 [redacted]

Notes 1: Section 2

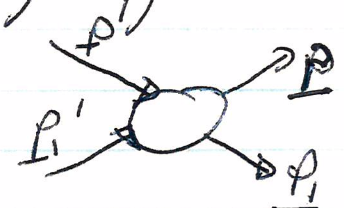
[redacted] Boltzmannia and H-Theorem

Now, can also write B.E. in terms collision operator based on scattering into + out of states: Q.M. formulating

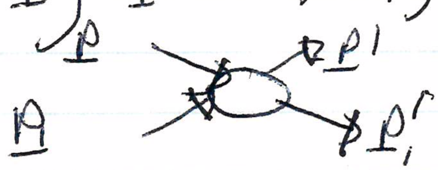
$\frac{d f(p)}{dt}$ = rate of change of f, due collisions

= rate in − rate out

$$\text{in} = \int dp' \int dp_1' \int dp' \; f(p')\, f(p_1')\, w(p', p_1'; p, p_1)$$



$$\text{out} = \int dp_1 \int dp' \int dp_1' \; f(p)\, f(p')\, w(p, p_1; p', p_1')$$



so

$$\frac{df(p)}{dt} = \int dp_1 \int dp' \int dp_1' \; W(p, p_1; p', p_1') \left(f(p')\, f(p_1') - f(p_1)\, f(p) \right)$$

⇒ B.E.

$w = wT$

note: $\rightsquigarrow$ $\underline{p}+\underline{p}_1 = \underline{p}'+\underline{p}_1'$

$\Rightarrow$ $w = w^T$

Observe!

- $C(f)=0$ for $f=f_0$

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

[Collision ops annihil. Maxwellian]

due conservation of energy and momentum.

- will show Maxwellian renders $dS/dt=0$ ✓

This brings us to:

H-Theorem [See end]

[Essence — [illegible] Macro irreversibility from micro reversib.]

- a gas, left alone, will evolve to an equilibrium of maximal entropy
- evolution accompanied by entropy production

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

{ local
  global

- evolution is to uniform Maxwellian
- $dS/dt \geq 0$

for ideal gas

$$S \cong \int d\underline{x} \int d\underline{p}\; f \ln(e/f)$$

$$\cong \int dx \int dp \left[-f \ln f \right]$$

see notes on entropy, next lecture.

will show $dS/dt \geq 0$.

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

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

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

→ entropy production due explicitly to collisions

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

Lemma

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

where notational shorthand $\Rightarrow$

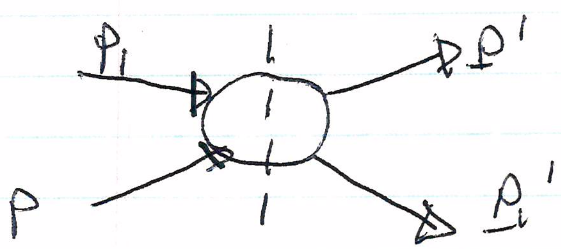
$$d^4 p = d\underline{p}\, d\underline{p}_1\, d\underline{p}_1'\, d\underline{p}'$$

Now, explicitly:

$$\int d\underline{p}\, \varphi(\underline{p})\, C(\underline{p}) = \int \varphi\, \overset{(1)}{w}(\underline{p},\underline{p}_1;\underline{p}',\underline{p}_1')\, f' f_1'\, d^4 p$$
$$- \int \varphi\, \overset{(2)}{w}(\underline{p}',\underline{p}_1';\underline{p},\underline{p}_1)\, f f_1$$

now, in (2):

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



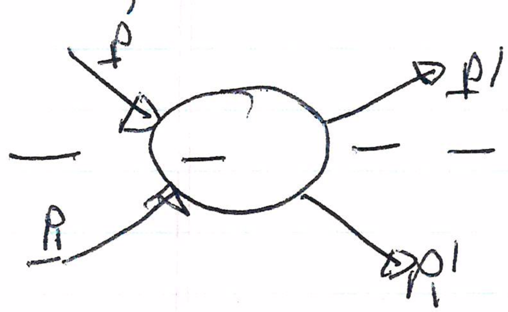
flip / rotate } about !

use T symmetry

so

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

Now, consider:



and interchange about - - -

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

N.B. up-down symmetry equivalent

so

$$\int dp\, C(f)\, \varphi = [illegible]$$

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

this proves Lemma!

Now, let $\varphi = \ln f$,

so Lemma $\Rightarrow$

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

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

$$x \equiv f' f_1' / f f_1$$

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

Now since $\int c(f)\, d\Gamma = 0$

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

i.e. write zero in complex way. C laid out so adding:

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

gives entropy production rate.

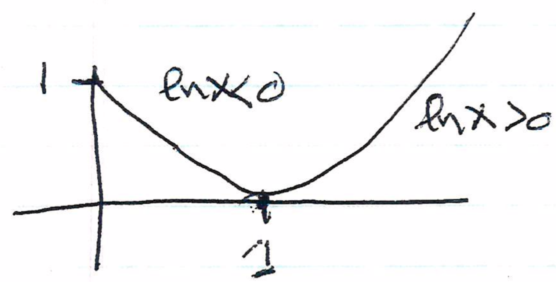
$F(x) = x \ln x - x + 1$

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

$F(0) = 1$

$F(1) = 0$

so



so

$\boxed{dS/dt \geq 0}$

yay!

Boltzman H-thm!

- $dS/dt = 0$ for $\underline{x=1}$

$f f_1 = f' f_1' \quad / \quad \Delta$

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

$\Rightarrow \quad \ln f + \ln f_1 = \text{const}$

lin dep occurs

sum of logs conserved in collision

$\Rightarrow \ln f = c + \underline{\beta} \cdot \underline{V} \; \alpha E$

see next lecture

$\frac{dS}{dt} = 0$ determines Maxwellian

keys: → detailed balance $\Leftrightarrow$ w symmetry

→ molec. chaos

$f(1,2) = f(1) f(2)$

→ $dS/dt \geq 0$

$dS/dt = 0$ corresponds $C(f) = 0$

collisions drive system to equilibrium.

→ $d\underline{x}$ irrelevant !!

entropy produced locally

i.e. relaxation to local Maxwellian.

→ Essence of H-thm. is:

macroscopic irreversibility from microscopically reversible dynamics + molec. chaos (micro-chaos).

More on Boltzmann eq. / H-Theorem

→ Summary of Basic Boltzmann eq.

– Basic Eqn.

$$C(f) = \int d\underline{p}_2 \, \frac{\partial V_{1,2}}{\partial \underline{r}_1} \cdot \frac{\partial}{\partial \underline{p}_1} \left[f(1,t) \, f(2,t) \right]$$

↑
Collision operator

$$= \int d\underline{p}_1 \int d\underline{p}' \int d\underline{p}_1' \, w(\underline{p}', \underline{p}_1'; \underline{p}_1, \underline{p}) \big(f(\underline{p}') f(\underline{p}_1') - f(\underline{p}_1) f(\underline{p}) \big)$$

with

$w = w(\underline{p}', \underline{p}_1'; \underline{p}_1, \underline{p}) = w^T$ (time reversible)
as transition probability

⇒ B.E.

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

based on
– detailed balance $w^T = w$
– molecular chaos

Now, $\sigma = -\int d\underline{x} \int d\underline{p} \, f \ln f$ → entropy

and : $$\frac{dS}{dt} = \frac{1}{2} \int d^4\underline{p} \int d^3\underline{x} \; w \, f f_1 \left[x \ln x - x + 1 \right]$$

$$x = f' f_1' / f f_1 \qquad \geq 0.$$

[redacted]

$\dot{X}$

$$\frac{dS}{dt} \geq 0 \quad \rightarrow \quad H \text{ thm.}$$

Max entropy state, $\underline{x=1} \Rightarrow \underline{dS/dt=0}$.

⇒ Some observations:

(a)
→ $\underline{\text{never}}$ actually $\underline{\text{used}}$ concept of equilibrium or equilibrium distribution function in building Boltzmann eq, though did observe $C(f_{eq})=0$.

→ might ask: "If no a-priori knowledge of equilibrium distribution, could one $\underline{\text{derive}}$ it?"

Now:

$$\frac{dS}{dt} = 0 \quad \text{for} \quad x=1 \qquad \left\{ \text{point of maximal entropy} \right.$$

$$x=1 \quad \Rightarrow \quad f'f_1' = ff_1$$

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

as labels in collision are arbitrary, i.e.

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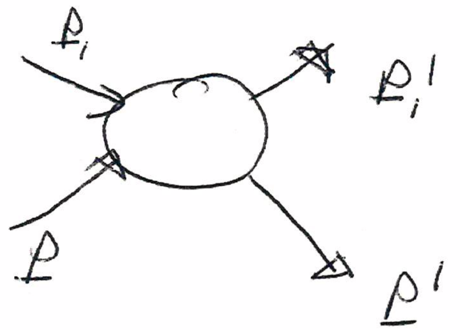


have, at equilibrium:

$$\ln f + \ln f_1 = \text{const}$$

$\left\{\begin{array}{l}\text{for equilibrium} \\ (ds/dt = 0)\end{array}\right.$

$\Rightarrow$ $\left\{\begin{array}{l}\text{sum of logs conserved} \\ \text{in collision.}\end{array}\right.$

Now, what is constant in collision:

- energy (kinetic for pt. particle)
- momentum
- number

$\Rightarrow$ **ln f can be expressed as a linear combination (with constant coeffs) of quantities conserved in a collision.**

so

$$\ln f = \underline{a} + \underbrace{\underline{b}\cdot\underline{p}}_{\text{momentum}} + \underbrace{c\,\frac{p^2}{2m}}_{\text{KE}}$$

Note: - $c < 0$ for normalizability of f

- conservation requires form of $\ln f$

- angular momenta not independent, as collision event occuring at 1 position.

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

$\rightarrow$ recovers Maxwell-Boltzmann distribution. ✓

$\rightarrow$ n, T, $\underline{V}$ all can be functions of x for $l_{mfp} < L$

$\rightarrow$ have derived form of eqbrm distribution from condition $dS/dt = 0$

(b)
$\rightarrow$ Boltzmann H-Thm exploited concept of entropy. Where from?

Fundamentally, Entropy $\leftrightarrow$ ln (Phase Volume)

$$\boxed{\sigma = \ln \Delta\Gamma} \rightarrow \text{fundamental definition}$$

$$= \ln \prod_i \frac{\Delta p \Delta q}{(2\pi\hbar)^s}$$

↳ ensures dimless.

Now, $f(\bar{E})\,\Delta\Gamma = 1$

weight factor, mean energy ⇒ assumes tightly localized f

and linearity of log:

$$\ln f(E) = \alpha + \beta E$$ (uses struct. of Eqbrm)

so $$\ln f(\bar{E}) = \alpha + \beta \bar{E}$$ ⇒ [can obtain from Liouville Eqn with sub-systems]

⇒
$$\ln f(\bar{E}) = \alpha + \beta \bar{E} = \langle \ln f(E) \rangle$$

thus

$$\sigma = \ln \Delta\Gamma = -\ln f(\bar{E}) = \ln \langle f(E) \rangle$$

⇒

$$\sigma = -\langle \ln f(E) \rangle = -\int f \ln f \, d\Gamma .$$

⇒ recovers entropy, used in H-Thm.

(c) How Reconcile?

- reversible laws of Hamiltonian mechanics, which govern gas
- $dS/dt \geq 0$.

related:

- whatever happened to Poincaré recurrence?

Key Point: Boltzmann introduces:

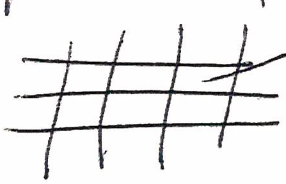
→ statistical description
i.e. $f(\underline{x}, \underline{p}, t)$ or probability

→ coarse graining (recall Lyapunov exponents!)

coarse graining essential to statistical description.

↓

i.e. partition



Δp, Δx.

↓

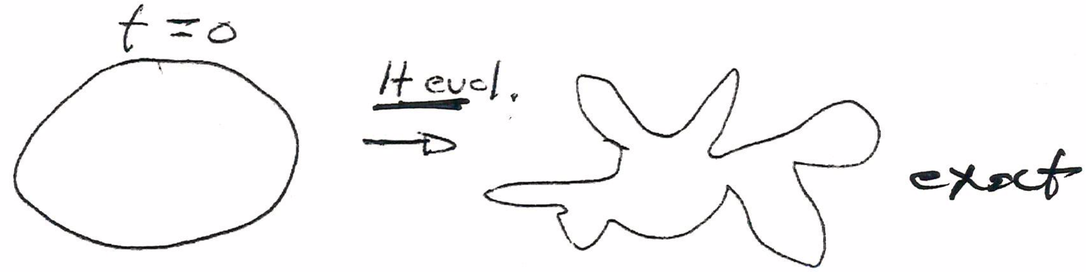
i.e. resolution scale

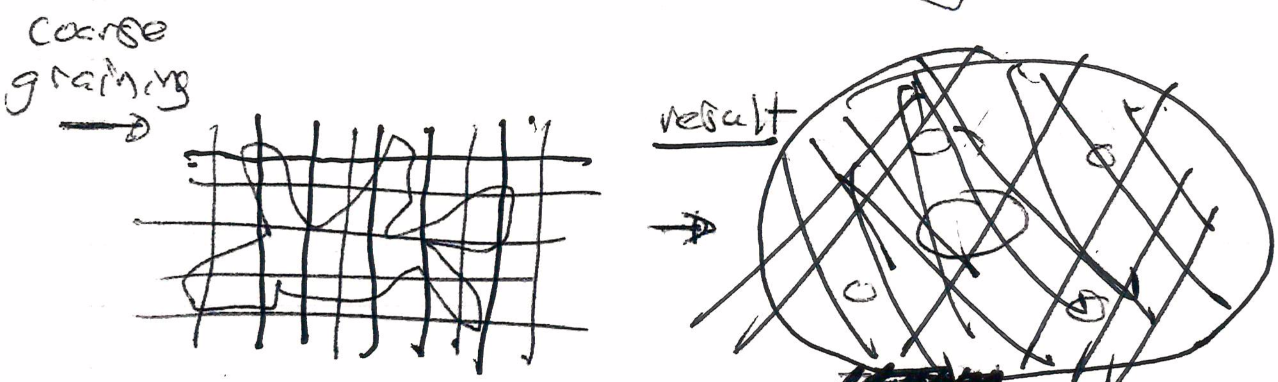
(recall S integrated)

Why significant ??

→ ~~partition~~ / coarse graining kills small details in phase volume evolution

i.e.





smeared by coarse graining

(i.e. phase space reconnection!) by coarse graining!

⇒ prediction of <u>very</u> <u>low</u> <u>probability</u> events is impossible, inaccurate and → $\boxed{\text{un-resolvable}}$

⇒ <u>recurrence</u> is <u>very</u> <u>low probability</u>.

(d) Why is statistical description valid?

→ chaos (even for $N=2$, not only $N = N_A$!)

i.e. $\tau_{relax} \gg \tau_{Lyap}$

$\downarrow$ mixing time

i.e. calculated Δ_M → it works.

→ what are the key assumptions:

→ reversible, conservative collisions

→ $f(1,2) = f(1)\,f(2)$

(Molecular chaos)

[chaos → correlation mixed

also:

Per Boltzmann: $\boxed{\text{Stosszahlansatz}}$

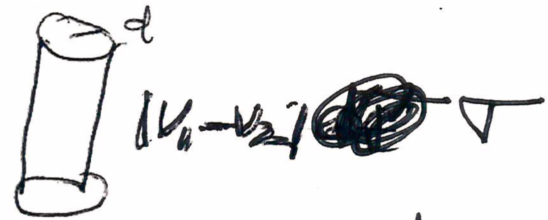
i.e.

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

= volume of $(\underline{v}_1, \underline{v})$ collision cylinder
* # particles with v_1, per volume

= $f(v_1)\,\delta |v_{rel}|$ —

Collision cylinder:



$\#$ in collision cylinder $\equiv v_{rel}\, \sigma\, f(\underline{v}_1)\, d^3v_1$

N.B.:

- dilute → non-overlapping cylinders
- collisions as 'point events'
  $d < \bar{r} < l_{mfp}$ ordering!
- $f(1,2)$ factorization

all buried here.

(small cylinder).

Also

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

relates transition to familiar items like cross-section.

→ for l_{mfp}, $l_{mfp} = 1/n\sigma$

σl_{mfp} = volume of collision cyl., for 1 collision.

i.e. $n \sigma l_{mfp} = \#\,\text{coll} = 1$

$l_{mfp} \sigma n = 1$

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

$\nu_{coll} = v_{th}/l_{mfp}$ → defines collision frequency.

n.b. crudely: $\sigma \sim d^2$.