L2b - H Theorem.

→ To H-Theorem!

→ Recall:

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

→ Key is diluteness ordering

$d < \bar{n}^{-1/3} < \text{mix} < L$

→ Molecular chaos Assumption
   Detailed Balance

$\Rightarrow f^N \text{ eqn.} \Rightarrow f^0 \text{ eqn.}$

→ Boltzmann Equation.
\frac{\partial f}{\partial t} + v \cdot \nabla f = C(f)

\text{Collision operator}

C(f) = \int dV_2 \ \frac{dV_2}{\omega_1} \cdot \frac{\partial}{\partial \omega_1} \left[ f_2^0 A f_3^0 \right]

\text{Nonlinear}

in reality, every particle (QOT) is both a test particle and a field particle.
2) 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 $\to \phi$

  $\text{i.e.} \quad \left[\text{consider as hard sphere collisions}\right]$

  \[
  \frac{d\Phi(\phi)}{dt} = \text{rate of change of } \phi \text{ due to collisions (interactions)}
  \]

  $\text{i.e.}$

  \[
  \frac{d\Phi(\phi)}{dt} = \text{rate scattering in}
  \]

  - rate scattering out

  (anticipates Master Equation)

$\text{in, out? :}$

\[
\begin{array}{c}
\text{P'} \\
\text{P} \\
\text{interaction} \\
\text{P}_1' \\
\end{array}
\]

$= \text{cin}$
\[ \text{in} = \int dp' \int dp_i \int dp_i' \ F(p') \ F(p_i') \ w(p, p_i; p', p_i') \]
\[ \text{out} = \int dp_i \int dp_i' \ F(p_i) \ F(p_i') \ w(p, p_i; p', p_i') \]

as
\[ w = w^T \] (reversible micro-dynamics)

\[ \frac{df(p)}{dt} = \int dp_i \int dp_i' \ w(p, p_i; p', p_i') \times \left( f(p') f(p_i') - f(p) f(p_i) \right) \]

N.B. - \( p + p_i = p' + p_i' \)

so detailed balance applies.

\[ p = p_0 \rightarrow = c e^{- \frac{(E + p \cdot v)}{T}} \]
So $C(f_0) = 0$ conservation energy momentum and will show Maxwellian renders $\frac{dS}{dt} = 0$.

**N.B.** - What about $V_{1/2}(x)$?

$\Rightarrow \text{Stark-Zehnderzatz}$ L. Boltzmann

**total # of $(u_1, v)$ collisions taking place in $dt$**

$= \left( \text{Volume of } u_1, v \text{ collision cylinder} \right) + \left( \# \text{ of particles with } u_1, \text{ per volume} \right)$

$\begin{array}{c}
\text{volume} \\
\text{of collision cylinder}
\end{array} = \sqrt{V_{rel}} f(C_{u_1}) \, d^3v_1$

$\Gamma \approx d^2$
and:

- dilute: non-overlapping cylinders
- collisions as 'point events'

\[ d \ll \bar{n} \ll \text{ampere ordering} \]

Also:

\[ \left[ V_1 \rightarrow \sigma \left( \frac{V_2}{V_3} - \frac{V_2}{V_4} \right) \right] \]

integrates.

\[- \omega d^3 \tau \cdot d^3 v_i = v_i d\tau \]

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

\[- \text{ampere} \cdot \text{ampere} = 1 / \text{amp}^2 \]

Onward... \( \Rightarrow \) H-Theorem.

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

- evolution accompanied by entropy production
\[ \dot{u} \geq \frac{ds}{dt} > 0 \]

- Evolution is to uniform Maxwellian

- Ideal gas:

\[ s = \int dx \int dp \ f \ln(e/p) \quad \text{(discussed later)} \]

\[ = \int dx \int dp \ f \ln f \]

\[ \frac{ds}{dt} = -\int dV \left[ \frac{df}{dt} \ln f + f \frac{df}{f} \right] \]

\[ = -\int dV \left[ c(\xi) \ln f + c(\xi) \right] \]

\[ \int dV \ c(\xi) = 0 \quad \text{(show)} \]

\[ \frac{ds}{dt} = -\int dV \ c(\xi) \ln f \]
\[
\frac{ds}{dt} = -\int dx \sum dp \sum dp' \sum dp'' \sum dp''' (\ln + M) w + \\
(\frac{\partial}{\partial q} \phi(q) - \frac{\partial}{\partial q'} \phi'(q'))^* \\
\text{Lemma} \\
\int u(q) v(q) dq = \frac{1}{2} \int e^{-\psi} (\psi + \psi' - \psi - \psi')^* \\
\text{explicitly:} \\
\int dp \ u(q) v(q) = \\
\int q w(q, \psi, \phi, \phi') \phi\phi' \ d^4 \phi \\
\int q' w(q', \psi', \phi, \phi') \phi\phi' \ d^4 \phi' \\
\text{To show:} \\
\text{Now, on } \circ: \\
\text{interchange } q, q' \rightarrow q', q \\
\text{flip about } \\
\text{use } w = w^T \\
\text{(micro-reversibility)
\[ \int_{\mathbb{R}^4} \left\{ \left( \psi(x) - \psi(x') \right) \psi'(x') \psi'(x) - \psi'(x) \psi'(x') \right\} + \psi(x) \psi'(x') \psi'(x) \psi'(x) \]
Now, let \( U = \ell \ln \ell \).

So, from Lemma:

\[
\frac{d\ell}{dt} = -\frac{1}{2} \int \frac{d\mathbf{p}}{d\ell} \frac{d^4 \mathbf{p}}{d\mathbf{p}} \left( \ln \ell + \ln \ell \frac{\mathbf{p}}{\ell} - \ell \frac{\mathbf{p}}{\ell} \right)
\]

\[
= \frac{1}{2} \int \frac{d\mathbf{p}}{d\ell} \frac{d^4 \mathbf{p}}{d\mathbf{p}} \left( \ln \left( \frac{\mathbf{p}}{\ell} \right) \right)
\]

Define \( x = \frac{\mathbf{p}}{\ell} \).

\[
\frac{d\ell}{dt} = \frac{1}{2} \int \frac{d\mathbf{x}}{d\ell} \frac{d^4 \mathbf{x}}{d\mathbf{x}} \ln \mathbf{x}
\]

Since: \( \int C \mathbf{x} \, d\mathbf{x} = 0 \)

have \( \int w \mathbf{R} (x - 1) \, d^4 \mathbf{p} \, dx = 0 \).
As a case of writing zero in a complicated way!
so adding 0 to $\frac{ds}{dt}$ expression:

\[
\frac{ds}{dt} = \frac{1}{2} \int \left[ x \ln x - x + 1 \right] dx
\]

is entropy production rate.

Then

\[
F(x) = x \ln x - x + 1
\]

\[
F'(x) = 1 + \ln x - 1
\]

\[
F(a) = -1
\]

\[
F(b) = 0
\]

\[
\begin{array}{c}
\text{graph}
\end{array}
\]

\[
\frac{ds}{dt} \geq 0
\]

\[
\rightarrow \text{H-Theorem}
\]
Now,
\[
\frac{dS}{dt} = 0 \quad \text{for} \quad x = 1
\]

\[
\frac{f}{f_1} = \frac{f'}{f'_1}
\]

\[
\ln f + \ln f_1 = \ln f' + \ln f'_1
\]

\[
\ln f + \ln f_1 \quad \text{[conserved in collision]}
\]

\[
\ln f = c + p \cdot v - x \in E
\]

\[
\frac{dS}{dt} = 0 \Rightarrow \text{Maxwellian Distribution}
\]

Note:

1) Keys: \( W = W_T \Rightarrow \text{Detailed Balance} \)

\( F(a, b) = F(a) \cdot R \cdot b \) \( \text{Factorization} \)

(Molecular Chaos)

2) \( \frac{dS}{dt} = 0 \Leftrightarrow \text{C(CF)} = 0 \)

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: $\frac{\partial}{\partial x}$)

Essence of $H$-Theorem:

Macroscopic irreversibility from microscopic reversibility dynamics

+ Molecular Chaos ("micro-chaos").
Some observations:

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

Recall: \( \frac{dS}{dt} = 0 \), \( \text{for } x = 1 \)

\[ x = 1 \Rightarrow x' f' = xf \]

\[ \ln f' + \ln f_i = \ln f + \ln f_i \]

as labels in collision arbitrary, i.e.

\( f \)

\[ \begin{array}{c}
  \text{+} \\
  \text{P} \\
  \text{P}
\end{array} \]

\[ \text{etc.} \]

so \( \ln f + \ln f_i = \text{const.} \), own laws conserved

What is conserved? (Dynamically):
- energy (kinetic energy / particle)
- momentum
- number

\[ \ln F = a + b \cdot p + c \frac{p^2}{2M} \]

C \geq 0 for normalizability

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

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

\[ c' = \mathbb{N} \]

\( n, T, V \) can be \( n(x), T(x), V(x) \) can all be functions of \( x \).
Thus, derived equilibrium distribution function from $H$-Thm.

② How reconcile?

- \text{reversible, Hamiltonian dynamics}
- \frac{dS}{dt} \leq 0.

Related: What happened to Poincare Recurrence?

Poinc:

- statistical description: \( f(x, y, t) \)

- \text{Coarse Graining:} \quad (\text{recall Lyapunov exponents})

\[ A \rightarrow \text{partition} \]

\[ \rightarrow \text{sets resolution scale} \]

(is it integrated quantity)
Why Significant?

- partition (tends to small details in phase volume evolution)

\[ \frac{\partial \omega}{\partial t} = 0 \]

\[ \omega \rightarrow \omega_{\text{exact}} \]

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

\[ \omega_{\text{initial}} \rightarrow \omega_{\text{coarse-grained}} \]

\[ \frac{\int \omega A_0}{A_{\text{coarse}}} = F \]

\[ F = \frac{\omega A_0}{A_{\text{coarse}}} \]

\[ F \ll \omega_0 \text{ as } A_0 \ll A_{\text{coarse}}. \]
So prediction of close recurrences impossible as partition sets resolution limit.

N.B.: \( \lambda_{\text{res}} = \frac{1}{\sqrt{n}} \)

\( \gamma_{c-1} = \gamma_c = \frac{\nu_m}{\lambda_{\text{res}}} \) etc