L2b - 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 dilueness ordering

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

  - → Molecular Chaos Assumption / Detailed Balance
    - → f^N eqn. → $f^{(1)}$ eqn.
      - ⇒ Boltzmann Equation.

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

↓

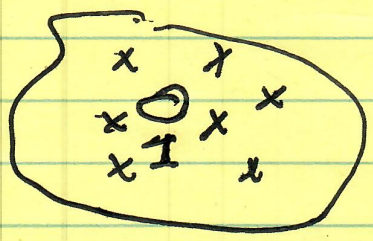
Collision operator

$$C(f) = \int d\Gamma_2 \; \frac{\partial V_{12}}{\partial \underline{r}_1} \cdot \frac{\partial}{\partial \underline{p}_1} \left[f(1,t)\, f(2,t) \right]$$

↓

Nonlinear

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



○ → 1 test particle

× → 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' $\leftrightarrow$ Δ

i.e. [consider as hard sphere collisions]

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

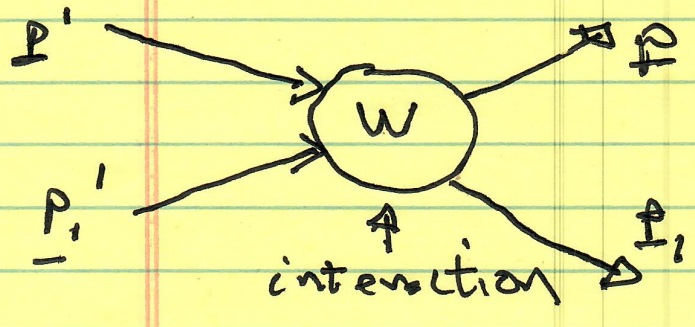
i.e.

$\frac{df(p)}{dt}$ = rate scattering in

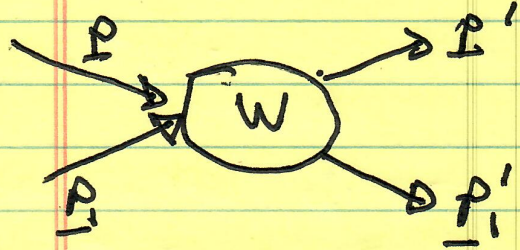
- rate scattering out

(anticipates Master Equation)

in, out?:



= in



$= \text{out}$

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

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

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

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

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

so detailed Balance applies.

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

So $C(f_0) = 0$ conservation { energy, momentum

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

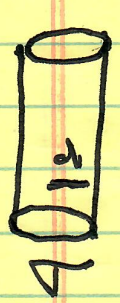
N.B. - What about $V_{1,2}(\underline{x})$?

$\Rightarrow$ {Stosszahlansatz} L. Boltzmann

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

= (Volume of $\underline{v}_1, \underline{v}$ collision cylinder)

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



$|\underline{v}_1 - \underline{v}_2|\sigma$

$\sigma \sim d^2$

in collision cylinder

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

and:

- dilute: non-overlapping cylinders.
- collisions as 'point events' (*)

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

Also: $\left[V_{1,2} \to \delta(\underline{r}_1 - \underline{r}_2) \right]$ integrates to 0.

- $W d^3V' d^3V_1 = v_{rel} d\Gamma$

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

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

Onward... ⇒ H-Theorem.

- a gas left alone, will evolve to an equilibrium of maximal entropy.

- evolution accompanied by entropy production

i.e. $\frac{dS}{dt} \geq 0$

- evolution is to uniform Maxwellian

- Ideal gas:

$$S' = \int dx \int dp \, f \ln(e/f)$$ (discussed later)

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

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

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

$$\int d\Gamma \, C(f) = 0 \qquad \underline{\text{show}} \; !_0$$

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

$$\frac{dS}{dt} = -\int dx \int dp \int dp_1 \int dp' \int dp_1' \, (\ln f)\, W \ast (f(p')f(p_1') - f(p)f(p_1))$$

Lemma

$$\int \varphi(p) C(p)\, dp = \frac{1}{2}\int d^4p \, (\varphi + \varphi_1 - \varphi' - \varphi_1') \ast W f' f_1'$$

explicitly:

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

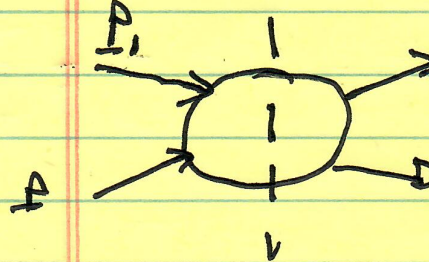
$$\textcircled{1} \quad \int \varphi\, W(p, p_1; p', p_1')\, f' f_1'\, d^4p$$

$$\textcircled{2} \quad -\int \varphi\, W(p', p_1'; p, p_1)\, f f_1\, d^4p$$

To Show:

Now, on ②:

→ interchange $p, p_1 \leftrightarrow p', p_1'$

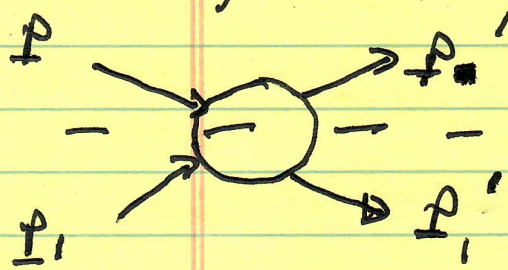


{ flip about ;
use $W = W^T$
(micro-reversibility

so

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

→ now, consider:



and interchange about
— — — —
i.e. p, p' with p_1, p_1'

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

so

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

Proves Lemma 1

Now, let $\varphi = \ln f$

so, from Lemma:

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

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

define $X = f' f_1' / f f_1$

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

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

have $\int w f f_1 (X - 1)\, d^4p\, dx = 0$

↝ a case of writing zero in a complicated way !

so adding 0 to dS/dt expression:

$$\frac{dS}{dt} = \frac{1}{2}\int d\Gamma_p \int dx \; w \, ff_i \left[x \ln x - x + 1 \right]$$

↝ entropy production rate.

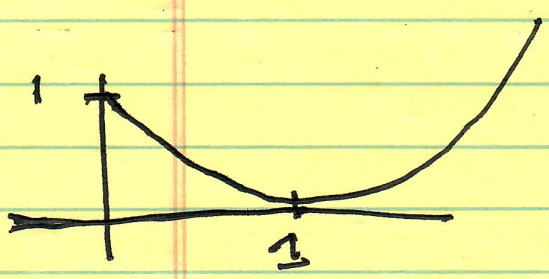
They

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

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

$F(0) = 1$

$F(1) = 0$



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

→ H-Theorem !

Now, $\frac{dS}{dt} = 0$ 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]

$\Leftrightarrow$ $\ln f = c + \underline{p} \cdot \underline{V} - \alpha \epsilon$

$\frac{dS}{dt} = 0 \Rightarrow$ Maxwellian Distribution

Note:

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

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

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

Collisions drive system to equilibrium.

3) dx irrelevant!

Entropy produced locally.

i.e. f relaxes to local Maxwellian,

then to uniform Maxwellian

(i.e. transport: $\frac{T(x)}{T(x)} \rightarrow \frac{\quad}{T(x)}$)

Essence of H-Theorem:

Macroscopic irreversibility from microscopically reversible dynamics

+ Molecular chaos ("micro-chaos").

→ Some observations:

(i)

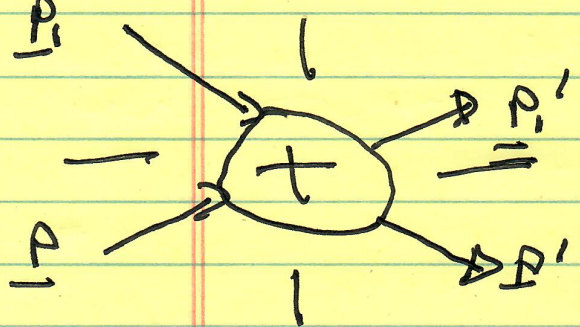
- If no a-priori concept/idea of equilibrium distribution, how derive it?

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

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

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

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

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

$c<0$ for normalizability

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

$\Rightarrow$

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

$c' \sim n$

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

Thus, derived equilibrium distribution function from H-Thm.

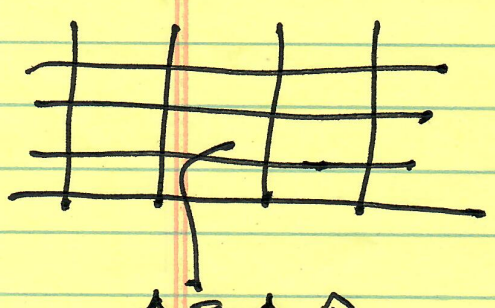
② How reconcile?

- reversible, Hamiltonian dynamics
- $dS/dt \geq 0$.

Related: What happened to Poincare Recurrence?

Point:

- statistical description: $f(\underline{x}, p, t)$
- Coarse Graining: (recall Lyapunov exponents)



→ Partition

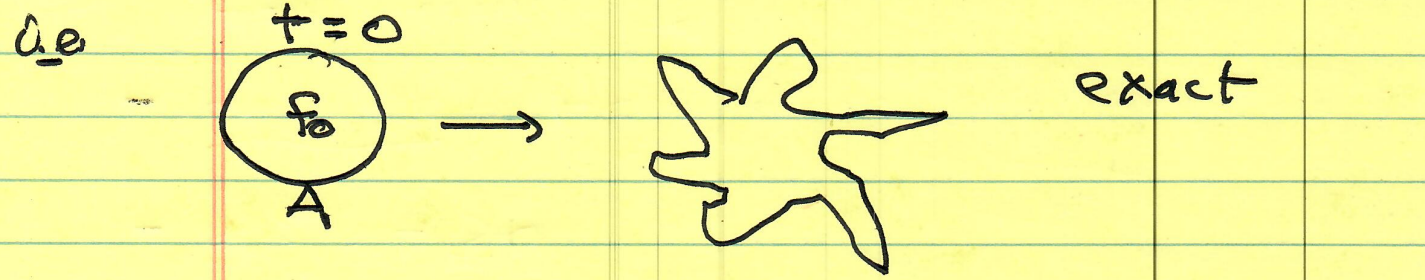
$\Delta x \Delta p$

↪ sets resolution scale.

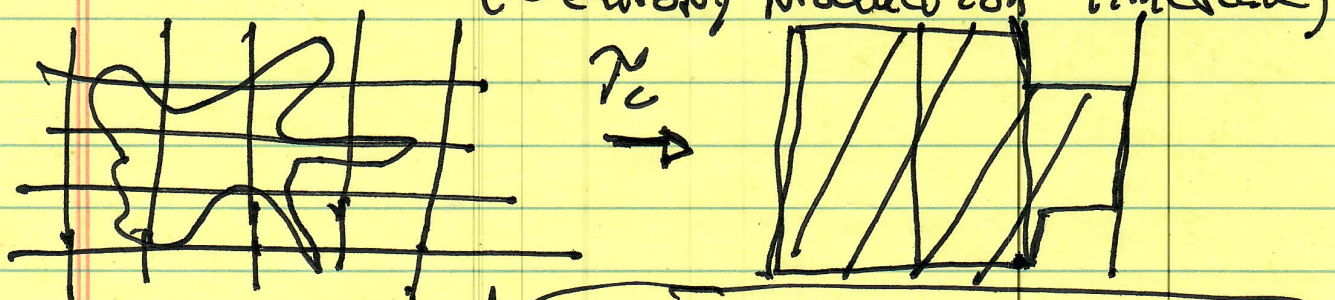
(S is integrated quantity)

Why significant?

→ partition kills small details in phase volume evolution



With coarse graining (smearing)
(≈ entropy production timescale)



coarse grained area.

critical

local phase space density modified by coarse graining

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

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

→ coarse grained distribution

$\bar{f} < f_0$ 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