L26 - H Theorem.

→ To H-Theorem!

→ Recall:

- Hamiltonian system
- Non-dissipative interactions
- From Liouville (for $N \sim N_A \gg 1$) to Boltzmann: BBGKY

→ key is diluteness ordering

$$\underbrace{d < \bar{n}^{-1/3}} < l_{mfp} < L$$

→ Molecular Chaos Assumption, Detailed Balance

→ f^N eqn. → $f^{(1)}$ eqn.

⇒ Boltzmann Equation.

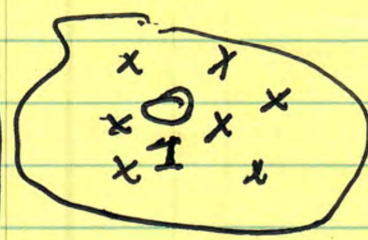
$$\frac{\partial f}{\partial t} + \underline{v} \cdot \underline{\nabla} f = C(f)$$

$C(f)$ ↓ collision operator

$$C(f) = \int d\Gamma_2 \, \frac{\partial V_{1,2}}{\partial \underline{r}_1} \cdot \frac{\partial}{\partial \underline{p}_1} \left[f(1,t)\, f(2,t) \right]$$

$[f(1,t)\, f(2,t)]$ ↓ Nonlinear

in reality,
every particle (DOF)
is both a
test particle and
a field particle



O → 1
test particle

x → field
particles

~> H-Theorem:

- What does it say/mean?

- What makes it remarkable?

- What does it rest upon?
  (Assumptions)

- How to prove?

Onward:

- Can also write Boltzmann Equation as change in occupation of 'state' $\leftrightarrow$ $\underline{p}$

i.e. [consider as hard sphere collisions]

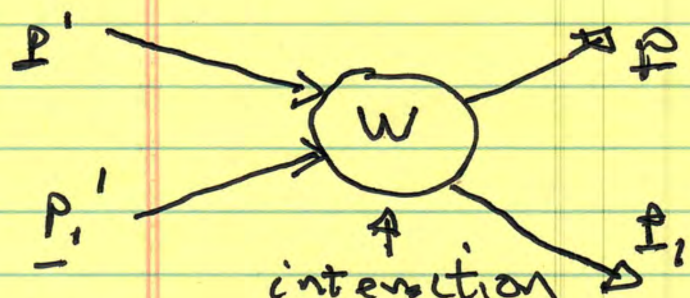
$$\frac{df(\underline{p})}{dt} = \text{rate of change of } f \text{ due collisions (interactions)}$$

i.e.

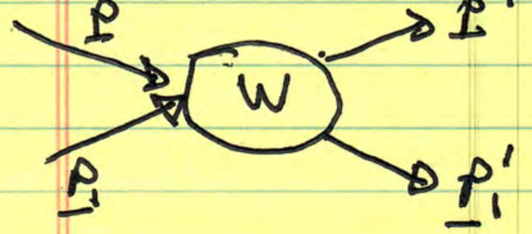
$$\frac{df(\underline{p})}{dt} = \text{rate scattering } \underline{\text{in}}$$
$$- \text{ rate scattering } \underline{\text{out}}$$

(anticipates Master Equation)

in, out?:



= $\underline{\text{in}}$



= out

$$\text{in} = \int d\underline{p}' \int d\underline{p}_1' \int d\underline{p}_1 \; f(\underline{p}')\, f(\underline{p}_1')\, W(\underline{p}', \underline{p}_1'; \underline{p}, \underline{p}_1)$$

$$\text{out} = \int d\underline{p}_1 \int d\underline{p}' \int d\underline{p}_1' \; f(\underline{p})\, f(\underline{p}_1)\, W(\underline{p}, \underline{p}_1; \underline{p}', \underline{p}_1')$$

as $W = W^T$ (reversible micro-dynamics)

$$\boxed{\frac{df(\underline{p})}{dt} = \int d\underline{p}_1 \int d\underline{p}' \int d\underline{p}_1' \; W(\underline{p}, \underline{p}_1; \underline{p}', \underline{p}_1') * \left(f(\underline{p}')\, f(\underline{p}_1') - f(\underline{p}_1)\, f(\underline{p}) \right)}$$

N.B. $-\ \underline{p} + \underline{p}_1 = \underline{p}' + \underline{p}_1'$

so detailed Balance applies.

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

So $C(f_0) = 0$ conservation $\Big\langle$ energy / momentum

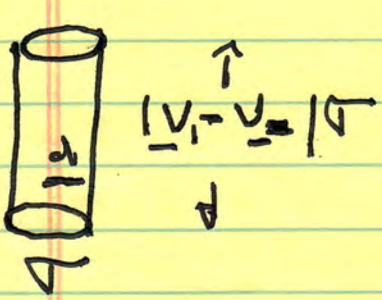
and will show Maxwellian renders $dS/dt = 0$.

N.B. - What about $V_{1,2}(\underline{x})$?

$\Rightarrow$ $\boxed{\text{Stosszahlansatz}}$ L. Boltzmann

total # $(\underline{v}_1, \underline{v})$ collisions taking place in dt

= (Volume of $\underline{v}_1, \underline{v}$ collision cylinder)
  * (# of particles with $\underline{v}_1$, per volume)



in collision cylinder

$= \sigma v_{rel} f(\underline{v}_1) \, d^3 v_1$

$\sigma \sim d^2$

and:

- dilute: non-overlapping cylinders.

- collisions as 'point events' (*)

  $d < \bar{r} < l_{mfp}$ ordering!

Also: $\left[V_{1,2} \to \delta(\underline{r}_1 - \underline{r}_2) \right]$
+ integrates.

- $w \, d^3v' \, d^3v_1' = v_{rel} \, d\sigma$

  relates transition (probability) to familiar items like cross-section.

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

Onward... ⇒ H-Theorem.

- a gas left alone, will evolve to an equilibrium of <u>maximal</u> <u>entropy</u>.

- evolution accompanied by <u>entropy</u> <u>production</u>

i.e. $\underline{\dfrac{dS}{dt} \geq 0}$

- evolution is to uniform Maxwellian
- Ideal gas:

$$S = \int d\underline{x} \int d\underline{p}\, f \ln(e/f) \qquad \text{(discussed later)}$$

$$= -\int dx \int dp\, f \ln f$$

$$\frac{dS}{dt} = -\int d\Gamma \left[\frac{df}{dt} \ln f + f \frac{1}{f} \frac{df}{dt} \right]$$

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

$$\int d\Gamma\, C(f) = 0 \qquad \underline{\text{show}}!$$

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

$$\frac{dS}{dt} = -\int d\underline{x} \int d\underline{p} \int d\underline{p}_1 \int d\underline{p}' \int d\underline{p}_1' \; (\ln f) \; w \, *$$
$$\left(f(\underline{p}') f(\underline{p}_1') - f(\underline{p}) f(\underline{p}_1) \right)$$

Lemma

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

explicitly:

$$\int d\underline{p} \; \varphi(\underline{p}) \, C(f) =$$

(1)

$$\int \varphi \, w(\underline{p}, \underline{p}_1; \underline{p}', \underline{p}_1') \, f' f_1' \, d^4\underline{p}$$

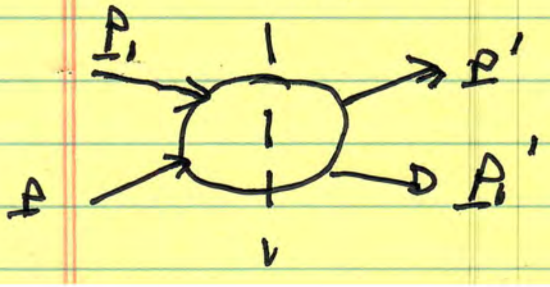
(2)

$$- \int \varphi \, w(\underline{p}', \underline{p}_1'; \underline{p}, \underline{p}_1) \, f f_1 \, d^4 p$$

To Show:

Now, on (2):

$\rightarrow$ interchange $\underline{p}, \underline{p}_1 \leftrightarrow \underline{p}', \underline{p}_1'$



flip about !

use $w = w^T$

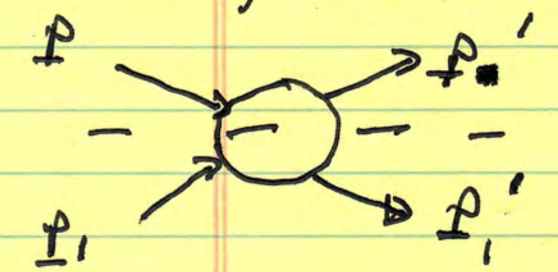
(micro-reversibility)

so

$$\int dp\, \varphi\, C(f)$$

$$= \int d^4p \left\{ (\varphi(p) - \varphi(p'))\, w\, (p, p_1; p', p_1') * f' f_1' \right\}$$

→ now, consider:



and interchange about

i.e. p, p' with p_1, p_1'

n.b.: up-down symmetry equivalent (no reason $\rightleftarrows$)

so

$$\int dp\, C(f)\, \varphi = \frac{1}{2} \int d^4p \left\{ (\varphi(p) - \varphi(p')) + \varphi(p_1) - \varphi(p_1'))\, w f' f_1' \right\}$$

Proves Lemma b

Now, let $\varphi = \ln f$

so, from Lemma:

$$\frac{dS}{dt} = -\frac{1}{2}\int d\underline{x} \int d^4 p \,\left(\ln f + \ln f_1 - \ln f' - \ln f_1'\right) w\, f' f_1'$$

$$= \frac{1}{2}\int d\underline{x} \int d^4 p \; w\, f' f_1' \ln\left(f' f_1' / f f_1\right)$$

define $x = f' f_1' / f f_1$

$$\frac{dS}{dt} = \frac{1}{2}\int d\underline{x} \int d^4 p \; w\, f f_1 \; x \ln x$$

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

have $\int w\, f f_1 \,(x - 1)\, d^4 p \; d\underline{x} = 0$

⇝ a case of writing zero in a complicated way!

so adding 0 to dS/dt expression:

$$\boxed{\frac{dS}{dt} = \frac{1}{2}\int d^4p \int dx \; w f f_1 \left[x \ln x - x + 1 \right]}$$

⇝ entropy production rate.

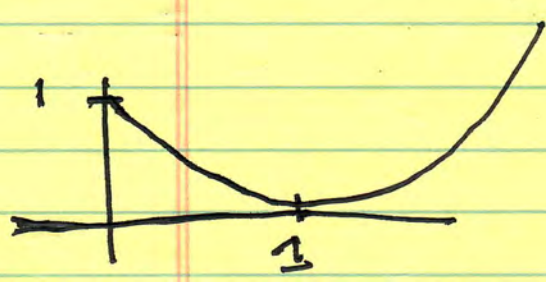
Then

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

$$F' = 1 + \ln x - 1$$

$F(0) = 1$

$F(1) = 0$



⇝ $\boxed{\frac{dS}{dt} \geq 0}$! → H-Theorem!

Now, $\dfrac{dS}{dt} = 0$ for $x = 1$

$$f f_1 = f' f_1'$$

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

so $\ln f + \ln f_1$ [conserved in collision]

$$\boxed{\begin{aligned} &\leftrightarrow \quad \ln f = c + \underline{p} \cdot \underline{V} - \alpha \epsilon \\ &\frac{dS}{dt} = 0 \Rightarrow \text{Maxwellian Distribution} \end{aligned}}$$

Note:

1.) Keys: $W = W^T \rightarrow$ Detailed Balance

$f(1,2) = f(1) f(2)$ factorization (Molecular chaos)

2) $\dfrac{dS}{dt} = 0 \leftrightarrow C(f) = 0$

collisions drive system to equilibrium.

3) $d\underline{x}$ irrelevant!

Entropy produced locally.

i.e. f relaxes to local Maxwellian,

then to uniform Maxwellian

(i.e. transport: $T(x)$ $\searrow$ $\rightarrow$ $\overline{}$ $T(x)$)

Essence of H-Theorem:

Macroscopic irreversibility from microscopically reversible dynamics
+ Molecular chaos ("micro-chaos").

→ Some observations:

①

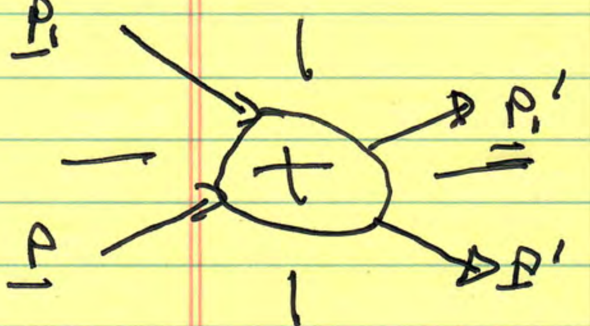
- If no a-priori concept/idea of equilibrium distribution, how derive it?

Recall: $\frac{dS}{dt} = 0$, for $x = 1$

$$x = 1 \quad \Rightarrow \quad f' f_1' = f f_1$$

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

as labels in collision arbitrary, i.e.



etc.

so $\ln f + \ln f_1 = \text{const.}$ sum logs conserved

What is conserved? (Dynamically):

- energy (kinetic energy / particle)

- momentum

- number

so

$\ln f$ can be expressed as a linear combination of conserved quantities

$$\ln f = a + \underline{b} \cdot \underline{p} + c \frac{p^2}{2m}$$

$c < 0$ for normalizability

N.B.: Angular momenta not independent as collision event at 1 position.

$\Rightarrow$

$$f = c' \left[\frac{-p^2}{2mT} + \frac{\underline{p} \cdot \underline{V}}{T} \right]$$

$c' \sim n$

$n, T, \underline{V}$ can be $n(\underline{x}), T(\underline{x}), V(\underline{x})$ can all be functions of $\underline{x}$ for $l_{mfp} \ll L$

Thus, derived equilibrium distribution function from H-Thm.

(2) How reconcile?

- reversible, Hamiltonian dynamics

- $dS/dt \geq 0$.

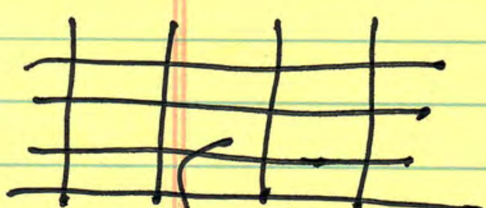
Related: What happened to Poincaré Recurrence?

Point:

- statistical description: $f(\underline{x}, \underline{p}, t)$

- Coarse Graining :

(recall Lyapunov exponents)



→ partition

$\Delta q \Delta p$

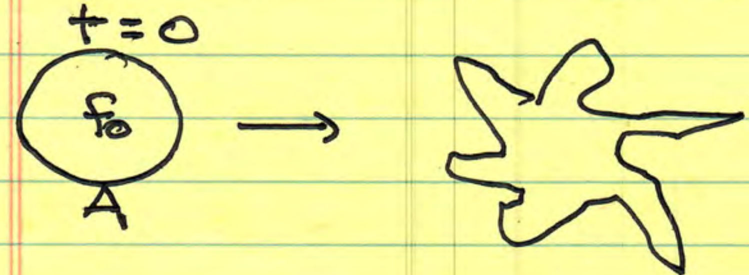
→ sets resolution scale.

(S is integrated quantity)

Why significant?

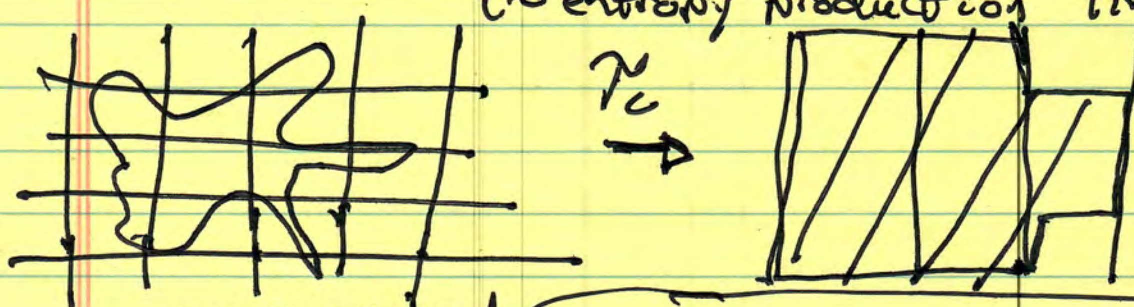
→ partition kills small details in phase volume evolution

i.e



exact

with coarse graining (smearing)
(~ entropy production timescale)



coarse grained area.

initial

local phase space density modified by coarse graining

$$f_0 A_0 = A_{CG} \bar{f}$$

↳ coarse grained distribution

$$\bar{f} = f_0 A_0 / A_{CG}$$

$\bar{f} < f_0$ as $A_0 < A_{CG}$.

so

- prediction of close recurrences impossible, as partition sets resolution limit.

N.B.: $l_{mfp} = 1/n\sigma$

$\tau_c^{-1} = \nu_c \cong v_{th}/l_{mfp}$ etc.