Physics 210B P. Diamond

I.) Kinetic Theory and Transport

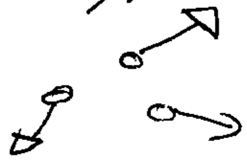
Goal: Physical Kinetics $\leftrightarrow$ Statistical Dynamics of Many-Body Systems

Descriptions:
- → Boltzmann Eqn. / collision operator
- → Hydrodynamic Eqns. / Transport Coefficients

Applications:
- → Dilute Gases (i.e. air)
- → Non-degenerate plasmas / collnal
- → Vlasov Plasmas
- → Fluids
- → Electron / Phonon Gases

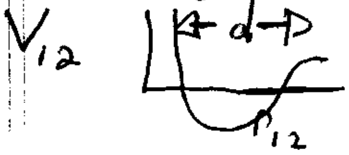
a.) Kinetic Theory of Gases; The Prototype

Ideal Gases:
- → molecules each move freely
- → interact only during close encounters



Scales:

1) d → range of inter-molecular interaction

i.e. 

$n \rightarrow$ density (#/volume)

3) $l_{mfp} \rightarrow$ mean free path (to be calculated)

i.e. typical distance between inter-molecular interactions

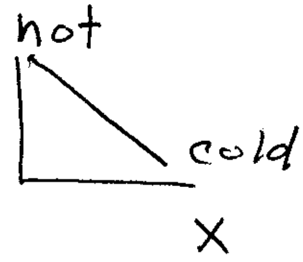
$$l_{mfp} = 1/n\sigma$$

σ ↓ cross-section for inter-molecular interaction

4) $L \rightarrow$ macroscopic scale length

i.e. characterizes distributions in problem

e.g. T



$$\frac{1}{T}\frac{dT}{dx} \equiv \frac{1}{L_T} \sim \frac{1}{L}$$

Orderings:

1.) $d \ll 1/n^{1/3} \Rightarrow n d^3 \sim d^3/\bar{r}^3 \ll 1$

↓ gaseousness parameter $\ll 1 \rightarrow$ dilute b.) $l_{mfp} \sim 1/n\sigma$

$\sim$ [illegible] $(\bar{r}/d)^2\,\bar{r}$

so

$l_{mfp} \gg \bar{r} \gg d \Rightarrow$ ideal gas

c.) $l_{mfp} < L \Rightarrow$ collisional system
- local transport
- hydro-description
- Chapman-Enskog Th.

$l_{mfp} > L \Rightarrow$ collisionless system
- transport non-local
- kinetic/Vlasov description

here: $d \ll \bar{r} \ll l_{mfp} \ll L$

Describe dilute gas in:

→ phase space: space of degrees freedom
- → translational
- → rotational
- → internal

i.e.

① translation: $(\underline{x}, \underline{v})$, $(\underline{x}, \underline{p})$

② rotation: $\underline{L}$, φ ⇒ rotational angle rapidly mixed, homogenized
→ exception: solution of rod-like polymers

∴ characterize molecule by L, alone

③ internal ⇒ vibrational states (quantum #'s)

∴ natural to define phase space distribution function:

$f(\Gamma)\, d\Gamma$ ⇒ # particles in $d\Gamma$ neighborhood / volume element of pt. Γ in phase space

f → phase space distrib.

$d\Gamma$ → phase volume element

i.e.

$$d\Gamma = d^3x\, d^3p\, 4\pi L^2\, dL\, d\varphi_L\, d\cos\theta$$

Usual pedagogical simplification:

→ 'point molecules' ↔ translation degrees freedom only

→ $f = f(\underline{x}, \underline{p}, t)$

$d\Gamma = d^3x\, d^3p$

∴ seek dynamical equation for $f(\underline{x}, \underline{p}, t)$

⇒

Boltzmann Equation

- B.E. : dynamical equation for phase space distribution
- rests on two great swindles:
  - → detailed balance
  - → molecular chaos
- allows:
  - H-Thm.
  - moment equations
  - transport equations and coefficients

→ aside: The Two Great Swindles of Kinetic Theory

a.) Detailed Balance

Detailed Balance ≡ in statistical eqbrm, (Γ excludes x here)

\# collisions $\Gamma, \Gamma_1 \to \Gamma', \Gamma_1'$ = \# collisions $\Gamma'^{T}, \Gamma_1'^{T} \to \Gamma^{T}, \Gamma_1^{T}$

i.e.

\# collisions $① \to ①'$ = \# collisions $①'^{T} \to ①$

[redacted]

$\Leftrightarrow$

$$W(\Gamma, \Gamma_1, \Gamma', \Gamma_1')\, f_{1,2}(\Gamma, \Gamma_1)\, d\Gamma\, d\Gamma_1\, d\Gamma'\, d\Gamma_1' = W(\Gamma', \Gamma_1'; \Gamma, \Gamma_1)\, f_{1,2}(\Gamma', \Gamma_1')\, d\Gamma'\, d\Gamma_1'\, d\Gamma\, d\Gamma_1$$

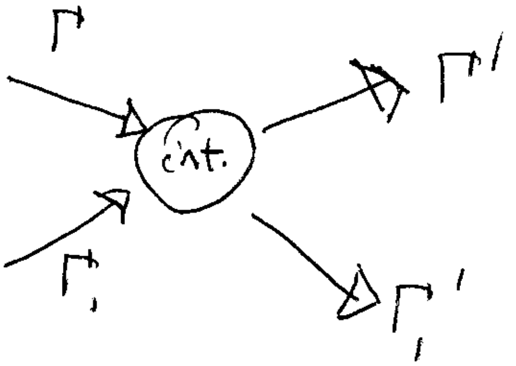
$f_{1,2}(\Gamma, \Gamma_1)$ ≡ two particle distribution function

i.e. ~ prob ① at Γ, ② at Γ_1

so

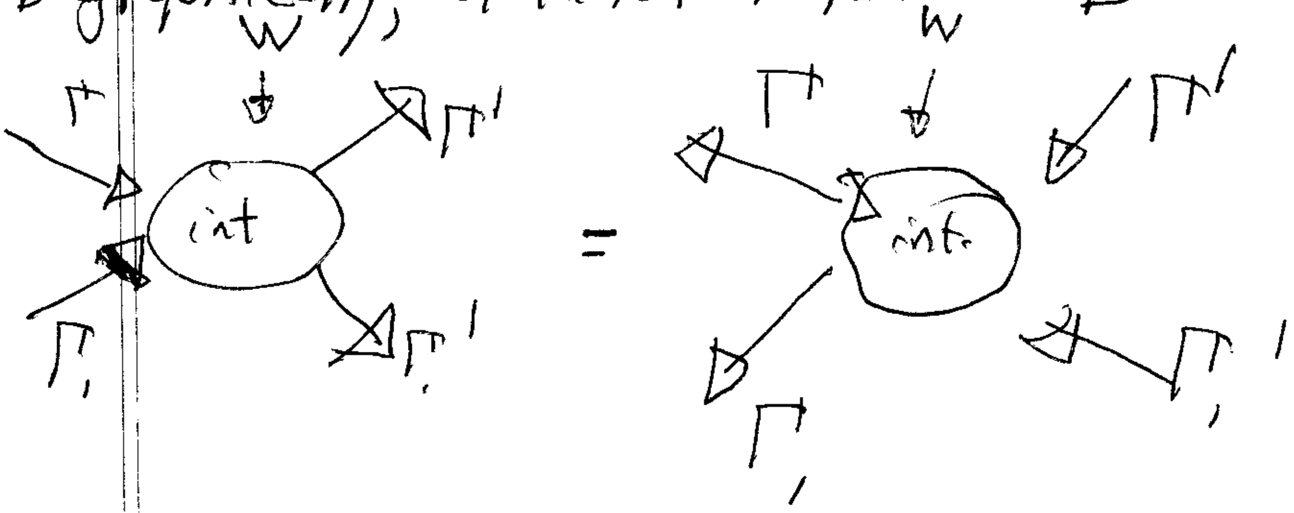
$\#$ particles at Γ which interact with others at Γ_1 is $= f_{1,2}(\Gamma, \Gamma_1)\, d\Gamma\, d\Gamma_1$

$W(\Gamma, \Gamma_1; \Gamma', \Gamma_1') \equiv$ transition probability



Notice:

→ graphically, detailed balance ⇒



i.e. as suggested by L→R = R→L, detailed balance is due time-reversal invariance of basic interaction dynamics.

i.e. if Γ^T = time reversal of Γ

$$\Gamma = (\underline{p}, \underline{L})$$

$$\Gamma^T = (-\underline{p}, -\underline{L})$$

then time reversal invariance ⇒

$$W(\Gamma', \Gamma_1'; \Gamma, \Gamma_1) = W(\Gamma, \Gamma_1; \Gamma', \Gamma_1')^T$$

(above graph)

if $W(\Gamma, \Gamma_1; \Gamma', \Gamma_1')^T = W(\Gamma', \Gamma_1'; \Gamma, \Gamma_1)$

$$= W(\Gamma, \Gamma_1; \Gamma', \Gamma_1')$$

(i.e. micro-dynamics reversible)

$$\# ① \rightarrow ①' \overset{?}{=} \# ①' \rightarrow ①$$

$$d\Gamma\, d\Gamma_1\, d\Gamma_1'\, d\Gamma'\, f(\Gamma, \Gamma_1)\, W(\Gamma, \Gamma_1; \Gamma', \Gamma_1')$$

$$\overset{?}{=} d\Gamma\, d\Gamma_1\, d\Gamma_1'\, d\Gamma'\, f(\Gamma', \Gamma_1')\, W(\Gamma', \Gamma_1'; \Gamma, \Gamma_1)$$

1ly need:

$$f(\Gamma^{+}, \Gamma_1^{+}) = f(\Gamma', \Gamma_1')$$

but in statistical eqbrm. (⟺ molecular chaos)

$$f(\Gamma^{+}, \Gamma_1^{+}) = f_0(\Gamma^{+})\, f_0(\Gamma_1^{+})$$

but

$$f_0(\Gamma) = \text{const}\ \exp\left[-\frac{\overset{\text{energy}}{\overset{\downarrow}{\epsilon}}(\Gamma^{+}) - \underline{p}\cdot\overset{\text{micro-flow}}{\overset{\downarrow}{\underline{V}}}}{T}\right]$$

$$f_0(\Gamma^{+})\, f_0(\Gamma_1^{+}) = \text{const}\ \exp\Big[-\big[\epsilon(\Gamma^{+}) + \epsilon(\Gamma_1^{+}) + \underline{V}\cdot(\underline{p}_{*} + \underline{p}_{*1})\big]\Big]$$

$$= \text{const}\ \exp\Big[-\big[\epsilon(\Gamma') + \epsilon(\Gamma_1') + \underline{V}\cdot(\underline{p}' + \underline{p}_1')\big]\Big]$$

by conservation $\begin{cases}\text{energy}\\ \text{momentum}\end{cases}$

$\therefore$ $f(\Gamma^{+}, \Gamma_1^{+}) = f(\Gamma', \Gamma_1')$ in stat eqbrm.

id thus: $\# \textcircled{1} \to \textcircled{1}' = \# \textcircled{1}' \to \textcircled{1}$

$\therefore$ detailed balance $\Longleftrightarrow$ $\begin{cases} \text{statistical eqbrm.} \\ \text{time-reversal of micro-interaction} \end{cases}$

observe: $\epsilon(\Gamma)$, $p \cdot \underline{V}$ invariant under T!

→ could generalize to $T \to T\underset{\substack{\downarrow \\ \text{parity inversion}}}{P}$

i.e.

$$\begin{cases} W(\Gamma,\Gamma_1;\Gamma',\Gamma_1') = W(\Gamma',\Gamma_1';\Gamma,\Gamma_1)^{TP} \\ \Rightarrow \text{detailed balance!} \end{cases}$$

requires: no stereoisomerism (i.e. new substance upon parity inversion of molecular structure).

→ can relate W to cross-section via:

$$\underset{\substack{\downarrow \\ \frac{d}{dt}\left(\text{Volume of interaction}\right)}}{d\sigma\,|V_{rel}|} = \underset{\substack{\downarrow \\ \text{transition probability}}}{W(\Gamma,\Gamma_1;\Gamma',\Gamma_1')}\, d\Gamma'\, d\Gamma_1'$$

v.) Molecular Chaos

Molecular chaos: $f(1,2)$ factorizes

$$\begin{cases} \rightarrow f(1,2) = f(1)\,f(2) \\ \rightarrow \frac{1}{2} m V_{Th}^2 \gg \overline{U(1,2)} \end{cases}$$

$\rightarrow d \ll \bar{r}$

$$\frac{\text{Volume of interaction}}{\text{Volume}} \ll 1$$

i.e. { gas (air), plasma in molecular chaos
crystals are not! }

(*) How enter theoretical construction (of B.E.)?

- Consider N particle system, $N \gg 1$
- For Hamiltonian dynamics; can write:

$$\frac{\partial f^N}{\partial t} + \sum_{i=1}^{N} \left\{ \frac{\partial}{\partial \underline{x}_i} (\dot{\underline{x}}_i f^N) + \frac{\partial}{\partial \underline{p}_i} (\dot{\underline{p}}_i f^N) \right\} = 0$$

$\hookrightarrow$ Liouville Eqn.

$$\Rightarrow \frac{\partial f^N}{\partial t} + \sum_{i=1}^{N} \left(\dot{\underline{x}}_i \cdot \frac{\partial}{\partial \underline{x}_i} f^N + \dot{\underline{p}}_i \cdot \frac{\partial}{\partial \underline{p}_i} f^N \right) = 0$$

uses Liouville Thm: phase space flow of Hamiltonian system is incompressible.

$f^N = f^N(t, x_1, p_1 \ldots\ldots x_N, p_N) \equiv$ N particle distribution

but $\dot{\underline{x}}_i = \underline{v}_i$

$\dot{p}_i = -\partial \sum_{\substack{j \\ j<i}} V_{ij} / \partial \underline{x}_i$

⇒

$$\frac{\partial f^N}{\partial t} + \sum_{i=1}^{N} \underline{v}_i \cdot \frac{\partial f^N}{\partial \underline{x}_i} - \frac{\partial f^N}{\partial \underline{p}_i} \cdot \sum_{j<i} \frac{\partial V_{ij}}{\partial \underline{x}_i} = 0$$

Now, can construct (BBGKY) hierarchy:

$f(t, x_1, p_1) = \int d\Gamma_2 \, d\Gamma_3 \ldots d\Gamma_N \; f^N \to$ 1 particle dist

$f(t; \underline{x}_1, \underline{p}_1; \underline{x}_2, \underline{p}_2) = \int d\Gamma_3 \ldots\ldots d\Gamma_N \; f^N \to$ 2 particle dist.

⇒ integrating out for 1 pdf: (Γ includes x here)

$$\frac{\partial f^{(1)}}{\partial t} + \underline{v}_1 \cdot \frac{\partial}{\partial x_1} f^{(1)} = \underbrace{(N-1)}_{\substack{(n-1) \\ \text{binary} \\ \text{pairs.}}} \int \underbrace{\frac{\partial V_{1,2}}{\partial \underline{x}_1}}_{\substack{\text{2-particle} \\ \text{int.}}} \cdot \underbrace{\frac{\partial f^{(2)}}{\partial p_1}}_{\substack{\text{2-particle} \\ \text{distrib}}} d\Gamma_2$$

i.e. RHS accounts for (1) evoln via all possible binary pair interactions!

Similarly:

$$\frac{\partial f^{(2)}}{\partial t} + \underline{v}_1 \cdot \frac{\partial}{\partial \underline{x}_1} f^{(2)} + \underline{v}_2 \cdot \frac{\partial}{\partial \underline{x}_2} f^{(2)} - \frac{\partial V_{1,2}}{\partial \underline{x}_1} \cdot \frac{\partial f^{(2)}}{\partial \underline{p}_1} - \frac{\partial V_{1,2}}{\partial \underline{X}_2} \cdot \frac{\partial f^{(2)}}{\partial \underline{p}_2}$$

$$= (N-2) \int d\Gamma_3 \left[\frac{\partial f^{(3)}}{\partial \underline{p}_1} \cdot \frac{\partial U_{1,3}}{\partial r_1} + \frac{\partial f^{(3)}}{\partial p_2} \cdot \frac{\partial U_{2,3}}{\partial r_2} \right]$$

note:

→ $N-1$, $N-2$ $\begin{cases} \text{from \# relabelings} \\ \sim N, \text{ as } N \gg 1 \end{cases}$

→ others yield surface terms!

Now:

→ yields coupled hierarchy; !? How truncate?

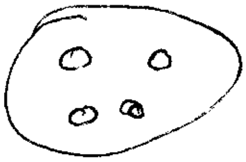
→ examine RHS of $f^{(2)}$ eqn:

$$\underset{p\text{ only}}{\int d\Gamma_3'}\ \frac{\partial f^{3}}{\partial p} \sim \frac{\partial f^{(2)}}{\partial p}\ \frac{1}{V} \xrightarrow{} \text{spatial norm factor}$$

d ≪ $l_p = \bar{r}$

So

$$RHS \sim \frac{\partial U}{\partial r}\ \frac{\partial f^{(2)}}{\partial p}\ \underbrace{\frac{d^3}{\bar{r}^3}}$$



interaction volume filling factor ~ $\frac{\text{volume } U \text{ significant}}{\text{total volume}}$

i.e.

$$\underset{\downarrow}{N}\int d\Gamma_3\ \frac{\partial f^{(3)}}{\partial p}\ \frac{\partial U}{\partial r} \sim N\ \frac{\partial U}{\partial r}\ d^3\ \frac{\partial f^{(2)}}{\underbrace{V\partial p}} \xrightarrow{} \text{norm factor}$$

$$\sim \frac{\cancel{V}}{\bar{r}^3}\ \frac{\partial U}{\partial r}\ d^3\ \frac{\partial f^{(2)}}{\cancel{V}\partial p}$$

$$\sim \frac{d^3}{\bar{r}^3}\ \frac{\partial U}{\partial r}\ \frac{\partial f^{(2)}}{\partial p}$$ ✓

∴ RHS/LHS terms $\sim d^3/\bar{r}^3$

$\ll 1$

So

$$\frac{d}{dt} f^{(2)}(t, \Gamma_1, \Gamma_2) = 0$$

is truncation of BBGKY hierarchy for dilute gas!

Now:

- $df^{(2)}/dt = 0$ is mechanical (no thought!)
- assume statistical independence of colliding particles

$\leftrightarrow$ serves as initial condition for

$df^{(2)}/dt=0$

i.e.
$$f^{(2)}(t,\Gamma_1,\Gamma_2)\Big|_{t=t_0} = f(t,\Gamma_1)\Big|_{t=t_0} \; f(t,\Gamma_2)\Big|_{t=t_0}$$

$\leftrightarrow$ ensures notion of "freely moving particles, interacting only within $d \ll r$"

$\therefore$ - molecular chaos assumption is;

$$f^{(2)}(1,2,t) = f^{(1)}(1,t)\, f^{(1)}(2,t)$$

- serves as i.c. for $df^{(2)}/dt=0$

- Boltzmann Equation

Consider 1 particle distribution function eqn:

$$\frac{\partial f}{\partial t} + \underline{v}\cdot\frac{\partial f}{\partial \underline{x}} = N\int d\Gamma_2 \, \frac{\partial U_{1,2}}{\partial \underline{r}_1}\cdot\frac{\partial f^{(2)}}{\partial \underline{p}_1}$$

$$= N\int d\Gamma_2 \, \frac{\partial U_{1,2}}{\partial r_1}\cdot\frac{\partial}{\partial p_1}\left[f^1(1,t)\, f^1(2,t)\right]$$

$\Rightarrow$

$$\frac{\partial f}{\partial t} + \underline{v}\cdot\frac{\partial f}{\partial \underline{x}} = \underset{\text{colln. operator}}{\underset{\downarrow}{C(f)}} \quad \rightarrow \text{Boltzmann Eqn}$$

$$C(f) = \int d\Gamma_2 \, \frac{\partial U_{1,2}}{\partial r_1}\cdot\frac{\partial}{\partial p_1}\left[f(1,t)\, f(2,t)\right]$$

(where have absorbed norm. factor!..)

alternatively:

$$\frac{df}{dt} = C(f)$$

i.e. f constant along phase space trajectories, up to collisions

∴ collisions determine <u>net</u> influx to point Γ in phase space:

$$\frac{df(\Gamma)}{dt} = \text{rate change } f \text{ due collisions}$$

$$= \#\text{ collisions scattering particles } \underline{\text{into}}\ \Gamma$$

$$\ominus\ \#\text{ collisions scattering particles } \underline{\text{out of}}\ \Gamma$$

$$\text{in} = \int d\Gamma' d\Gamma_1' d\Gamma_1\, \overset{\text{molecular chaos}}{\overset{\downarrow}{f(\Gamma') f(\Gamma_1')}}\, W(\Gamma', \Gamma_1'; \Gamma, \Gamma_1)$$

$$\text{out} = \int d\Gamma_1 d\Gamma' d\Gamma_1'\, f(\Gamma) f(\Gamma_1)\, W(\Gamma, \Gamma_1; \Gamma', \Gamma_1')$$

<u>so</u> exploiting <u>detailed balance</u>:

$$\boxed{\begin{aligned} \frac{df(\Gamma)}{dt} &= \int d\Gamma_1 d\Gamma' d\Gamma_1'\, W\left(f(\Gamma') f(\Gamma_1') - f(\Gamma) f(\Gamma_1)\right) \\ \frac{df}{dt} &= \frac{\partial f}{\partial t} + \underline{v} \cdot \frac{\partial f}{\partial \underline{x}} \end{aligned}}$$

Boltzmann Eqn.

an immediately note:

- B.E. conserves particle #

$$\int \frac{df}{dt} d\Gamma = \int d\Gamma\, C(f)$$

$$= \int d\Gamma\, d\Gamma_1\, d\Gamma'\, d\Gamma_1'\, W(\Gamma, \Gamma_1; \Gamma', \Gamma_1')\big(f(\Gamma')f(\Gamma_1') - f(\Gamma)f(\Gamma_1)\big)$$

$$= 0$$

using
- detailed balance
- $\Gamma, \Gamma_1 \leftrightarrow \Gamma', \Gamma_1'$ interchange antisymmetry

- B.E. (HW) conserves $\begin{cases} \text{energy} & \int C(f)\epsilon = 0 \\ \text{momentum} & \int C(f)p = 0 \end{cases}$ as micro-interaction (usually) does.

- note that gradients in distribution function entirely determines net evolution due collisions.

r Htd: note $C(f)$ vanishes for equilibrium distribution (Maxwellian)

$$C(f) = \int d\Gamma_1 \, d\Gamma' \, d\Gamma_1' \; w \left(f(\Gamma') f(\Gamma_1') - f(\Gamma) f(\Gamma_1) \right)$$

$$f = c \exp - \left[(\epsilon + p \cdot \underline{V}) / T \right]$$

due conservation energy, momentum during int.

$\underset{\approx}{\text{so}}$

→ <u>H-Theorem</u>

- gas, left alone, will evolve to eqbrm.
- such evolution accompanied by <u>entropy production</u>

∴ need show $dS/dt \geq 0$ for B.E.

- establishes system will evolve to equilibrium distribution.

Now, for ideal gas: $\Gamma \rightarrow$ momenta only

$$S = \int f \ln (e/f) \, dV d\Gamma = -\int f \ln f \, dV d\Gamma \qquad \begin{cases} f \sim c e^{-\epsilon/T} \\ dE = T dS \end{cases}$$

$$-\quad \frac{dS}{dt} = -\int \frac{df}{dt}\ln f\, dV d\Gamma - \int \cancel{f}\,\frac{1}{\cancel{f}}\,\frac{df}{dt}\, dV d\Gamma$$

$$= -\int C(f)\ln f\, dV d\Gamma - \cancel{\int C(f)\, dV d\Gamma} \quad \text{\# conservation}$$

$$\Rightarrow \frac{dS}{dt} = -\int C(f)\ln f\, dV d\Gamma$$

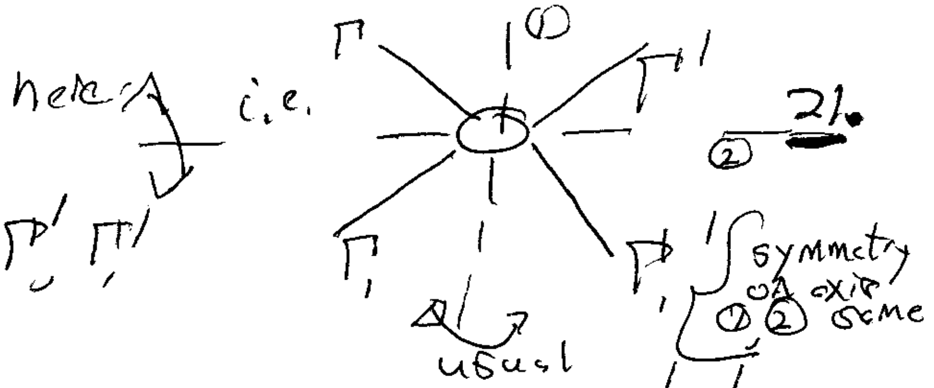
$$C(f) = \int d\Gamma_1\, d\Gamma'\, d\Gamma_1'\; w\,\big(f(\Gamma')f(\Gamma_1') - f(\Gamma)f(\Gamma_1)\big)$$

$$\frac{dS}{dt} = \int dV \int d\Gamma\, d\Gamma_1\, d\Gamma'\, d\Gamma_1' \ln f\; w\,\big(f(\Gamma')f(\Gamma_1') - f(\Gamma')f(\Gamma_1')\big)$$

Lemma: Consider $\int \underbrace{\varphi(\Gamma)}_{\underline{\text{any}}\text{ fctn }\Gamma} C(f)\, d\Gamma$

$$\int \varphi(\Gamma)\, C(f)\, d\Gamma = \int \varphi\, w(\Gamma, \Gamma_1; \overset{①}{\Gamma'}, \Gamma_1')\, f' f_1'\, d^4\Gamma - \int \varphi\, w(\overset{②}{\Gamma'}, \Gamma_1'; \Gamma, \Gamma_1)\, f f_1\, d^4\Gamma$$

$$d^4\Gamma = d\Gamma\, d\Gamma_1\, d\Gamma'\, d\Gamma_1'$$



in ②, $\Gamma, \Gamma_1 \leftrightarrow \Gamma', \Gamma_1'$

$$\Rightarrow \int \varphi(\Gamma)\, C(f)\, d\Gamma = \int (\varphi - \varphi')\, w(\Gamma, \Gamma_1; \Gamma', \Gamma_1')\, f' f_1'\, d^4\Gamma$$

Now, interchange $\Gamma, \Gamma' \leftrightarrow \Gamma_1, \Gamma_1'$ and symmetrizing (up/down, instead Left-Rt.)

$$\Rightarrow \int \varphi(\Gamma)\, C(f)\, d\Gamma = \frac{1}{2} \int (\varphi + \varphi_1 - \varphi' - \varphi_1')\, w' f' f_1'\, d^4\Gamma$$

now, applying to dS/dt

$$dS/dt = -\frac{1}{2} \int (\ln f + \ln f_1 - \ln f' - \ln f_1') * w' f' f_1'\, d^4\Gamma\, dV$$

$$= \frac{1}{2} \int d^4\Gamma\, dV\, w' f' f_1' \ln (f' f_1' / f f_1)$$

$$= \frac{1}{2} \int d^4\Gamma\, dV\, w' f f_1\, X \ln X$$

$X = f' f_1' / f f_1$

$\therefore \int C(f)\, d\Gamma = 0$

$\Rightarrow \int w' f f_1 \, (X-1)\, dv\, d^4\Gamma = 0$

$\therefore$ subtraction $\Rightarrow$

$$\frac{dS}{dt} = \frac{1}{2}\int d^4\Gamma\, dv\; w' f f_1 \left[X \ln X - X + 1 \right]$$

$f(x) = x \ln x - x + 1$

$f' = \ln x \cancel{+1} \cancel{-1}$

$\left.\begin{array}{l} f(0) = 1 \\ f(1) = 0 \end{array}\right\}$

$\therefore \quad f(x) > 0$ for all $x > 0$

$\Rightarrow \boxed{dS/dt \geq 0}$ as $f(x)$, w, $f f_1 > 0$.

$\Downarrow$

Boltzmann H-Thm.

hus:

- $dS/dt \geq 0$; entropy increases except at equilibrium

- collisions drive system toward eqbrm

$$C(f) = -\nu (f - f_0)$$

$$\downarrow$$

Krook Model

(C)

\# conserving Krook Model:

$$C(f) = -\nu \delta f + \nu f_0 \int dv \, \delta f$$

- dV irrelevant ⇒ entropy produced locally!

Now, construct macro-equations!

→ Fluid Equations

Seek macroscopic description of gas → hydrodynamic equations for $n(\underline{x},t)$, $\underline{V}(\underline{x},t)$, $p(\underline{x},t)$, etc.
→ held together (against dispersion) by collisions

- describe 'blobs' of gas s/t $L > l_{mfp}$, $\omega < \nu$
- local, Eulerian description
- parametrizes dynamics in terms structure of distribution

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

⇒ works best for slight deviation from eqbrm.
⇒ sacrifices info re: higher moments (usual truncation at energy)

recall:

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

demand: (of $C(f)$)

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

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

$$\int C(f)\, \epsilon = 0 \qquad (\text{energy conservation})$$

define: $n = \int d^3v \, f$ → density

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

$\bar{\epsilon} = \frac{1}{n}\int d^3v \, \epsilon f$ → energy density

$$\frac{\partial f}{\partial t} + \frac{\partial}{\partial x_i}(v_i f) = C(f)$$

⇒ taking moments:

(1) $$\frac{\partial n}{\partial t} + \nabla \cdot \underset{\underset{\text{mass flux}}{\downarrow}}{(n\underline{V})} = \underset{\underset{\text{\# cons.}}{\downarrow}}{0}$$ (continuity)

(2) $$\frac{\partial}{\partial t}(n V_\alpha) + \underset{\underset{\substack{\text{momentum flux}\\ \text{stress tensor}}}{\downarrow}}{\frac{\partial}{\partial x_\beta}} \Pi_{\alpha\beta} = \underset{\underset{\text{mom. cons.}}{\downarrow}}{0}$$ (momentum balance)

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

$$\frac{\partial}{\partial t}(n\bar{\epsilon}) + \underbrace{\underline{\nabla}\cdot\underline{q}}_{\text{energy flux}} \underbrace{= 0}_{\text{energy conservation}} \qquad \text{(energy balance)}$$

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

can furthur simplify by observing:

$$\underline{v} = \underbrace{\underline{V}(x,t)}_{\substack{\text{mean/bulk}\\ \text{flow}\\ (\sim\text{ body forces})}} + \underbrace{\underline{\acute{v}}}_{\substack{\text{thermal fluctuation}\\ \text{about mean } (\sim\sqrt{T/m})}}$$

so ①

$$\Pi_{\alpha\beta} = \int d^3v\ m\,(V_\alpha(\underline{x},t) + \acute{v}_\alpha)(V_\beta(\underline{x},t) + \acute{v}_\beta)\overset{\text{centered on }\underline{V}(\underline{x},t)}{f}$$

$$= mn\,(V_\alpha(\underline{x},t)\,V_\beta(\underline{x},t) + \langle \acute{v}_\alpha \acute{v}_\beta\rangle)$$

$$\langle \acute{v}_\alpha \acute{v}_\beta\rangle = \frac{1}{3}\langle \acute{v}^2\rangle\,\delta_{\alpha\beta} \qquad (\sim\text{isotropic } f \text{ abt. } \underline{V})$$

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

<u>so</u>, can define $\overset{\substack{\text{pressure tensor}\\ \downarrow}}{\underline{\underline{P}}} = mn\langle V'_\alpha V'_\beta\rangle$

isotropy (collisional isotropization) $\Rightarrow$ $= \frac{1}{3} mn\langle V'^2\rangle \delta_{\alpha,\beta}$

$p = nT$ (usual ✓)

<u>So</u>

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

<u>but</u>: $\frac{\partial n}{\partial t} + \underline{\nabla}\cdot(n\underline{V}) = 0$ (continuity)

so subtraction $\Rightarrow$

$$\left. n\left(\frac{\partial \underline{V}}{\partial t} + \underline{V}\cdot\underline{\nabla}\,\underline{V}\right) = -\underline{\nabla}p \right\}$$ Navier-Stokes Eqn.

$\underline{\nabla}\cdot\underline{V} = 0$ defines p (incompressible Eqn. St.)

② Similarly,

$$\epsilon = \frac{1}{2} m v^2 + \epsilon'$$

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

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

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

$$= \underline{V}(\underline{x},t)\left(\tfrac{1}{2} m n \underline{V}^2 + \underbrace{p + n\overline{\epsilon}'}_{\substack{\Downarrow \\ W \,\to\, \text{internal energy}}}\right)$$

$\underline{\text{and}}$

$$\underbrace{\frac{\partial}{\partial t}(n\overline{\epsilon})}_{\Downarrow} + \underline{\nabla}\cdot\left[\underline{V}(\underline{x},t)\left(\tfrac{1}{2} m n \underline{V}^2 + p + n\epsilon'\right)\right] = 0$$

can similarly simplify.

Note:

→ angular momentum <u>not</u> conserved by $C(f)$

$\underline{\text{i.e.}}$ deflection ⟶ ∘ ⇒ ∘

→ most truncations stop at 3rd moment

Next: Transport coeffs.

⇒ Transport Coefficients

→ Introduction

- Now, can write fluid equations as conservation laws for density $n(\underline{x},t)$, momentum density $\underline{g}(\underline{x},t) = nm\underline{V}(\underline{x},t)$ and energy density $\epsilon(\underline{x},t)$

i.e.

$$\frac{\partial n(\underline{x},t)}{\partial t} + \nabla\cdot\underline{g}(\underline{x},t) = 0$$

$$\frac{\partial \underline{g}(\underline{x},t)}{\partial t} + \underline{\nabla}\cdot\underbrace{\underline{\underline{\Pi}}}_{}(\underline{x},t) = 0 \quad \text{→ stress tensor}$$

$$\frac{\partial \epsilon(\underline{x},t)}{\partial t} + \nabla\cdot\underline{j}^{\epsilon}(\underline{x},t) = 0$$

↳ energy current.

Now, questions are:

→ how relate $\underline{g}$, $\underline{\underline{\Pi}}$, $\underline{j}^{\epsilon}$ to fields consistent with level of truncation, i.e. n, $\underline{V}$, P, ϵ, T?

→ how represent variation of macroscopic fields, i.e. $\underline{V}(\underline{x},t)$, $T(\underline{x},t)$ given that fluid equations describe dynamics of blobs of scale l_{mfp}?

i.e. note parallel :

Non-Markovian Stochastic Process	Fluid
time	space
$\tau_{ref}\,\gamma_j > 1 \Rightarrow$ irrelevant $\Rightarrow$ equilibrate	$l < l_{mfp} \rightarrow$ collisions coarse-grain $l > l_{mfp} \rightarrow$ fluid equations describe
$\tau_{ref}\,\gamma_j < 1 \rightarrow$ relevant $\Rightarrow$ dynamics	$\Rightarrow \omega \geq \nu \rightarrow$ coarse grained $\omega \lesssim \nu \rightarrow$ dynamic
time scale ordering $L_b\, P(a,b,t) = 0 \Rightarrow$ $p = S(a,t)\, \underset{\downarrow \text{ Const. Mtn.}}{P_{eq.}(b)}$	time scale ordering $C(f) = 0 \Rightarrow f = f_{Max}$ $f = \frac{n(\underline{x},t)}{(2\pi v_m)^{3/2}} \exp\left[\frac{m(\underline{v}-\underline{V}(\underline{x},t))^2}{T(\underline{x},t)}\right]$
$\Rightarrow$ F.P.E. coefficients	$\Rightarrow$ fluid eqns. with transp coeffs.

$\Rightarrow$ yields constitutive relations: (microscopic)

$$\langle \underline{g}(\underline{x},t)\rangle_{micro} = mn\,\underline{V}(\underline{x},t)$$

$$\langle T_{ij}(\underline{x},t)\rangle_{micro} = p(\underline{x},t)\,\delta_{ij} - \overset{\text{shear viscosity}}{\eta}\Big[\underbrace{\nabla_i V_j(\underline{x},t) + \nabla_j V_i(\underline{x},t)}_{\text{strain tensor.}}$$

$$-\tfrac{2}{3}\,\underline{\nabla}\cdot\underline{V}(\underline{x},t)\,\delta_{ij}\Big] - \underset{\text{bulk viscosity (compression)}}{\zeta}\,\nabla\cdot\underline{V}\;\delta_{ij}$$

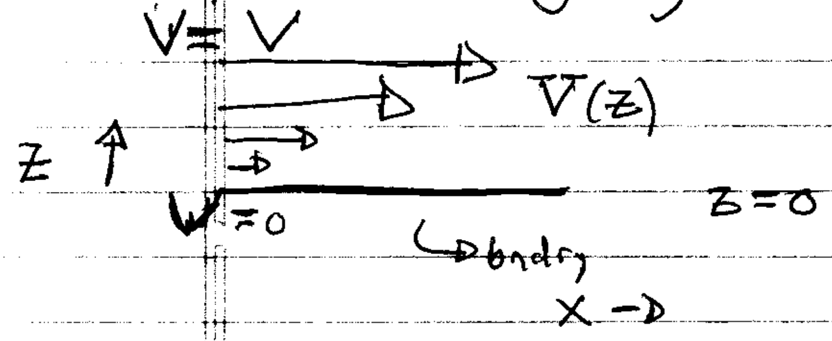
$$\langle \underline{j}^{\epsilon}(\underline{x},t)\rangle = (\epsilon+p)\,\underline{V}(\underline{x},t) - \underset{\substack{\downarrow \\ \text{thermal diffusivity}}}{\kappa}\nabla T(\underline{x},t)$$

∴ how calculate η (@, κ ? how construct equation of state for p etc.
⇒ underlying kinetic theory.

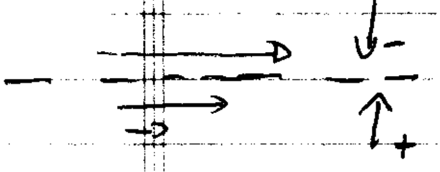
→ Chapman-Enskog Expansion

- simple physics of transport coefficients :

Consider viscous gas ;



→ For transport of p_x thru imaginary surface,



$$\left.\begin{aligned}\Gamma_+ &= \int_+ d\underline{v}\, m\bar{V}_x v_z f \sim v_{Th}\bar{V} n m \\ \Gamma_- &= \int_- d\underline{v}\, m\bar{V}_x v_z f \sim v_{Th}\bar{V} n m\end{aligned}\right\}$$

± define domains of integration yielding +, − flux

At first glance, would appear $\Gamma_+ = \Gamma_-$, but

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

i.e.  lmfp ~> $\bar{V}(z)\hat{x}$ has gradient across this

$$\to \quad \Gamma \cong - V_{Th}\, n m \left[\bar{V}\left(z + \frac{l_{mfp}}{2}\right) - \bar{V}\left(z - \frac{l_{mfp}}{2}\right) \right]$$

$$\cong - n m V_{Th}\, l_{mfp} \frac{\partial V_x(z)}{\partial z}$$

i.e. $\cong - \eta \dfrac{\partial V_x(z)}{\partial z}$

$\eta \cong n m \underbrace{V_{Th}\, l_{mfp}}_{D}$ → shear viscosity

→ key points:

- equal # random walkers in +, − direction but
- more momentum (velocity gradient) brought in from above

⇒ viscous momentum transport.

→ Calculation

Consider Boltzmann equation for stationary flow

<u>i.e.</u>

$$\cancel{\frac{\partial f}{\partial t}} + \underset{\substack{\downarrow \\ V_{Th}/L_f}}{\underline{v}\cdot\underline{\nabla} f} = \underset{\substack{\downarrow \\ \nu_{eff} = \frac{V_{Th}}{l_{mfp}}}}{C(f)}$$

Seek : $$\underset{\substack{\downarrow \\ \text{x-direction} \\ \text{flux of z momentum}}}{\tilde{T}_{xz}} = \int d^3v \, \underset{\substack{\downarrow \\ \text{flux in z-direction}}}{V_z} \, \underbrace{V_x m f(\underline{x},\underline{v})}_{\hat{x}\text{ momentum}},$$

How calculate ?

- Premise of Chapman - Enskog expansion.

$$l_{mfp} \ll L \iff \nu_{eff} \gg \frac{V_{Th}}{L}$$

⇒ - f remains very close to Maxwellian (<u>i.e.</u> equilibrium)

- seek calculate deviation from equilibrium i.e.

$$f = \underset{\sim\text{local Maxwellian}}{f_0} + \underset{\text{perturbation}}{\delta f}$$

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

l.o. $\Rightarrow$ $C(f_0) = 0$

$\therefore$ $f_0 = f_{0\,max}$

1st order $\underline{v}\cdot\nabla f_{0\,max} = C(\delta f)$

$\therefore$ $\delta f = C^{-1}\left[\underline{v}\cdot\nabla f_{0\,max}\right]$

and thus

contribution vanishes by symmetry

$$\Pi_{xz} = \int d^3v\; v_z\, v_x\, m \left[f_{0\,max} + \delta f\right]$$

$$= \int d^3v\; v_z\, v_x\, m\; C^{-1}\left[\underline{v}\cdot\underline{\nabla} f_{0\,max}\right]$$

$$\cong -\eta\,\frac{\partial \underline{V}_{0x}(z)}{\partial z}$$

To calculate η:

$C(\delta f) = -\nu(f - f_0)$ "Crook" model

$= -\nu\,\delta f$

$\hookrightarrow \nu = \nu(v)$

$\therefore \quad \delta f = \frac{-1}{\nu}\,\underline{v}\cdot\nabla f_{0\,max}$

$\rightarrow$ from $\bar{V}(z)\,\hat{x}$

$$= -\frac{1}{\nu}\, v_z \frac{\partial}{\partial z} f_0(\underline{v}, z)$$

$\rightarrow$

$$\tilde{T}_{x,z} = -\int d^3v \; v_z v_x \frac{m}{\nu} v_z \frac{\partial}{\partial z} f_0$$

$$f_0 = \frac{n(x)}{\left(\sqrt{2\pi}\,v_{Th}\right)^3}\exp\left[-m\frac{\left(\underline{v}-\bar{V}(z)\,\hat{x}\right)^2}{2T}\right]$$

$$\therefore \quad \tilde{T}_{xz} \cong -\#\, n m \frac{v_{Th}^2}{\nu}\frac{\partial}{\partial z}\bar{V}_x(z)$$

$$\tilde{T}_{x,z} = -\#\, n m\, v_{Th}\, l_{mfp}\frac{\partial}{\partial z}\bar{V}_x(z)$$

$$= -\#\, n m\, D_{eff}\frac{\partial}{\partial z}\bar{V}_x(z)$$

Note:

→ $\underset{\substack{\downarrow \\ \text{transp.} \\ \text{coeff}}}{\eta} \sim nm \frac{l_{mfp}^2}{\tau} \sim nm \underset{\substack{\downarrow \\ \text{diffn} \\ \text{coeff.}}}{D}$ $\left\{ \begin{array}{l} 1/\tau = \nu_{eff} \Rightarrow \Delta T \sim \nu^{-1} \\ L \sim l_{mfp} \end{array} \right.$

→ $\tilde{\Gamma}_{x,z} = \underbrace{\# n m D}_{\mu\text{-process}} \frac{\partial V_x(z)}{\partial z}$

↓ thermodynamic flux (macroscopic)

↳ thermodynamic force (deviation from max. entropy state) (macroscopic)

Constitutive relations ↔ thermodynamic flux – force relation

→ In general, have vector relation

$$\underline{\Gamma} = - \underline{\underline{K}} \cdot \underline{\nabla} G$$

⇒ $\frac{\partial V_x(z)}{\partial z}$ drives thermal flux, too, etc

$\underline{\Gamma}$ ↓ vector of fluxes

$\underline{\underline{K}}$ ↓ matrix of transport coefficients. (Onsager Matrix) → symmetric.

$\underline{\nabla} G$ ↳ vector of gradients

→ flux down gradient ⇔ relaxation to f_{max} (H-thm.)

→ can have flux up a particular gradient, so long as total entropy production is > 0

Chemotaxis

→ More on { Onsager Symmetry
Calculating Transport Coefficients (Chapman – Enskog).

Recall have discussed :

→ Boltzmann collision integral, equation, H thm.

→ hydrodynamic equations

and

→ collision driven fluxes ↔ { Chapman Enskog expansion ↳ to linear response theory ---

i.e. $\underline{q} = -K \underline{\nabla} T$

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

from $\frac{l_{mfp}}{L}$ expansion

(concerned with "relaxation of fluctuation")

In general:

→ inhomogeneities (i.e. gradients in T, n, V etc.)
⇒ deviation from equilibrium.

i.e. maximal entropy state is uniform state

so

→ gradients tend to relax ⇒ { transport, entropy production

⇒ useful to understand flux – force relations for transport

i.e. $$\underbrace{\underline{\Phi}}_{\text{flux vector}} = -\underbrace{\underline{\underline{D}}}_{\text{transport coefficient matrix}} \cdot \underbrace{\underline{\nabla} X}_{\text{force vector}} \Rightarrow \text{vector of gradients}$$

nd entropy production rate:

$$\dot{S} = -\frac{1}{2}\left\langle \underline{\Phi} \cdot \underline{\nabla} X \right\rangle$$

$$= \frac{1}{2}\left\langle \underline{\nabla} X \cdot \underline{\underline{D}} \cdot \underline{\nabla} X \right\rangle$$

i.e. $\underline{\Phi} \leftrightarrow \underline{q}$

$\underline{\nabla} X \leftrightarrow \underline{\nabla} T$

$\underline{\underline{D}} = \underline{\underline{\kappa}}$

$$2\dot{S} = \int d^3x \left[\underline{\nabla} T(x) \cdot \underline{\underline{D}} \cdot \underline{\nabla} T(x) \right]$$

→ Onsager symmetry ⟺ symmetry of $\underline{D}$ matrix
→ time reversal symmetry of underlying dynamics.

i.e. $D_{ij} = D_{ji}$

Onsager Symmetry ⟺ $\left\{ \begin{array}{l} \text{Entropy} \\ \text{Fluctuations} \\ \text{Relaxation and Correlations.} \end{array} \right.$

so, some review is useful...

Review of Entropy and Fluctuations (Brief)

Liouville Thm ⇒ $\frac{d}{dt} f(q_i, p_i, t) = 0$

$\therefore \quad f = f(\underline{\text{I}}\text{OM})$ ⟺ dependence of distribution function

and since, for two distinct subsystems:

$$f_{1,2} = f_1 f_2$$

$$\ln f_{1,2} = \ln f_1 + \ln f_2$$

⇒ $\ln f$ should be additive.

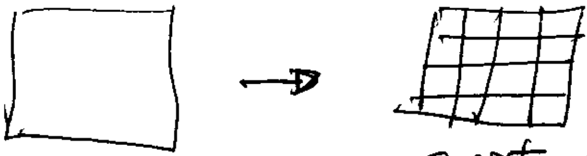
as $f = f(\mathrm{IOM})$

can always "view" in stationary frame

$$\ln f_\alpha = \alpha_\alpha + \beta E_\alpha + \cancel{\gamma \cdot \underline{P}_\alpha} + \cancel{\delta \cdot \underline{L}_\alpha}$$

$$= \alpha_\alpha + \beta E_\alpha$$

For entropy:



w_n = p.d.f. for n^{th} subsystem

$w_n = w_n(E)$

↳ subsyst energy

so

$$\rho(E)\,dE = w_n(E)\,(\#\text{ states})$$

↓

{prob. of subsyst energy in range $(E, E+dE)$

$\Gamma(E)$ = # states with energy $< E$

$$(\#\text{ states}) = \frac{d\Gamma(E)}{dE}\,dE$$ (shell)

so

$$\boxed{\rho(E) = \frac{d\Gamma(E)}{dE}\,w(E)}$$

Classically; $\Delta\Gamma = \Delta p \, \Delta q / (2\pi\hbar)^s$

{ statistical weight of phase volume

s = # degrees freedom

[$\hbar$ ensures S is dimensionless]

so define $\boxed{S = \ln \Delta\Gamma}$ → entropy

Now, need relate to distribution function: i.e.,

for subsystem: $\ln w(E_n) = \alpha + \beta E_n$

as $\ln w(E_n)$ is linear in E_n (additivity property!)

$$\ln \underset{\text{prob}}{w}(\overset{\text{avg. energy}}{\bar{E}}) \overset{\text{tight dist}}{=} \alpha + \beta \bar{E} = \overline{\ln w}$$

$$= \underbrace{\langle \ln w(E_n) \rangle}_{\text{statistical avg.}}$$

$$= -\sum_n w_n \ln w_n$$

so $\boxed{S = -\int d\Gamma \, f \ln f}$

defines entropy in terms dist.

Note: → $\Delta\Gamma = \Delta\Gamma_1 \Delta\Gamma_2 \dots \Delta\Gamma_\alpha$

→ $S = \sum_\alpha S_\alpha$

→ Entropy is function of exact value of energies of subsystem.

Now: $$\boxed{w(E) = e^{S(E)}}$$

pdf of energies.

for general quantity X ; $$\boxed{w(x) = c\, e^{S(x)}}$$

state variable

Now:

→ entropy (at eqbrm) maximal for $X = \text{const} = 0$

i.e. $$\left.\frac{\partial S}{\partial x}\right|_{x=0} = 0 \quad , \quad \left.\frac{\partial^2 S}{\partial x^2}\right|_{x=0} < 0$$

defines equilibrium.

→ note that "most probable state" is one of constant state variable ↔ uniform state.

∴ deviation from uniformity ↔ relaxation to equilibrium ...

- given $\partial S/\partial x = 0$, $\partial^2 S/\partial x^2 < 0$;

$$\left.\begin{aligned} w(x)dx &= \sqrt{\beta/2\pi}\; e^{-\beta x^2/2}\,dx \\ \langle x^2\rangle &= 1/\beta. \end{aligned}\right\}\ \text{distribution structure.}$$

- for multi-variable system: (n)

$$S = S_0 - \tfrac{1}{2}\sum_{i,k=1}^{n} \beta_{ik}\, x_i x_k$$

with summation convention,

$$S - S_0 = -\tfrac{1}{2}\,\beta_{ik}\, x_i x_k$$

Now, define: $\underset{\substack{\uparrow \\ \text{thermodynamic conjugate to } x_i}}{\underline{X}_i} = -\partial S/\partial x_i$

$(\underline{X}_i \to \text{flux},\ x_i \to \text{force})$.

$$\underline{X}_i = \beta_{ik}\, x_k$$

Motivating analogy: $\underset{\substack{\uparrow \\ \text{canonically} \\ \text{conjugate momentum}}}{p} = \partial S/\partial q$ in H-J theory so if write ⇒

$$W = \frac{\sqrt{\beta}}{(2\pi)^{n/2}} \exp\left[-\beta_{ik}\frac{x_i x_k}{2}\right]$$

$$\langle x_i X_k \rangle = \langle x_i \beta_{kj} x_j \rangle$$

$$= \delta_{ik}$$

$$\langle x_i x_k \rangle = \beta^{-1}_{ik} \qquad \left(\underline{\beta}^{-1}\underline{\beta} = \underline{\underline{I}}\right).$$

Now, for fluctuations, {i.e. seek pdf, moments.

$$W \cong e^{S} \text{ and actually, } \underset{\text{probability of fluctuation.}}{W} \cong e^{\overset{\text{amount entropy differs from maximum due to fluctuation}}{\Delta S}}$$

$$W \cong \exp\left[-\underset{\text{free energy change .....}}{R_{min}}/T\right]$$

$$R_{min} = \underbrace{\Delta E - T\Delta S + P\Delta V}_{\text{change induced by fluctuation ....}}$$

Now, can expand:

$$\Delta E - T\Delta S + p\Delta V = \frac{\partial E}{\partial S}\Delta S + \frac{\partial E}{\partial V}\Delta V + \frac{1}{2}\left[\frac{\partial^2 E}{\partial S^2}(\Delta S)^2 + 2\frac{\partial^2 E}{\partial S\partial V}(\Delta S\Delta V) + \frac{\partial^2 E}{\partial V^2}(\Delta V)^2\right] - T\Delta S + p\Delta V$$

$$\boxed{\begin{aligned}\frac{\partial E}{\partial S} &= T \\ \frac{\partial E}{\partial V} &= -p\end{aligned}}$$

$$= \frac{1}{2}\left[\Delta S\,\Delta\left(\frac{\partial E}{\partial S}\right)_V + \Delta V\,\Delta\left(\frac{\partial E}{\partial V}\right)_S\right]$$

$$= \frac{1}{2}\left[\Delta S\,\Delta T - \Delta p\,\Delta V\right]$$

$$W \sim \exp\left[\frac{\Delta p\Delta V - \Delta T\Delta S}{2T}\right]$$

and now can consider various cases. . .

if V, T are independent variables,

$$\Delta S = \left(\frac{\partial S}{\partial T}\right)_V \Delta T + \left(\frac{\partial S}{\partial V}\right)\Delta V = \frac{C_v}{T}\Delta T + \left(\frac{\partial p}{\partial T}\right)_V \Delta V$$

$$\Delta p = \left(\frac{\partial p}{\partial T}\right)_V \Delta T + \left(\frac{\partial p}{\partial V}\right)_T \Delta V$$

so . . . .

$\Rightarrow$

$$W \cong \exp\left[-\frac{C_V}{2T^2}(\Delta T)^2 + \frac{1}{2T}\left(\frac{\partial p}{\partial V}\right)(\Delta V)^2\right]$$

$\Rightarrow$

$$\begin{cases} \langle(\Delta T)^2\rangle = T^2/C_V \\ \langle(\Delta V)^2\rangle = -T\,(\partial V/\partial p)_T \end{cases}$$

and can consider other pairs independent variables...

Now, $(\Delta V)^2$ determines volume fluctuation in some part of body containing N particles. So, volume-per-particle fluctuation

$$\underbrace{\langle(\Delta(V/N))^2\rangle}_{\text{fluctuation in volume-per-particle.}} = -\frac{T}{N^2}\left(\frac{\partial V}{\partial p}\right)_T$$

Now, can hold volume fixed,

$$\Delta(V/N) = -\frac{T}{N^2}\frac{\partial V}{\partial p}$$

so $\langle(\Delta N)^2\rangle = -T\frac{N^2}{V^2}\left(\frac{\partial V}{\partial p}\right)_T$

but for ideal gas $pV = NT$

$$\Rightarrow \begin{cases} \langle (\Delta N)^2 \rangle \sim N \\ \left(\left\langle \frac{(\Delta N)^2}{N^2} \right\rangle \right)^{1/2} \sim 1/\sqrt{N} \end{cases}$$

basic # scalings of fluctuation levels

This brings us to dynamics .....

→ Some Basic Ideas of Dynamics ...

- correlation function ↔ measures $\begin{cases}\text{memory} \\ \text{rate of relaxation}\end{cases}$

$$\phi(t', t) = \langle X(t)\, X(t') \rangle$$

here: $\langle A \rangle = \int_0^{T_0} \frac{d\tau}{T_0} A(\tau)$

i.e. average is time on ensemble (statistical) average (ergodic hypothesis)

Now, for stationary process;

$$\phi(t) = \langle X(0)\, X(t) \rangle$$

\- correl'n. function depends only on time difference in multi-variable case:

$$\phi_{ik}(t'-t) = \langle x_i(t')\, x_k(t)\rangle$$

and 'trivial' symmetry property follows i.e.

$$\phi_{ik}(t'-t) = \langle x_i(t')\, x_k(t)\rangle$$

$$= \langle x_k(t)\, x_i(t')\rangle$$

$$= \phi_{ki}(t-t') = \phi_{ki}(-(t'-t))$$

$$\phi_{ik}(\tau) = \phi_{ki}(-\tau)$$

but, if particles motion in system is time reversal symmetric, then

have non-trivial symmetry, i.e.

$$\phi_{ik}(t) = \phi_{ik}(-t)$$

as

$$\langle x_i(t')\, x_k(t)\rangle = \langle x_i(t)\, x_k(t')\rangle$$

i.e. order at earlier/later time irrelevant.

This, at long last, brings us to Onsager symmetry ---

consider <u>relaxation</u> associated with slight deviation from equilibrium

$$\dot{x}_i = -\lambda_{ik} x_k \quad \rightarrow \text{ "generic relaxation equation"} \rightarrow \text{linear.}$$

More useful to express in terms conjugate variables,

$$\overline{\underline{X}}_i = -\partial S/\partial x_i$$

equilibrium, $\overline{\underline{X}}_i = 0$ (no entropy gradients)!

in **weak** deviation from equilibrium:

$$\overline{\underline{X}}_i = \beta_{ik} x_k \quad , \quad \text{where } x_k \text{ "small" (i.e. "near zero")}$$

of course, β_{ik} are quadratic coefficients of S, so $\beta_{ik} = \beta_{ki}$

Now,

$$\overline{\underline{X}}_i = \beta_{ik} x_k$$

$$x_k = \beta^{-1}_{ki} \overline{\underline{X}}_i$$

and plugging into relaxation equation ⇒

$$\boxed{\underbrace{\dot{x}_i}_{\text{evoln.}} = -\underbrace{\gamma_{ik}}_{\text{kinetic coefficient.}} \underbrace{X_k}_{\text{flux}}}$$

relaxation equation in terms conjugate variables.

$$\boxed{\gamma_{ik} = \lambda_{il}\,\beta^{-1}_{lk}}$$

Onsager Principle: $\gamma_{ik} = \gamma_{ki}$ if micro-dynamics (i.e. x_i evolution) reversible.

To prove:

- define $\mathcal{E}_i(t) \equiv$ mean of fluctuating quantities x_i at t

$\Theta_i(t) \equiv$ mean of X_i at t

then

$$\dot{\mathcal{E}}_i(t) = -\gamma_{ik}\,\Theta_k(t) \qquad t > 0.$$

If time-reversal symmetry:

$$\langle x_i(t)\,x_k(0)\rangle = \langle x_i(0)\,x_k(t)\rangle$$

or, stating in terms $\mathcal{E}$,

$$\langle \varepsilon_i(t)\, x_k \rangle = \langle x_i\, \varepsilon_k(t) \rangle$$ (avg. as ensemble)

take d/dt $\Rightarrow$

$$\langle \dot{\varepsilon}_i(t)\, x_k \rangle = \langle x_i\, \dot{\varepsilon}_k(t) \rangle$$

and use "ε" form of relaxation equation:
$\Rightarrow$

$$\gamma_{il} \langle \theta_l(t)\, x_k \rangle = \gamma_{kl} \langle x_i\, \theta_l(t) \rangle .$$

At $t=0$, $\theta_i = X_i$, so at $t=0$;

$$\gamma_{il} \langle X_l\, x_k \rangle = \gamma_{kl} \langle x_i\, X_l \rangle$$

$$\langle X_l\, x_k \rangle = \delta_{lk}$$ (quad. form)

$\Rightarrow$

$$\gamma_{il}\, \delta_{lk} = \gamma_{kl}\, \delta_{il}$$

$$\boxed{\gamma_{ik} = \gamma_{ki}}$$ Q.E.D.

$\rightarrow$ have proved Onsager relation.

Note:

- key to proof: time reversal symmetry of equations of motion

Onsager symmetry ⟺ detailed balance have same fundamental underpinning.

- rotation / gyration break (simple) Onsager symmetry (relevant exception)

if reverse time, need flip sign Ω, B_0

if not $\gamma_{ik} = -\gamma_{ki}$ (anti-symmetry).

- now, can express net dissipation ⟺ entropy production

let $f = \frac{1}{2} \gamma_{ik} x_i x_k$

so $\dot{x}_i = -\partial f/\partial x_i = -1/2\, \gamma_{ik} x_k$.

if $S = S(x_i)$

so $\dot{S} = \frac{\partial S}{\partial x_i}\dot{x}_i = -x_i\frac{\partial f}{\partial x_i}$

as f quadratic,

$$\boxed{\dot{S} = 2f} \longrightarrow \text{relates entropy production to dissipation}$$

i.e. $$\boxed{\dot{S} = \gamma_{ik}\, x_i\, x_k}$$

if $\underline{X} = \nabla T$

$\underline{\gamma_{ik}} = \underline{\underline{K}}$

$\Rightarrow \dot{S} = \int d^3x\ \underline{\nabla}T \cdot \underline{\underline{K}} \cdot \underline{\nabla}T$

in general,

$$\begin{cases} \dot{S} = -\overset{\substack{\text{force}\\ \downarrow}}{\underline{\nabla}X} \cdot \overset{\substack{\text{flux}\\ \downarrow}}{\underline{\Phi}} \\ \quad = \underline{\nabla}X \cdot \underline{\underline{D}} \cdot \underline{\nabla}X \end{cases} \Rightarrow \boxed{\text{relates to entropy production}}$$

N.B. Onsager symmetry facilitates variational calculation (relies on self-adjointness) of transport coefficients.

→ Transport Coefficients and Chapman-Enskog Theory, in detail .....

have discussed:
→ Boltzmann equation, H-thm.
→ thermodynamic force-flux relations, Entropy production, Onsager symmetry
→ basics of derivation of fluid equations from Boltzmann equation, and of Chapman-Enskog theory of transport coefficients.

Now, consider Chapman-Enskog theory, in detail ...

→ point of Chapman-Enskog theory is calculating
- rates of relaxation due collisions (i.e. on f)
→ - fluxes, transport coefficients (i.e. macroscopics)
→ - entropy production (key principle)

Entropy production ⇒ $X_\alpha = -\partial S/\partial x_\alpha \neq 0$
i.e. - finite thermodynamic force (i.e. gradient) present
- system departs Maxwellian

∴ → system will relax, ala:

$$\dot{x}_\alpha = -\gamma_{\alpha\beta} X_\beta$$

↳ Onsager matrix

→ underpinning of system relaxation is relaxation of distribution function → decay of perturbation from Maxwellian

<u>so</u>

$$f = f_0 + \delta f$$

generic phase space variables

$$\delta f = -\frac{\partial f_0}{\partial \epsilon}\chi(\Gamma) = \frac{f_0}{T}\chi(\Gamma)$$

↳ rescaled perturbed distribution

Now, $\chi(\Gamma)$ must satisfy <u>conservation</u> laws/constraints

<u>i.e.</u> number, momentum, energy } conserved ⇒ $\int f_0 \, d\Gamma$, $\int p \, f_0 \, d\Gamma$, $\int \epsilon \, f_0 \, d\Gamma$ } constrained

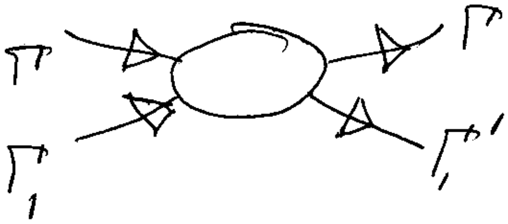
<u>so</u> perturbation must not violate constraint ⇒

$$\int d\Gamma \, \delta f \begin{pmatrix} 1 \\ p \\ \epsilon \end{pmatrix} = \int d\Gamma \, f_0 \begin{pmatrix} 1 \\ p \\ \epsilon \end{pmatrix} = 0$$

For Chapman-Enskog procedure, recall Boltzmann equation:

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

$$C(f) = \int d\Gamma_1\, d\Gamma'\, d\Gamma_1'\, \underset{\text{transition probability}}{w'}\left(\overset{\text{final}}{f' f_1'} - \overset{\text{initial}}{f_1 f}\right)$$



$$f = f_0 + \delta f$$
$$= f_0\left(1 + \frac{\chi}{T}\right)$$

$$\therefore\ C(f) = \int d\Gamma_1 \int d\Gamma' \int d\Gamma_1'\, w'\Bigg(f_0' f_{0,1}'\left(1+\frac{\chi'}{T}\right)\left(1+\frac{\chi_1'}{T}\right)$$
$$- f_{0,1} f_0\left(1+\frac{\chi}{T}\right)\left(1+\frac{\chi_1}{T}\right)\Bigg)$$

$$\cong \int d\Gamma_1 \int d\Gamma' \int d\Gamma_1'\, w'\, f_{0,1} f_0 \left(\cancel{1} + \frac{\chi' + \chi_1'}{T} - \cancel{1} - \frac{\chi - \chi_1}{T}\right)$$

as $f_0' f_{0,1}' = f_{0,1} f_0$ (equilibrium distribution)

$$\cong f_0 \int d\Gamma_1 \int d\Gamma' \int d\Gamma_1'\, \frac{w f_{0,1}}{T}\left(\chi' + \chi_1' - \chi - \chi_1\right)$$

to l.o. in P.T.

$$\equiv \frac{f_0}{T} I(\chi)$$ → defines collision effect on δf

where operator $I(\chi)$ (collisional relaxation of perturbation) is:

$$\boxed{I(\chi) = \int w' \cdot f_{0,1} \, (\chi' + \chi_1' - \chi - \chi_1) \, d\Gamma_1 \, d\Gamma' \, d\Gamma_1'}$$

Now, can observe:

if $\chi = \text{const} \Rightarrow I(\chi) = 0$

$\chi = \epsilon \Rightarrow I(\chi) = 0$ as

$\epsilon' + \epsilon_1' = \epsilon + \epsilon_1$ (energy conservation)

$\chi = \underline{p} \cdot \underset{\text{boost}}{\delta \underline{V}} \Rightarrow I(\chi) = 0$ as

$\delta \underline{V} \cdot (\underline{p}_1' + \underline{p}' = \underline{p} + \underline{p}_1)$ (momentum conservation)

$I(\chi)$ consistent with conservation constraints.

→ Now can make progress by relating Boltzmann equation to macroscopics.

For gas at rest:

$$f_0 = \exp\left(\frac{\overset{\text{chem. potential}}{\mu} - \epsilon(\Gamma)}{T}\right)$$

energy associated with internal degrees freedom

$$\downarrow$$

and $\epsilon(\Gamma) = \frac{1}{2} m v^2 + \epsilon_{int}$

so in moving gas;

$$f_0 = \exp\left[\frac{(\mu - \epsilon_{int})}{T}\right] \exp\left[-\frac{m}{2T}(\underline{v}-\underline{V})^2\right]$$

as transport coefficients independent $\underline{V}$, can examine in frame where $\underline{V} = 0$ (but $\underline{V}' \neq 0$)

so . . .

$$\frac{1}{f_0}\frac{\partial f_0}{\partial t} = \left[\left(\frac{\partial \mu}{\partial T}\right)_p - \frac{(\mu - \epsilon(\Gamma))}{T}\right]\frac{\partial T}{\partial T} + \left(\frac{\partial \mu}{\partial p}\right)_T \frac{\partial p}{\partial t}$$

$$+ \; m\underline{v} \cdot \frac{\partial \underline{V}}{\partial t}$$

Now, thermo $\Rightarrow$ $\left(\frac{\partial \mu}{\partial T}\right)_p = -S$ (entropy per particle)

$\left(\frac{\partial \mu}{\partial p}\right)_T = 1/N$ (volume per particle)

$\mu = W - TS$ (heat fctn. $(W = c_p T)$)

$$\underline{\otimes}\ \underline{\underline{(1)}} \quad \frac{\partial f_0}{\partial t} = \frac{f_0}{T}\left[\left(\frac{\epsilon(\Gamma)-w}{T}\right)\frac{\partial T}{\partial t} + \frac{1}{N}\frac{\partial p}{\partial t} + m\underline{v}\cdot\frac{\partial \underline{V}}{\partial t}\right]$$

and similarly:

$$\underline{\underline{(2)}} \quad \underline{v}\cdot\underline{\nabla} f_0 = \frac{f_0}{T}\left[\left(\frac{\epsilon(\Gamma)-w}{T}\right)\underline{v}\cdot\underline{\nabla}T + \left(\frac{1}{N}\right)\underline{v}\cdot\underline{\nabla}p + m\, v_\alpha v_\beta V_{\alpha\beta}\right]$$

where $V_{\alpha\beta} = \frac{1}{2}\left(\frac{\partial V_\alpha}{\partial x_\beta} + \frac{\partial V_\beta}{\partial x_\alpha}\right)$ → strain tensor

$$V_{\alpha\alpha} = \underline{\nabla}\cdot\underline{V}$$

and used $v_\alpha v_\beta \frac{\partial V_\beta}{\partial x_\alpha} = v_\alpha v_\beta V_{\alpha;\beta}$

As $\frac{\partial f_0}{\partial t} + v\cdot\nabla f_0 = \frac{f_0}{T}\left(I(\chi)\right)$

will add $\underline{\underline{(1)}}$ and $\underline{\underline{(2)}}$. Observe that

$\underline{\underline{(1)}}$, $\underline{\underline{(2)}}$ add to form fluid equations i.e. $$\frac{\partial T}{\partial t} + \underline{V}\cdot\nabla T \; - - - - -$$

$$\frac{\partial P}{\partial t} + \underline{V}\cdot\underline{\nabla} P \; - - - - -$$

{ forms emerge from addition

etc.

Now, use:

$$\frac{\partial \underline{V}}{\partial t} = \frac{-1}{\rho}\underline{\nabla P} = -\frac{1}{Nm}\underline{\nabla P}$$ (Euler)

$$\frac{\partial N}{\partial t} = -N\,\underline{\nabla}\cdot\underline{V}$$ (Continuity)

As $N = P/T$ for gas,

$$\frac{1}{N}\frac{\partial N}{\partial t} = \frac{1}{P}\frac{\partial P}{\partial t} - \frac{1}{T}\frac{\partial T}{\partial t} = -\underline{\nabla}\cdot\underline{V}$$

Also, entropy conservation $\Rightarrow$

$$\frac{\partial s}{\partial t} + \underline{V}\cdot\underline{\nabla} s = 0$$

and $V = 0 \Rightarrow \partial s/\partial t = 0$

$$\frac{\partial s}{\partial t} = 0 = \frac{\partial}{\partial t}\left(\left(\frac{\partial s}{\partial T}\right)_p T + \left(\frac{\partial s}{\partial p}\right)_T p \right)$$

$$0 = \frac{c_p}{T}\frac{\partial T}{\partial t} - \frac{1}{p}\frac{\partial p}{\partial t} \qquad (*)$$

as $\left(\frac{\partial s}{\partial T}\right)_p = \frac{c_p}{T}$, $\left(\frac{\partial s}{\partial p}\right)_T = -\frac{1}{p}$

with:

$$\frac{1}{p}\frac{\partial p}{\partial t} - \frac{1}{T}\frac{\partial T}{\partial t} = -\underline{\nabla}\cdot\underline{V} \qquad (*)$$

$\Rightarrow$ can combine starred equations:

$$\frac{1}{T}\frac{\partial T}{\partial t} = -\frac{1}{c_v}\underline{\nabla}\cdot\underline{V} , \quad \frac{1}{p}\frac{\partial p}{\partial t} = -\frac{c_p}{c_v}\underline{\nabla}\cdot\underline{V}$$

$$c_p - c_v = 1$$

So, can add results for $\partial f_0/\partial t$, $\underline{v}\cdot\underline{\nabla} f_0$ and exploit macroscopic relations to obtain:

$$\frac{\partial f_0}{\partial t} + \underline{v}\cdot\underline{\nabla} f_0 = \frac{f_0}{T}\left\{ \frac{\epsilon(\Gamma) - w}{T}\, \underline{v}\cdot\underline{\nabla} T + m v_\alpha v_\beta \overline{V}_{\alpha\beta} + \left(\frac{w - T c_p - \epsilon(\Gamma)}{c_v}\right) \underline{\nabla}\cdot\underline{V} \right\}$$

with $W = c_p T$, can re-write Boltzmann equation for gas as:

$$\boxed{\left(\frac{\epsilon(\Gamma) - c_p T}{T}\right) \underline{v}\cdot\underline{\nabla} T + \left[m v_\alpha v_\beta - \delta_{\alpha\beta}\frac{\epsilon(\Gamma)}{c_v}\right] \overline{V}_{\alpha\beta} = I(\chi)}$$

→ Boltzmann eqn. in Chapman-Enskog expansion, expressed in macro-scopics.

→ Application: Calculating the Thermal Conductivity .....

Now, → need determine $\underline{K}$ s/t

$$\underbrace{\underline{Q}}_{\text{heat flux}} = -\underbrace{\underline{\underline{K}}}_{\text{conductivity tensor}} \cdot \underbrace{\underline{\nabla} T}_{\text{temperature gradient}}$$

→ need solve simplified Boltzmann equation, with $\nabla T \neq 0$.

taking $V_{\alpha,\beta} \to 0$,

$$\boxed{\frac{\epsilon(\Gamma) - C_p T}{T}\, \underline{v}\cdot\nabla T = I(\chi)}$$

transport equation

- note that this is integral equation.
- obtain $\underline{\underline{\chi}}$, then $\delta f = f_0 \frac{\chi}{T}$
  ↳ "the answer"

Now solution must have form:

$$\chi = \underline{g}\cdot\underline{\nabla} T$$

as - non-equilibrium is $\underline{\nabla} T$-driven

- $\underline{\nabla} T$ factor on both sides transport equation

so $\underline{g} = \underline{g}(\Gamma)$, i.e. independent of $\underline{\nabla} T$

key: χ must be linear in ∇T!
⟺ Perturbation / linear response.

So

$$\frac{\epsilon(\Gamma) - c_p T}{T}\, \underline{v}\cdot\underline{\nabla} T = I(\chi) = I\left(\underline{g}\cdot\underline{\nabla} T\right)$$

$$= I(\underline{g})\cdot\underline{\nabla} T$$

as temp. gradient necessarily outside collision integral.

So

$$\boxed{\underline{v}\left(\frac{\epsilon(\Gamma) - c_p T}{T}\right) = I(\underline{g})}$$

Also, χ must satisfy conservation laws, i.e.:

$$\int d\Gamma\, f_0 \begin{pmatrix} \chi \\ \epsilon\chi \\ \underline{p}\chi \end{pmatrix} = 0 \quad , \qquad \chi = \underline{g}\cdot\underline{\nabla} T$$

Can observe straight out:

for number or energy perturbation, need:

$$\left.\begin{array}{l} \int d\Gamma\, f_0\, \underline{g} \neq 0 \\ \int d\Gamma\, f_0\, \epsilon\, \underline{g} \neq 0 \end{array}\right\rangle \text{ must specify ``direction'' of vector integrals.}$$

but transport equation gives no vector parameters which set direction.

$\therefore$ $\underline{\underline{\text{no}}}$ $\begin{pmatrix}\text{number}\\ \text{energy}\end{pmatrix}$ perturbation, as must be.

Momentum conservation requires: $\int d\Gamma\, f_0\, \underline{v}\cdot g = 0.$

Now calculate $\underline{\underline{K}}$ by calculating energy flux <u>due</u> <u>collisions</u> (i.e. neglect bulk motion)

↳ meaning ?

Now, $\underline{q} = \int d\Gamma\, \underline{v}\, \epsilon \,(\underset{\text{no direction}}{\cancel{f_0}} + \delta f)$

$$= \int d\Gamma\, \underline{v}\, \epsilon\, \frac{\chi f_0}{T}$$

$$= \int d\Gamma\, \underline{v}\, \epsilon\, \frac{f_0}{T}\, g\cdot \underline{\nabla} T$$

<u>So</u>

$$\boxed{\begin{aligned} q_\alpha &= -K_{\alpha\beta}\frac{\partial T}{\partial x_\beta} \\ K_{\alpha\beta} &= -\frac{1}{T}\int f_0\, \epsilon\, v_\alpha\, g_\beta\, d\Gamma \end{aligned}}$$

general expression for conductivity

For isotropic gas (i.e. equilibrium)

→ $K_{\alpha\beta}$ diagonal

→ $K = \frac{1}{3} K_{\alpha\alpha}$

$$\boxed{\underline{q} = -K\,\underline{\nabla}T \;, \quad K = -\frac{1}{3T}\int d\Gamma\, f_0\, \epsilon\, \underline{v}\cdot\underline{g}}$$

Note that $\chi = g\cdot\underline{\nabla}T$

$$I(\chi) = \frac{\epsilon(\Gamma) - c_p T}{T}\, \underline{v}\cdot\underline{\nabla}T$$

makes $K>0$, as flux opposite to temperature gradient.

Note: In general, is total X-flux necessarily opposite $\underline{\nabla}X$??.

So, finally:
$$\boxed{K = -\frac{1}{3T}\int d\Gamma\, f_0\, \epsilon\, \underline{v}\cdot\underline{g}}$$

→ Estimates

$$K = -\frac{1}{3T}\int d\Gamma\, f_0\, \epsilon\, \underline{v}\cdot\underline{g}$$

In simple monatomic gases, g must have form:

$$\underline{g} = \frac{\underline{v}}{v}\, g(v)$$

, as $\underline{v}$ is only vector "available" to $\underline{g}$.

At this point, must employ some approximate collision operator, i.e.

$$C(f) = -\nu\,(f - f_0)$$

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

So

$$\underline{q} = \int d\Gamma\, \delta f\, \epsilon$$

$$= \int d\Gamma \left(\frac{-\underline{v}\cdot\nabla f_0}{\nu}\right)\epsilon$$

$f_0 \equiv$ Maxwellian with $T = T(x)$

so ⇒ $g \sim \frac{v_{Th}}{\nu} \sim l_{mfp}$

⇒ $K \sim \underset{\substack{\downarrow \\ \text{specific} \\ \text{heat per molecule}}}{c} \, N \overbrace{l_{mfp} v_{Th}}^{D}$

⇒ can re-write as:

$l_{mfp} \sim 1/N\underset{\substack{\hookrightarrow \text{collisional} \\ \text{cross section}}}{\sigma}$, $v_{Th} \sim \sqrt{T/m}$

$K \sim (1/\sigma)\sqrt{T/m}$ [$\sigma(T)$ generally decreases with T]

⇒ P.T. ⇒ $\delta f/f_0 \ll 1$

→ $\frac{\chi}{T} \overset{?}{\ll} 1 \Rightarrow \frac{g \cdot \nabla T}{T} \overset{?}{\ll} 1$

$\Rightarrow l_{mfp} \frac{\nabla T}{T} \ll 1$

condition for P.T. is $l_{mfp}/L_T \ll 1$. ✓

(refer basic orderings)

Aside: Physical interpretation of $g \sim l_{mfp}$

Recall: $\text{Fluxes} \longleftrightarrow \int d^3\underline{v}\,\overset{\text{moment}}{\{\underline{v}\}}\,\delta f$

↓
response to fluctuation in f
induced by gradient (thermodynamic force)

where: $\left\{ \begin{array}{l} \delta f = \dfrac{f_0}{T}\chi \\ \chi = \underline{g}\cdot\underline{\nabla}T \end{array} \right.$ from general structural arguments

and correspondence with result of Krook operator calculation or simple dimensional analysis ⇒

$$g \sim l_{mfp}$$

One can 'understand' this result heuristically by considering 'collisional mixing' of the temperature gradient, i.e.

$$\delta f = \left(\frac{\partial f}{\partial T}\right)\delta T = -\frac{f_0}{T}\,\delta T$$

$$\underset{\text{fluctuation in } T}{\delta T} = T(x - l_{mfp}) - T(x) = -l_{mfp}\,\underset{\text{gradient drive}}{\partial T/\partial x}$$

so $$\delta f = \frac{\partial f}{\partial T}\left(-l_{mfp}\frac{\partial T}{\partial x}\right) = \frac{f_0}{T}\,l_{mfp}\frac{\partial T}{\partial x}$$

$\therefore \quad \delta f/f_0 \cong \frac{l_{mfp}}{T}\frac{\partial T}{\partial x} \sim \frac{l_{mfp}}{L_T} \sim \frac{\omega_{stream}}{\nu} \ll 1.$

and $g \sim l_{mfp}$.

Generically: $\chi \sim 1/\sigma \, v_{th}$

- how far will χ scaling persist as T increases assuming σ decreases with increasing T?
- what happens at "flux limit" i.e. $l_{mfp} \sim L_T$?

Furthur Discussion of Transport Theory and Chapman - Enskog Expansion

ⓐ → Onsager symmetry revisited
⇒ self-adjointness of $I(\chi)$ operator

ⓑ → systematic solution of transport equation

Why? → Deeper insight into structure of the theory ....

⑨ Onsager Symmetry, Revisited

recall generic flux ⟺ force relation (abstract form)

$$\dot{x}_a = -\sum_b \gamma_{ab} \underline{X}_b$$

$\dot{x}_a$ ⟶ flux

$\underline{X}_b$ ⟶ force $\sim -\partial S/\partial x_b$

if a, b physical processes time reversal invariant ⟺

$\gamma_{ab} = \gamma_{ba}$ → Onsager Symmetry

for entropy production rate:

$$\dot{S} = -\underline{X}_a \dot{x}_a = \sum_{a,b} \gamma_{ab} \underline{X}_a \underline{X}_b$$

Example: Heat Flux, Thermal diffusivity, etc.

$\dot{x}_a \to \underline{q}$ → heat flux

$\underline{X}_a \to \frac{1}{T^2}\frac{\partial T}{\partial x}$ → temperature gradient as thermodynamic force $\left(S \sim \frac{1}{T}\right)$

$\therefore \gamma_{a,b} = T^2 \kappa_{\alpha\beta}$ → thermal conductivity is kinetic coefficient.

Now – in explicit calculation performed, symmetry of $R_{\alpha\beta}$ follows from isotropy of f_0

- here, demonstrate that Onsager symmetry follows from fundamental structure of Boltzmann equation

?: But who cares?? We know hard sphere gas collisions are time reversible, so transport matrix MUST be Onsager symmetric?!

A: Direct proof establishes:
→ approximations made in Chapman-Enskog theory don't violate/mutilate time reversal symmetry of dynamics

? How is it that Chapman-Enskog theory, which calculates irreversible process producing entropy, is consistent with time reversal symmetry which underpins Onsager symmetry?

→ self-adjointness of approximated collision operator which is useful in formulating variational principle and more general solution.

→ Recall: Chapman-Enskog seeks $\int d\Gamma \, \underline{v} \, v^n \, \delta f$

where $\delta f = \frac{f_0}{T} \chi$ and, in general:

$$\chi = \sum_a \underset{\substack{\uparrow \\ \text{response (i.e. } \delta\chi/\delta \underline{X}_a) \\ \text{(contains transport coeff)}}}{g_a(\Gamma)} \; \overset{\text{force}}{\underline{X}_a}$$

i.e. for temperature, thermal conduction:

$\chi = \underline{g} \cdot \underline{\nabla} T$, where g obeys:

$$\left(\frac{\epsilon(\Gamma) - c_p T}{T} \right) \underline{v} \cdot \underline{\nabla} T = I(\chi)$$

$\Rightarrow$

$$I(g) = \underline{v} \, \frac{\epsilon(\Gamma) - c_p T)}{T} \rightarrow$$ "transport equation, 'appropriately linearized'"

with T^2, $$\boxed{\underline{I}(g_\alpha) = T(\epsilon(\Gamma) - c_p T) v_\alpha}$$

and must have: $$\int f_0 \, g_\alpha \begin{pmatrix} 1 \\ \epsilon \\ p \end{pmatrix} d\Gamma = 0$$

to maintain conservation laws.

Now, can also observe:

(1) $L_a = I(g_a)$ is generic form of transport equation

($\underline{\text{i.e.}}$ $L_a = T(\epsilon - c_p T)V_a$, for heat)

and also generically;

(2) $\dot{x}_a = -\sum_b \gamma_{ab} \overline{X}_b$

$= \int d\Gamma\, \underline{v} \overset{\text{general moment}}{\{(\underline{v}^n)\}}\, \delta f$

flux

$\underline{\underline{\text{i.e.}}}$ $\underline{q} = \frac{1}{T} \int f_0 \epsilon \underline{v} g \cdot \nabla T d\Gamma$

where:

$$\delta f = \frac{f_0}{T}\chi = \frac{f_0}{T} \sum_a g_a \overline{X}_a$$

so

(3) $\dot{x}_a = -\sum_b \gamma_{ab} \overline{X}_b$

$$= \int d\Gamma\, \underline{v} \{(\underline{v}^n)\} \left(\frac{f_0}{T} \sum_b g_b \overline{X}_b \right)$$

Now, note $\underline{V}\{\underline{V}'\} \overset{\text{corresponds}}{\longleftrightarrow} \underline{L}$.

i.e. for heat, can write: $L_a = V_a(\epsilon - c_p T)T$

so can write, in general (by correspondence):

$$\boxed{T^2 \gamma_{\alpha,\beta} = -\int d\Gamma\, f_0\, L_\alpha\, g_\beta}$$

{ general matrix element in Chapman-Enskog theory

→ general form of Onsager matrix element, in terms { → L_α ⇔ transport equation evolution operator
→ g_β ⇔ δf (i.e. $\chi = \sum_\beta g_\beta \underline{X}_\beta$)

→ to show Onsager symmetry, need show:

$$\gamma_{\alpha\beta} = \gamma_{\beta\alpha} \rightarrow \boxed{\int d\Gamma\, f_0 L_b g_a = \int d\Gamma\, f_0\, g_a L_b}$$

Proceed via:

- showing self-adjointness of collision operator

then

- Onsager symmetry

→ First: Self-Adjointness $\underline{I}(\chi)$

Need show: $\boxed{\int d\Gamma f_0\, \varphi\, I(\psi) = \int d\Gamma f_0\, \psi\, I(\varphi)}$

Now:

$d\Gamma d\Gamma_1 d\Gamma' d\Gamma_1'$

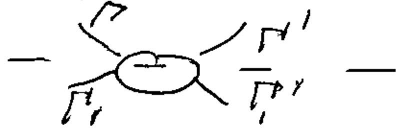
$\int$

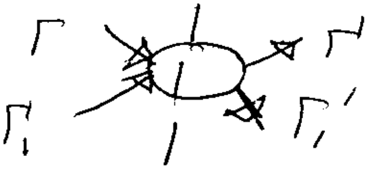
$$\int f_0\, \varphi\, \underline{I}(\psi)\, d\Gamma = C$$

$$= \int f_0 f_{0_1} W' \varphi \left(\psi' + \psi_1' - \psi - \psi_1\right) d^4\Gamma$$

now, as $\Gamma, \Gamma_1, \Gamma', \Gamma_1'$ all integrated over:

- interchange $\Gamma, \Gamma' \Longleftrightarrow \Gamma_1, \Gamma_1'$
- interchange $\Gamma, \Gamma_1 \Longleftrightarrow \Gamma', \Gamma_1'$





so

$$C = \frac{1}{4} \int f_0 f_{0_1} \left[W'(\varphi + \varphi_1) - W(\varphi' + \varphi_1')\right] *$$
$$\left[(\psi' + \psi_1') - (\psi + \psi_1)\right] d^4\Gamma$$

Consider similar integral with:

$T \equiv$ time reversal

$$\psi(\Gamma) \to \varphi(\Gamma^T)$$

$$\varphi(\Gamma) \to \psi(\Gamma^T)$$

with:

$\rightarrow \Gamma, \Gamma_1, \ldots \rightarrow \Gamma^T, \Gamma_1^T \ldots$

and:

$\rightarrow$ detailed balance

$\Rightarrow$

$$\int f_0 \psi^T I(\varphi^T) d\Gamma = \frac{1}{4} \int f_0 f_{01} \left[w(\psi + \psi_1) - w'(\psi' + \psi_1') \right] \left[(\varphi' + \varphi_1') - (\varphi + \varphi_1) \right] d^4\Gamma$$

and had:

$$\int f_0 \varphi I(\psi) d\Gamma = \frac{1}{4} \int f_0 f_{01} \left[w'(\varphi + \varphi_1) - w(\varphi' + \varphi_1') \right] * \left[(\psi' + \psi_1') - (\psi + \psi_1) \right] d^4\Gamma$$

Noting:

$$\int f_0 f_{01}\, w\, (\psi + \psi_1)(\varphi + \varphi_1) d^4\Gamma = \int f_0 f_{01}\, w'\, (\psi + \psi_1)(\varphi + \varphi_1) d^4\Gamma$$

[n.b. not yet imposing detailed balance].

we then have:

$$\boxed{\int f_0 \varphi I(\psi)\, d\Gamma = \int f_0 \psi^T I(\varphi^T)\, d\Gamma}$$

Now, using detailed balance:

$$\int d\Gamma\, f_0 \psi^T \underline{I}(\varphi^T) = \int f_0 \psi \underline{I}(\varphi)\, d\Gamma$$

so

$$\boxed{\int f_0 \varphi I(\psi)\, d\Gamma = \int f_0 \psi I(\varphi)\, d\Gamma}$$

$\Rightarrow$ $\boxed{\underline{I}(\psi) \text{ is self-adjoint!}}$

$\Rightarrow$ message is that approximations must respect self-adjointness!.

Now proceed to Onsager proof $\Rightarrow$ consider kinetic coefficients.

Recall need: $\int f_0 L_a g_b\, d\Gamma = \int f_0 L_b g_a\, d\Gamma$

Now, $L_a(\Gamma^{+T}) = \pm L_a(\Gamma^{+})$

$+ \rightarrow$ viscosity $(\sim vv)$
$- \rightarrow$ thermal conduction $(\sim v)$

so

$$\int f_0 g_b L_a \, d\Gamma = \pm \int f_0 g_b^{T} I(g_a) \, d\Gamma^{+T}$$

as $L_a = I(g_a)$ (transport equation)

Using self-adjointness

$$\int f_0 g_b L_a \, d\Gamma = \pm \int f_0 g_a^{T} I(g_b) \, d\Gamma^{+T}$$
$$= \pm \int f_0 g_a^{T} L_b(\Gamma) \, d\Gamma^{+T}$$

using transport equation again.

Finally, using time reversal again $\Rightarrow$
$(\Gamma \Leftrightarrow \Gamma^{+T})$

$$\boxed{\int f_0 g_b L_a \, d\Gamma = \int f_0 g_a L_b \, d\Gamma}$$

and have shown Chapman-Enskog theory consistent with Onsager symmetry.

Finally, can also:

→ relate diagonal coefficients to entropy production

→ show diagonal coefficients must be positive definite

Now, $S = -\int d\Gamma\, f \ln f$

so $$\frac{dS}{dt} = -\int d\Gamma \left[\frac{df}{dt} \ln f + \frac{df}{dt} \right]$$

$$= -\int d\Gamma \left[C(f) \ln f \right]$$

[N.B. Why $\int d\Gamma \frac{df}{dt} = 0$?]

Now; $f = f_0 \left(1 + \frac{x}{T} \right)$

$$C(f) = \frac{f_0}{T} I(x)$$

$$\frac{dS}{dt} = -\int d\Gamma \left[\frac{f_0}{T} I(x) \ln \left(f_0 \left(1 + \frac{x}{T} \right) \right) \right]$$

and expanding ---

$$\frac{dS}{dt} = \overset{\textcircled{1}}{-\int d\Gamma \left[\frac{f_0}{T} I(\chi) \ln f_0 \right]} - \overset{\textcircled{2}}{\int d\Gamma \left[\frac{f_0}{T} I(\chi) \ln\left(1 + \frac{\chi}{T}\right)\right]}$$

but $\ln f_0 = -\frac{\epsilon}{T}$ so

$$\textcircled{1} = -\int d\Gamma \left[\frac{f_0}{T} I(\chi) \ln f_0 \right]$$

$$= +\int d\Gamma \left[\frac{f_0}{T} \epsilon\, I(\chi) \right] = 0 \, !$$

as collision operator is energy conserving !.

so

$$\frac{dS}{dt} = -\int d\Gamma \frac{f_0}{T} I(\chi) \ln\left(1 + \frac{\chi}{T}\right)$$

$$\cong -\int d\Gamma \frac{f_0}{T} I(\chi) \frac{\chi}{T}$$

so $\frac{dS}{dt} > 0 \Leftrightarrow -\int d\Gamma f_0\, \chi\, I(\chi) > 0$.

Now recall: $L_a = I(g_a)$

$$\gamma_{a,b} = -\frac{1}{T^2} \int f_0\, L_a\, g_b\, d\Gamma$$

$$\therefore \quad \gamma_{ab} = \frac{-1}{T^2}\int f_0 \, I(g_a)\, g_b \, d\Gamma$$

and thus diagonal coefficients ⇒

$$\gamma_{a,a} = \frac{-1}{T^2}\int d\Gamma \, f_0 \, g_a \, I(g_a)$$

so for $x = g_a$, on $-\int d\Gamma f_0 \, x \, I(x) > 0$

have $$\boxed{\gamma_{a,a} > 0 \quad \text{for} \quad \frac{dS}{dt} > 0}$$

so diagonal components of Onsager matrix are positive definite!

② Systematics of Calculating Transport Coefficients

→ up till now, have focused on:
1) general structure, properties of Boltzmann equation
2) simple approximations to solution - i.e. Krook operators

Now, seek to discuss more general solution and variational structure, exploiting self-adjointness of $I(\chi)$, already proved.

Recall the fundamental problem: Linearized Boltzmann equation is an integral equation, i.e. (for K):

$$\left.\begin{aligned}
&\underset{\substack{\uparrow \\ \underline{v}\cdot\underline{\nabla} f_0}}{\frac{\epsilon(\Gamma) - c_p T}{T}\, \underline{v}\cdot\nabla T} = \underset{\substack{\uparrow \\ \text{collision operator}}}{I(\chi)} \\
&\text{where: } I(\chi) = \int w' f_{0 1}(\chi' + \chi_1' - \chi - \chi_1)\, d\Gamma_1\, d\Gamma'\, d\Gamma_1'
\end{aligned}\right\}$$

(? - explain constituents)

with solution of form $\chi = \underline{g}\cdot\underline{\nabla} T$, transport equation becomes:

$$-\underline{v}\left(5/2 - \beta v^2\right) = I(\underline{g})$$

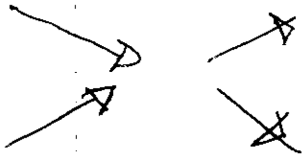
$\left\{ c_p = 5/2 \text{ for Monatomic gas} \right.$

where can re-write $I(\chi)$ as:

$$I(g) = \int d\Gamma_1 \int d\Gamma' \int d\Gamma_1' \, f_{0,1} \, (g' + g_1' - g - g_1) \, w'$$

Now, can exploit definition, for simple collisions:

$$\int d\Gamma' \int d\Gamma_1' \, w'(\Gamma', \Gamma_1'; \Gamma, \Gamma_1) = \int \underset{\substack{\uparrow \\ \text{differential} \\ \text{cross-section}}}{d\sigma} \; \overset{\text{relative velocity}}{V_{rel}}$$



so

$\{ g = g(\underline{V})$, recall

$$I(g) = \int d\underline{p}_1 \int d\sigma \, V_{rel} \, f_{0,1} \, (g' + g_1' - g - g_1)$$

$$f_0(v) = \left(N \beta^{3/2} / m^3 \, \pi^{3/2}\right) e^{-\beta v^2}$$

Now, convenient to expand $g(\underline{V})$ in Sonine polynomials (i.e. related to generalized Laguerre polynomials) → complete set

i.e.

$$g(\underline{V}) = \frac{\beta}{N} \, \underline{V} \sum_{s=1}^{\infty} \overset{\text{coeff}}{A_s} \; \underset{\substack{\uparrow \\ \text{Sonine Polynomial.}}}{S_{3/2}^{s}} (\beta V^2)$$

where: $\left\{ S_r^{s}(x) = \frac{1}{s!} e^{x} x^{-r} \frac{d^s}{dx^s}\left(e^{-x} x^{r+s}\right) \right.$

defines polynomial. Here $\left\{ \begin{array}{l} r = \text{any number} \\ s = \text{nonnegative integer} \end{array} \right.$

So

$$S_r^0 = 1, \quad S_r^1(x) = r+1-x$$

Orthogonality (for same r, different s) is:

$$\int_0^\infty e^{-x} x^r S_r^s(x) S_r^{s'}(x)\,dx = \delta_{s,s'} \Gamma(r+s+1)/s!$$

N.B.: Omitting $s=0$ guarantees momentum conservation.

Observe LHS of transport equation related to $S^1_{3/2}(\beta v^2)$ so can re-write:

$$-\underline{v}\, S^1_{3/2}(\beta v^2) = (\beta/N) \sum_{s=1}^{\infty} A_s\, I(\underline{v}\, S^s_{3/2})$$

and can proceed using orthogonality.

$$\int \left[\underline{v}\, f_0(\underline{v})\, S^{\ell}_{3/2}(\beta v^2) \cdot \left(-\underline{v}\, S^{1}_{3/2}(\beta v^2)\right)\right] d^3p =$$

$$\int \left[\underline{v}\, f_0(v)\, S^{\ell}_{3/2}(\beta v^2) \cdot \frac{\beta}{N} \sum_{s=1}^{\infty} A_s\, I(\underline{v}\, S^{s}_{3/2}) \right] d^3p$$

$\Rightarrow$

$$\frac{15}{4}\, \delta_{\ell,1} = \sum_{s=1}^{\infty} a_{\ell,s}\, A_s$$

where $a_{\ell s} = -\beta^2/N^2 \int f_0\, \underline{v} \cdot S^{\ell}_{3/2}\, I(\underline{v}\, S^{s}_{3/2})\, d^3p$

→ this mess defines a set of algebraic equations for coefficients A_s

→ then: $g(\underline{v}) = \frac{\beta}{N}\, \underline{v} \sum_{s=1}^{\infty} A_s\, S^{s}_{3/2}(\beta v^2)$

and,

$$\kappa = -\frac{1}{3T} \int f_0\, \epsilon\, \underline{v} \cdot \underline{g}\, d\Gamma$$

gives exact, series solution for thermal conductivity. Grinding the crank gives

$\kappa = 5A_1/4$.

→ Now, series expansion gives systematic, approximate solution, converging to exact solution.

Useful to note that values of transport coefficients so obtained, approach exact solution from below, i.e.

⇒ Variational Principle for Transport Coefficients:

The solution of $\underline{L} = I(\underline{g})$ (i.e. the linearized Boltzmann equation) gives a maximum of the functional $-\int f_0\, g\, I(g)\, d^3p$, and so an upper bound, on the transport coefficient.

The point:

→ actual transport equation is:

(1) $I(\underline{g}) = \underline{L}$ (integro-differential equation)

and transport coefficient (i.e. K) satisfies:

$$D \sim -\int f_0 g I(g)\, d^3p > 0$$

R,T:

→ series solution rests on orthogonality property ✓ and integral relation

(2) $\int d^3p\, f_0 g I(g) d^3p = \int d^3p\, f_0 L g$

Claim that "maximal D" results from solution of (1) among class of functions which satisfy (2).

∴ can maximise D subject to constraint of satisfying (2) i.e. meaning?

- determine a g (parametrically dependent) which satisfies (2)

then

- maximise $-\int f_0 \, g \, I(g) \, d^3p$ with respect to parameter in g.

$\Rightarrow$ variational calculation of transport coefficient.

To show, need show:

$$-\int f_0 \, g \, I(g) \, d^3p > -\int f_0 \, \varphi \, I(\varphi) \, d^3p$$

where g satisfies (1) and φ satisfies (2).

Now, consider

$$R = -\int f_0 (g-\varphi) I(g-\varphi) \, d^3p$$

$dS/dt > 0 \Rightarrow R > 0$, as shown earlier.

Now, expanding ....

$$R = -\int f_0 \left\{ g\,I(g) + \varphi I(\varphi) - \varphi I(g) - g\,I(\varphi) \right\} d^3p > 0$$

Now, as shown previously, I is self-adjoint, so:

$$\Rightarrow \int d^3p\, f_0\, \varphi I(g) = \int d^3p\, f_0\, g\, I(\varphi)$$

$$R = -\int f_0 \left\{ g\,I(g) + \varphi I(\varphi) - 2\varphi I(g) \right\} d^3p > 0$$

but $I(g) = L$ so

$$R = -\int d^3p\, f_0 \left\{ g\,I(g) + \varphi I(\varphi) - 2L\varphi \right\} > 0$$

but have (2) $\Rightarrow \int f_0 L \varphi\, d^3p = \int f_0\, \varphi I(\varphi)\, d^3p$

so

$$R = -\int d^3p\, f_0 \left\{ g\,I(g) + \varphi I(\varphi) - 2\varphi I(\varphi) \right\} > 0$$

$$= -\int d^3p\, f_0 \left\{ g\,I(g) - \varphi I(\varphi) \right\} > 0$$

as $R > 0$, have:

$$-\int d^3p \, f_0 \, g \, I(g) > -\int d^3p \, \varphi \, I(\varphi)$$

so transport coefficient "D", computed from (1), is maximal.

This proves variational principle and completes our discussion of kinetic theory of gases.