v_{th} + \underline{V}) - M_1 (v_{th} - \underline{V})$$

$$\sim M_1 \underline{V}$$

change in heavy momentum

so for force:

light-heavy colln freq.

$$\frac{\Delta \underline{P}_H}{\Delta t} \sim \nu_{c\,LH} \, (\underline{\Delta P}) \sim (M_1 \underline{V}) \frac{v_{th}}{l_{mfp}}$$

mom change/colln.

rate momentum change/time

$$\sim (M_1 \underline{V}) \, v_{th} \, n \, \sigma_{LH}$$

$\rho = M_1 n_1$

$$\boxed{\underline{F} \sim (\rho \, v_{th} \, \sigma_{LH}) \, \underline{V}}$$

so $$\boxed{\mu = 1/\rho \, \sigma \, v_{th}}$$

is the mobility.

have established mobility of heavies in lights.

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→ What is Diffusivity of Heavies?

- Heavies diffuse, as thermally agitated lights will randomly kick them, akin to thermal fluctuations kicking Brownian particle.

- Diffusive flux requires gradient in heavies.

i.e.

$$\Gamma_H = -D_H \frac{dn_2}{dx}$$

$$\Downarrow$$

?

now

$$\boxed{\underline{\Gamma}_H = n_2 \underline{V}} \qquad \text{(flux)}$$

but $\underline{V} = \mu \underline{F}$ → mobility.

so

$$\underline{\Gamma}_H = \mu \underline{F} \qquad \mu = 1/C_L \tau_{LH} v_{ThL}.$$

What is F?

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expect $\underline{F}$ must be thermodynamic
i.e. $\sim -dn_H/d\underline{x}$. How estimate?

Now, if force acts on H, then H moves in potential U. So near eqbrm.

potential

$$n_2(\underline{x}) \cong \exp\left[-U(\underline{x})/T\right]$$

$$\frac{1}{n_2}\frac{dn_2}{d\underline{x}} \simeq -\frac{1}{T}\frac{dU}{d\underline{x}} \cong \frac{+1}{T}\underline{F}$$

defines force!

So

$$\underline{F} = -\frac{T}{n_2}\frac{dn_2}{d\underline{x}}$$ (force down gradient)

$$\Gamma_H = -D_H\frac{dn_2}{d\underline{x}} = n_2\mu\underline{F} = -n_2\mu\frac{T}{n_2}\frac{dn_2}{d\underline{x}}$$

$\Rightarrow$ D_H given by μT.

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$$\boxed{D_H = \mu T}$$ ~ Einstein Relation

~ Relates mobility and Diffusion

$$\boxed{\mu_H = 1/\rho_L \sigma_{LH} v_{TL}}$$ ~ Related FDT

Lights are thermal fluctns in fluid, kicking Brownian particle.

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

$$\sim \left(T_L^3/M_L\right)^{1/2} \frac{1}{\rho\, \sigma_{LH}}.$$

Note: Lights mobilize heavier here!

⇒ Can calculate $\left\{\begin{array}{l}\text{heat}\\ \text{momentum}\end{array}\right.$ transport coefficients

i.e. thermal conductivity

$$\left\{\begin{array}{ll} q = -\chi\, dT/dx \;; & \nabla T \text{ driver.} \\ \pi_{xy} = -\eta\, \partial v_y/\partial x \;; & \nabla v \text{ driver} \end{array}\right.$$

momentum flux.

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Now, heat flux q:

$$q = \underbrace{E(T)}_{\text{thermal energy/particle}} n v$$

if dT/dx, and $E(T)$ absorbs $T(x)$ in V

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

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

$$\boxed{\begin{aligned} q &= -c\,(v n \ell)\, dT/dx = -c\, D\, dT/dx \\ c &\equiv n\, dE/dT \rightarrow \text{heat capacity/volume of gas.} \\ \lambda &= cD = c\, v_{th}\, \ell_{mfp} \end{aligned}}$$

Now; $c \sim n\, dE/dT$

$dE/dT \sim O(1)$

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

can also compute viscosity, etc.