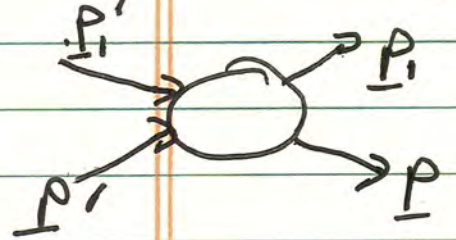
Notes I ; Section III →

- → Fluid Equations (Ideal)
- → Transport Coefficients
- → Viscous Fluids

Recall:

- classical, { hard sphere iteraction
  dilute gas



local ⇒ W

$nd^3 \ll 1$

⇒

- Boltzmann Equation

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

$$C(f) = \int d\underline{p}' \int d\underline{p}_1' \int dp_1 \left[f(\underline{p}')f(\underline{p}_1') - f(\underline{p}_1)f(\underline{p}) \right] \underbrace{W(\underline{p}', \underline{p}_1'; \underline{p}, \underline{p}_1)}_{\text{transition probability}}$$

- use: { $nd^3 \ll 1$
  detailed balance
  Molecular Chaos

– cont'd to truncate BBGKY hierarchy.

⇒ Eqn. $f(1,t)$.

– H-Theorem

$$S = \int d\underline{x}\, s = \int d\underline{x}\, d\underline{p}\, (-f \ln f)$$

– entropy

showed:

$$\frac{dS}{dt} \geq 0$$

Macroscopic order from microscopic reversibility and molecular chaos.

key: Detailed Balance
Molecular Chaos

Some up-shots:

– $\frac{dS}{dt} = 0$ ⇒ $\frac{ds}{dt} = 0$

locally $f' f_1' = f_1 f$

$$\Rightarrow \ln f' + \ln f_1' = \ln f_1 + \ln f$$

so at equilibrium, $\ln f$ must be additive for collision.

so collision operator conserves:

- number
- momentum
- energy

and must be normalizable.

$$\ln f = c + \alpha \underline{V}\cdot\underline{p} - \beta\epsilon \qquad \beta > 0$$

$$\epsilon_1 + \epsilon = \epsilon_1' + \epsilon'$$

$$\underline{p}_1 + \underline{p} = \underline{p}_1' + \underline{p}'$$

$$f_0 = c\, n_0 \exp\left[-\frac{(\epsilon - \underline{p}\cdot\underline{V})}{T}\right]$$

equilibrium is Maxwellian.

- i.e. local equilibrium, scale l_{mfp}

$$f = c\, n_0(\underline{x}) \exp\left[-(\underline{v} - \underline{V}(\underline{x}))^2 m / T(\underline{x})\right]$$

$n \to$ density

$\underline{V} \to$ flow

$T \to$ temperature

— "global equilibrium"

$n, T, \underline{V}$ constant.

Note:
f_{eq} local
does <u>not</u>
solve Boltzmann
equation unless
$\underline{V} \cdot \nabla f_{eq} = 0$
(homogeneous)

$C(f)$: → drives to local
equilibrium on
collision time scale

Inhomogeneity
→
deviation from
maximum
entropy state.

$\nu_c \sim \frac{v_{Th}}{l_{mfp}} \sim$ [redacted].

$\sim v_{Th}\, n\, \sigma$

Recall $W \sim v_{rel}\, d\sigma$.

→ global equilibrium on

$$\frac{1}{\tau_{relax}} \sim \frac{D}{L^2} \sim \frac{v_{Th}\, l_{mfp}}{L^2}$$

$1/\tau_{relax} \sim \nu_c \left(\frac{l_{mfp}}{L}\right)^2$ $\tau_c \ll \tau_{relax}$

Recall: $d < \bar{r} < l_{mfp} < L$

Global Relaxation ⇒ transport!
⇒ how calculate transport coefficients?

N.B. - Collision is $\underline{\underline{local}}$ (Stosszahl-ansatz) - $d < l_{mfp}$ -
so establish local equilibrium on ν_c^{-1} scale

- Later relax to constant n, T, $\underline{V}$

Simplified Collision Operator

→ Collision operator is nonlinear and complex.

→ convenient to use reduced form:

$$\frac{\partial f}{\partial t} + \underline{v}\cdot\underline{\nabla} f = C(f)$$
$$= -\nu_{eff}\left(f - f_{eq}\right)$$

f_{eq} → *local* Maxwellian. $\left(f_{eq} \neq f\right)$

$\nu_{eff} = \nu =$ collision frequency

⇒

$C(f)$ as local relaxation process

- Krook Model, Operator

  BGK Model: $\left\{\begin{array}{l}\text{Bhatnagar}\\ \text{Gross}\\ \text{Krook}\end{array}\right.$

  ($\neq$ BGK mode, plasma).

- also a "*Crook*" model

  - does not conserve momentum, energy

  - nonlinearity buried.

⇒ Krook models are crooked, but useful.

⇒ How use Boltzmann Eqn ?

— f evolution → 6 D (painful).

— recall scale ordering:

$$d < \bar{r} < l_{mfp} < v_{Th}$$

so

For $l \geq l_{mfp}$ — macroscopic scales

— $f \sim f_{eq}$.

Why solve for f ?

Solve for parameters of f_{eq}

$$\left.\begin{array}{l} \rightarrow n(\underline{x}, t) \\ \underline{V}(\underline{x}, t) \\ T(\underline{x}, t) \end{array}\right\rangle \Rightarrow \text{fields for fluid model.}$$

$k_b = 1$.

→ $\boxed{\text{Fluid Equations}}$

- what to do with B.E. ⇒ [not a substitute for proper study of fluid mechanics

{ fluid eqns. [illegible]
{ transport coefficients → flux – force proportionality
$\Gamma = -D\nabla n$

- replace B.E. by set of equations which evolve thermodynamic parameters (f_eq param.)

⇒ hydrodynamic equations for $n(\underline{x},t)$, $\underline{V}(\underline{x},t)$, $P(\underline{x},t)$ etc.

- local, Eulerian description (lab frame)
→ held together by collisions vs. dispersion
- describes 'blobs' of gas, held together by collisions ; $L > l_{mfp}$, $\omega < \nu_{coll}$ } scales of relevance

fluid element

- parametrizes dynamics in terms structure of distribution

$$f = \frac{n(\underline{x})}{(2\pi)^{3/2}\, v_{th}(\underline{x})^3} \exp\left[-\left(\underline{v}-\underline{V}(\underline{x},t)\right)^2 / v_{th}^2(\underline{x},t)\right]$$

$n,\ \underline{V},\ T;\quad P = nT$

- works for slight deviation from equilibrium.

Total Distr:

i.e. $f = f_{eq} + \delta f$

$\Downarrow$ local Maxwellian $\Downarrow$ ideal equations

$\hookrightarrow \delta f = -\frac{\underline{v}\cdot\nabla f_{eq}}{\nu} \sim l_{mfp}\nabla f_{eq}$

$\Downarrow$ viscous dissipative eqns.

sacrifices info re: higher moments (usual energy truncation). → why care?/ i.e. heat flux, beyond?

now, **recall:**

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

demand: $\int d^3\underline{v}\, C(f) = 0$ (# conservation)

(easily shown) $\int d^3\underline{v}\, m\underline{v}\, C(f) = 0$ (momentum conservation)

$\int d^3\underline{v}\, \epsilon\, C(f) = 0$ (energy conservation)

then define:

$n = \int d^3v\, f$ → density

$\underline{V} = 1/n \int d^3v\, \underline{v}\, f$ → velocity / momentum

10.

$$\bar{\epsilon} = \frac{1}{n}\int d^3\underline{v}\ \epsilon f \rightarrow \text{energy density}$$

phase space

$$\downarrow$$

and $\partial_t f + \partial_{x_i}(v_i f) = C(f)$

taking moments:

conservative form

$$\frac{\partial n}{\partial t} + \underset{\substack{\text{mass}\\ \text{flux}}}{\underbrace{\nabla\cdot(n\underline{v})}} = \underset{\#\text{ cons.}}{\underbrace{0}}$$

(number conservation)

$$\frac{\partial}{\partial t}(m v_\alpha) + \underset{\left[\substack{\text{momentum}\\ \text{flux}}\right]}{\underbrace{\frac{\partial}{\partial x_\beta}\Pi_{\alpha\beta}}} = \underset{\text{mom. cons.}}{\underbrace{0}}$$

(<u>mom</u>entum <u>bal</u>ance)

$$\Pi_{\alpha,\beta} = \int d^3v\ m v_\alpha v_\beta f$$

$$\frac{\partial(n\bar{\epsilon})}{\partial t} + \underset{\substack{\text{energy}\\ \text{flux}}}{\underbrace{\underline{\nabla}\cdot\underline{q}}} = \underset{\substack{\text{energy}\\ \text{cons.}}}{\underbrace{0}}$$

(<u>energy</u> <u>balance</u>)

$$\underline{q} = \int d^3\underline{v}\ \underline{v}\,\epsilon f$$

[redacted]

note form: conservation

$$\boxed{\frac{\partial}{\partial t}(\text{stuff}) + \underline{\nabla}\cdot(\text{Flux of stuff}) = 0}$$

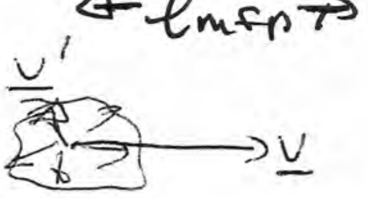
→ essence is calculation of fluxes.

Further simplify by:

$$\underline{v} = \underset{\text{macro}}{\underline{V}(\underline{x},t)} + \underset{\text{micro}}{\underline{v}'}$$

$\underline{V}$ ↓ mean/bulk flow (~ linked to body forces)

$\underline{v}'$ ↓ thermal fluctuation about mean $(\sim\sqrt{T/m})$



realistically! $|\underline{V}| \ll |\underline{v}'|$

{ but v''s cancel

so

$$\Pi_{\alpha,\beta} = \int d^3v\, m\,(V_\alpha(\underline{x},t) + v'_\alpha)\,(V_\beta(\underline{x},t) + v'_\beta)\, f$$

$$f = f_{eq.} + \cancel{\delta f}$$

here ↔ "ideal" fluid.

$f_{eq.}$ ↓ loc. Maxwellian, as above.

$\cancel{\delta f}$ → neglected

so

$$\Pi_{\alpha,\beta} = mn\left(V_\alpha(\underline{x},t)\,V_\beta(\underline{x},t) + \langle v'_\alpha v'_\beta\rangle\right)$$

[redacted]

now, $$f = \frac{n(\underline{x})}{(2\pi)^{3/2} v_{th}^3(x)} \exp\left[-\frac{(\underline{v}-\underline{V}(\underline{x},t))^2}{v_{th}(x)^2}\right]$$

(assumption ?)

$$\langle v'_\alpha v'_\beta \rangle = 1/3\, v'^2 \delta_{\alpha,\beta}$$ (~ isotropic f_{eq}, $\forall \underline{v}$)

$$\langle v'^2 \rangle = 3T/m$$

(collisions isotropize pressure)

so, can define:

~~stress~~

$$\underline{\underline{P}} = mn \langle v'_\alpha v'_\beta \rangle$$ → ~~[illegible]~~ tensor

stress tensor

$$= \frac{1}{3} mn \langle v'^2 \rangle \delta_{\alpha,\beta}$$

$$p = nT$$

(Diagonal for ideal fluid)

so

$$\frac{\partial}{\partial t}(n\underline{V}) + \underline{\nabla}\cdot\left(n\underline{V}\,\underline{V} + \underline{\underline{I}}\,p\right) = 0$$

but:
$$\frac{\partial n}{\partial t} + \nabla\cdot(n\underline{v}) = 0$$

Euler Eqn:

subtracting →

$$\boxed{n\left(\frac{\partial}{\partial t}\underline{v} + \underline{v}\cdot\nabla\underline{v}\right) = -\underline{\nabla} p}$$

"Euler Eqn."

(+ visc → Navier-Stokes)

incompressible $\underline{\nabla}\cdot\underline{V} = 0$

13.

[redacted]

$\underline{\nabla}\cdot\underline{V} = 0$ <u>defines</u> p. (incompressible fluid).

Similarly,

$$\epsilon = \tfrac{1}{2}mv^2 + \epsilon'$$

$$= \frac{1}{2}m\,(\underline{V}(\underline{x},t) + \underline{v}')^2 + \epsilon'$$

so $$\underline{Q} = \int \epsilon\, \underline{v}\, f\, d^3\underline{v}$$

$$\cong \int \epsilon\, v\, f_0\, d^3\underline{v}$$

$$\underline{Q} = \int d^3\underline{v}\ (\underline{V}(\underline{x},t) + \underline{v}')\,(\epsilon' + \underset{\to p\underline{V}}{\tfrac{1}{2}m}(\underline{V}(\underline{x},t) + \underline{v}')^2)f$$

$$= \underline{V}(\underline{x},t)\,(\tfrac{1}{2}nmV^2 + \underbrace{p + n\bar{\epsilon}}_{\hookrightarrow\ w \to \text{[redacted] enthalpy}})$$

so

$$\frac{\partial}{\partial t}(n\bar{\epsilon}) + \underline{\nabla}\cdot\left[\underline{V}(\underline{x},t)\left(\frac{1}{2}mnV^2 + p + n\bar{\epsilon}\right)\right] = 0$$

↓

can <u>simplify</u> as for <u>momentum</u>.

→ angular momentum not conserved by $C(f)$!

⇒ $\boxed{\text{most truncations stop at 3rd moment}}$

Now, for transport: [Flux – Gradient Relations !

→ what if f_0 has gradient ? $T(x)$

⇒ drives δf

i.e. Chapman-Enskog expansion

$$\Rightarrow \delta f = -\frac{1}{\nu_c}\,\underline{v}\cdot\underline{\nabla} f_{eq}$$

→ then $f_0 + \underline{\underline{\delta f}}$ set fluxes, so

$$\text{Flux} = \underset{\overset{\uparrow}{f_{eq}}}{\text{ideal part}} + \underset{\overset{\uparrow}{\delta f}}{\text{collisional part}}$$

⇒ transport.

Key Point: How relate fluxes to gradients in thermodynamic quantities ?

Non-Ideal Fluids, Transport, Chapman-Enskog [redacted]
(Viscous) [redacted]

Applications of the Boltzmann Equation [redacted]

→ Chapman-Enskog ⇝ Basics (C-E Light)

- a major application of B.E. is calculation of transport coeffs.

- recall, fluid equations [redacted] involve momentum, heat flux

i.e. really $\frac{\partial \underline{v}}{\partial t} = -\nabla\cdot\underline{\underline{\Pi}}$, etc.

continuity form

here:

$$\Pi_{\alpha,\beta} = mn\,(u_\alpha V_\beta + \langle v'_\alpha v'_\beta\rangle)$$

$$\langle v'_\alpha v'_\beta\rangle = \int d^3v\; f\; v'_\alpha v'_\beta$$

if $f = f_{eq} = \frac{n(x)}{(2\pi)^{3/2} v_{Th}(x)^3}\exp\left[-\frac{(\underline{v}-\underline{V}(x))^2}{2 v_{Th}^2}\right]$

⇒

$$\langle v'_\alpha v'_\beta\rangle = \frac{1}{3}\langle v^2\rangle\,\delta_{\alpha,\beta}$$

$$\langle v^2\rangle = 3T/m$$

but [redacted] is f = f_{eq} ?!

recall, f satisfies:

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

f_{eq} is soln. to $C(f) = 0$.

$\Rightarrow$ $\boxed{\text{$f_{eq}$ cannot solve B.E. unless } \underline{\nabla f_0 = 0}}$!

can assign time scales:

$\partial_t f \rightarrow \omega$

$\underline{v} \cdot \underline{\nabla} f \Rightarrow v_{Th}/L$

$C(f) \rightarrow \nu$;

Collisional regime has $\nu > \frac{v_{Th}}{L}, \omega$

$d < \bar{r} < l_{mfp} < L$

$\nu = \frac{v_{Th}}{l_{mfp}}$ $\quad \frac{v_{Th}}{L} < \nu.$

$l_{mfp} = 1/n\sigma$

$\Rightarrow$ $\boxed{\text{$f_{eq}$ is 0th order solution.}}$

then if f_0 is homogeneous $\Rightarrow$ [stationary solution has correction!

$f = f_0 + \delta f$

$\hookrightarrow$ ~ inhomogeneity $\Downarrow$ $\Rightarrow$ [more precisely response to inhomogeneity

i.e. $\nabla T, \nabla V$

$\Downarrow$

and $\langle v'_\alpha v'_\beta \rangle = \int d^3v \, (\underset{\uparrow}{f_0} + \delta f) \, v'_\alpha v'_\beta$

$\Downarrow$

$= \underset{\uparrow}{p} \, \delta_{\alpha,\beta} + \underline{\underline{\text{Viscous stress}}}$

$\sim \nabla \bar{V}$

$$\text{viscosity} \sim mn\,D \qquad D \sim l_{mfp} V_{th}$$

$$\text{i.e.}\quad mn\langle V'_\alpha V'_\beta\rangle_{visc} = -\overset{\downarrow}{\eta}\,\frac{\partial \langle V_\alpha\rangle}{\partial x_\beta} + \cdots$$

↳ generic form of viscous stress → flux-grad-rel'n.

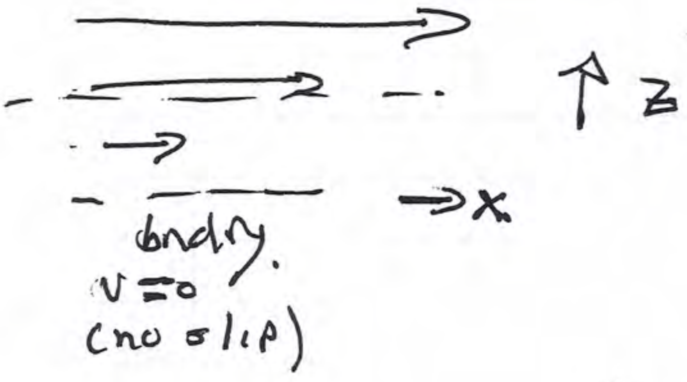
so, need:

- understand viscosity, etc.
- see how calculate δf and then transport coeffs (viscosity)

so what is viscosity about?

- simple physics of transport coeffs!

Consider collisional gas:

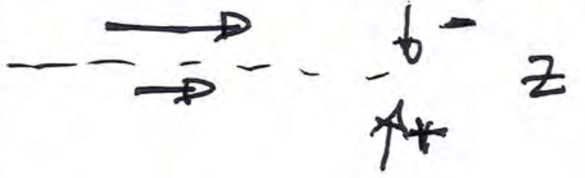


mean flow

$$\underline{V} = V(z)\,\hat{x}$$

i.e. shear flow (gradient ⊥ flow)

choose imaginary surface:



Calculate transport of $\hat{x}$ momentum thru surface:

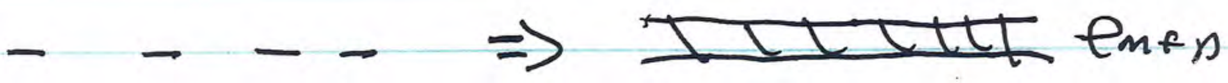
$$\Pi_+ = \int_{v_z>0} d\underline{v}\; m V_x v_z f$$

$$\sim v_{Th} \bar{V} n m_+$$

$$\Pi_- = \int_{V_z<0} d\underline{v}\; m V_x V_z f$$

at first glance, would appear $\Pi_+ = \Pi_-$

so $\Pi_{tot} = 0$?! but! :



→ "scale of resolution" for imaginary surface is ℓmfp ⇒ defines effective thickness.

→ $\boxed{V(z) \text{ has gradient across this!}}$

so

$$\Pi_{tot} = \Pi_- + \Pi_+$$

⊗

$$\Pi \cong \overbrace{-n m v_{Th} \bar{V}\left(z + \frac{l_{mfp}}{2}\right)}^{\Pi_-} \underbrace{+ n m v_{Th} \bar{V}\left(z - \frac{l_{mfp}}{2}\right)}_{\Pi_+}$$

$$\cong -n m v_{Th} l_{mfp} \frac{\partial \bar{V}}{\partial z}$$

$$\cong -n m \overset{\sim l_{mfp} v_{Th}}{D} \frac{\partial \bar{V}}{\partial z}$$

$$= -\nu \frac{\partial \bar{V}}{\partial z}$$

ν → viscosity (shear)

$\sim \underline{\rho D}$ $\qquad D \sim v_{Th} r$

→ Key Points:

- equal # collisional kicks in +, - direction, but
- more momentum kicked down from above, the velocity gradient.

⇒

- net viscous momentum transport via collisions to relax gradient

[redacted]

How calculate systematically?

⇒ Chapman-Enskog expansion!

now

$$\frac{\partial f}{\partial t} + \underbrace{\underline{v}\cdot\underline{\nabla} f}_{\frac{v_{Th}}{L}} = \underbrace{C(f)}_{\nu_{eff.}}$$

{ multiple time scales

$\nu > \frac{v_{Th}}{L}$

f norm ton

and seek:

$$\underbrace{\Pi_{z,x}}_{} = \int d^3v\, v_z\, (m v_x f)$$

z direction flux of $\hat{x}$ momentum

$$f = f_{eq} + \delta f$$

$$\Pi_{zx} = \int d^3v\, v_z\, (m\, v_x\, (f_0 + \delta f))$$

if $f_{eq} \cong \frac{n_0}{v_{Th}^3} \exp\left[-\frac{(\underline{v} - V(z)\hat{x})^2}{2 v_{Th}(x)^2}\right]$

{i.e. local Maxwellian}

→ f_{eq} contribution vanishes by symmetry !

so

$$\Pi_{z,x} = \int d^3v \, v_z \, (m \, v_x) \, \delta f$$

↑ drives the flux.

How get δf ?

⇒ Perturbative solution !?

$\underline{v} \cdot \nabla f = C(f)$ → really an integral equation !

l. O.: $C(f) = 0$

$f = f_{eq}$ → Local Maxwellian

1st O. :

$\underline{v} \cdot \underline{\nabla} f_0 = C(\delta f)$

$\therefore \quad \delta f = C^{-1} \left[\underline{v} \cdot \nabla f_{eq} \right]$

How ?

→ lengthy calculation

→ Krook (crook) Model !

$$C(f) = -\nu\left(f - f_{eq}\right)$$

↓

collisional decay to
local Maxwellian
caveat Emptor!

or

$$\underline{v}\cdot\underline{\nabla} f = C(f) = -\nu\left(f - f_{eq}\right)$$

$$f = f_{eq} + \delta f$$

$$\underline{v}\cdot\underline{\nabla}\left(f_{eq} + \delta f\right) = -\nu\left(f - f_{eq}\right)$$

l.o. ; $-\nu\left(f - f_{eq}\right) = 0$

$$f = f_{eq}$$

1st order :

$$\underline{v}\cdot\underline{\nabla} f_{eq} = -\nu\,\delta f$$

$$\delta f = -\frac{\underline{v}\cdot\underline{\nabla}}{\nu} f_{eq}$$

↓

perturbative correction to fo ; $O\left(\frac{v_{Th}}{L\nu}\right)$

So

$$\Pi_{z,x} = \int d^3v \; v_z \; m v_x \; \delta f$$

$$= \int d^3v \; v_z m v_x \left(- \frac{v_z}{\nu} \frac{\partial}{\partial z} f_0 \right)$$

$$\bar{V}\hat{x} = V(z)\hat{x}$$

now $$f_0 \cong \frac{n(\underline{x})}{v_{Th}^3(\underline{x})} \exp\left[- \frac{(v - V(z)\hat{x})^2}{2 v_{Th}^2(\underline{x})} \right]$$

$$= \frac{n}{v_{Th}^3} \exp\left[- \frac{(v - V(z))^2}{2 v_{Th}^2} \right]$$

$$\frac{\partial f_0}{\partial z} = \frac{n}{v_{Th}^3} \frac{v_x}{v_{Th}^2} \frac{\partial V(z)}{\partial z} \exp[\;\;]$$

linear response.

$$- 2 \frac{V(z)}{v_{Th}^2} \frac{\partial V(z)}{\partial z} \exp[\;\;]$$

see [redacted] next

[redacted]

dropped ⇒ interested in only linear response of flux to gradient.

⇒ $$\frac{\partial f_0}{\partial z} = f_0 \frac{v_x}{v_{Th}^2} \frac{\partial V(z)}{\partial z}$$

[redacted]

Note:

→ here seek linear relation between flux and gradient

→ presumes weak distortion from Maxwellian, i.e.

$$f_{eq} = \frac{n}{v_{Th}^3} \exp\left[-\frac{(v - \bar{V}(z)\hat{x})^2}{2 v_{Th}^2} \right]$$

$$= \frac{n}{v_{Th}^3} \exp\left[-\frac{(v^2 - 2v\bar{V} + V^2)}{2 v_{Th}^2} \right]$$

$$\cong \frac{n}{v_{Th}} \exp\left[\frac{-v^2}{2 v_{Th}^2} \right] \left[1 + \frac{v_x \bar{V}}{v_{Th}^2} \right]$$

$$= f_{eq}\left(1 + \frac{v_x \bar{V}}{v_{Th}^2} \right)$$

↑ e.o. factor on expansion

yields result.

up-coming → "Linear Response Theory"

Green-Kubo Relation

so

$$\Pi_{z,x} = \int d^3x \; v_z \, m v_x \left(-\frac{v_z}{\gamma} \frac{v_x}{v_{Th}^2} \times f_{eq} \frac{\partial V(z)}{\partial z} \right)$$

$$= -\# \frac{mn}{\gamma} v_{Th}^2 \frac{\partial V(z)}{\partial z}$$

$$= -\# \, mn \underbrace{\left(\frac{v_{Th}}{\gamma}\right)}_{l_{mfp}} v_{Th} \frac{\partial V(z)}{\partial z}$$

$$D = v_{Th} \, l_{mfp}$$

$$\boxed{\begin{aligned} \Pi_{z,x} &= -\# \, mn D \frac{\partial V(z)}{\partial z} \\ &= -\# \rho D \frac{\partial V(z)}{\partial z} \end{aligned}}$$

$$\eta = -\# \rho D$$

⇒ basic result for collisional shear viscosity!

[redacted]

Note form of result:

$$\underset{\substack{\downarrow \\ \text{flux}}}{\Pi_{zx}} = -\underbrace{\#nmD}_{\substack{\text{microscopics} \\ \downarrow \\ \text{transport} \\ \text{coefficient}}} \frac{\partial V_x(z)}{\partial z}$$

↳ gradient of thermo. quantity (dist.)
↓
thermodynamic force.

⇒ example of thermodynamic flux - force relation.

⇒ $\boxed{\text{constitutive relation}}$. proportionality is transport coefficient

In general, have vector relation:

$$\underset{\substack{\downarrow \\ \text{vector} \\ \text{of fluxes}}}{\underline{\Gamma}} = -\underset{\substack{\downarrow \\ \text{matrix of transport} \\ \text{coefficients — Onsager matrix)}}}{\underline{\underline{K}}} \cdot \underset{\substack{\downarrow \\ \text{vector of} \\ \text{gradients}}}{\underline{\nabla} C}$$

(n.b. "Onsager symmetry" → $\underline{\underline{K}}$ symmetric)

⇒ Observe:

- $f_{Max,\,eq}$ annihilates collision operator, and corresponds to $\frac{dS}{dt} = 0$ state ⇒ maximal entropy.

but

- $f_{Max}[n(\underline{x}), T(\underline{x}), V(\underline{x})]$ does not satisfy Boltzmann eqn. ⇒ δf needed.

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

$$\Rightarrow \quad f = f_{Max} + \delta f$$

why?: → gradients in thermodynamic quantities ⇒ system is not in maximum entropy state i.e. $\delta f \neq 0$

- so $\delta f \sim \underline{\nabla} C$ ⇒ relaxation to maximum entropy state will occur by collisional transport.

- can describe relaxation macroscopically, i.e.

$$\underset{\text{flux}}{\underset{\downarrow}{\Pi_{\alpha,\beta}}} = -\rho D \underset{\text{force}}{\underset{\downarrow}{\frac{\partial V_\beta}{\partial x_\alpha}}}$$

$$\frac{\partial \rho V}{\partial t} = -\nabla\cdot\underline{\underline{\Pi}}$$

$$-\frac{\partial V_\beta}{\partial x_\alpha}\Pi_{\alpha,\beta} = \rho D\left(\frac{\partial V_\beta}{\partial x_\alpha}\right)^2 \qquad \partial_t \int \mathcal{E}_{V} = \int \underline{\Pi}\cdot\underline{\nabla V}$$

$$\Rightarrow \boxed{\frac{dS}{dt} = \frac{\rho D}{T}\left(\frac{\partial V_\beta}{\partial x_\alpha}\right)^2}$$

- entropy production due transport-induced relaxation

Note time scales:

(i.) to form local Maxwellian, H-thm. $\Rightarrow \tau_{coll} \sim \nu^{-1}$

(ii.) to form global [redacted] maximum entropy state:

$$1/\tau_{relax} \sim D/L_V^2 \sim \nu\,\frac{l_{mfp}^2}{L_V^2}$$

$$L_V^{-1} = \frac{1}{V}\frac{\partial V}{\partial x}$$

$$\tau_{relax} \sim \left(L_v / l_{mfp}\right)^2 \tau_{coll}.$$

⇒ entropy production / relaxation is multiple time scale process!.

More generally, can write:

$$\underbrace{J_i}_{\underline{i\text{th flux}}} = -\sum_{j=1}^{n} \underbrace{\alpha_{ij}}_{\text{kinetic coefficient}} \underbrace{x_j}_{\text{driving force}}$$

$$\frac{dS}{dt} = \varphi = \text{"Dissipation Function"}$$

⇒

$$\frac{dS}{dt} = \sum_{i=1}^{n} \sum_{j=1}^{n} \alpha_{i,j}\, x_i x_j$$

<u>i.e.</u>

$$\frac{dS}{dt} = -x_j J_i$$

so, for 2x2:

$$\frac{dS}{dt} = \sum_{i=1}^{2} \sum_{j=1}^{2} \alpha_{1,1} x_1^2 + (\alpha_{1,2} + \alpha_{2,1}) x_1 x_2 + \alpha_{2,2} x_2^2$$

clearly need:

$$\begin{matrix} \alpha_{1,1} \geq 0 \\ \alpha_{2,2} \geq 0 \end{matrix} \quad \rightarrow \text{ i.e. diffusion down gradient}$$

and $\alpha_{1,1}\,\alpha_{2,2} - \frac{1}{4}\left(\alpha_{1,2} + \alpha_{2,1}\right)^2 \geq 0.$

(i.e. descr → diag.)

N. B. Off-diagonals ?!

i.e. Can ∇T drive a density flux ?

$$\Gamma = \int d^3v \; \underline{v} \; \delta f$$

$$\delta f = -\frac{1}{\nu} \underline{v} \cdot \nabla f_0$$

$$\Rightarrow \Gamma = \int d^3v \; \underline{v} \left(-\frac{1}{\nu} v_x \frac{\partial}{\partial x} \left(\frac{n_0}{v_{th}(x)^3} \exp\left[-\frac{m v^2}{2T(x)} \right] \right) \right)$$

clearly can get contribution to Γ_x.
→ Thermal diffusion.
Message: Gradient in distribution function is the key! ... but integration symmetries matter.