H - Thm and convergence towards Equilibrium

① Conservation Laws.

② H-Theorem,

③ global equilibrium.

④ Thermodynamics and H- Thm.

⑤ Apparent 'objections' to the H-thm.

Useful lit: Huang, Statistical Mechanics.

Villani, H thm and beyond (Math references)

Cercignani, Boltzmann Legacy.

Jaynes, Violation of H thm.

⋮

etc.

Objective here is to analyze the Boltzmann equation from the point of view of conservation laws and convergence towards equilibrium. In particular, we will show how the collision term drives the statistics of f_1 towards Maxwell-Boltzmann distribution.

① Conservation Laws

Recall the Boltzmann equation: (Smooth Potential)

$$\partial_t f + \{f, H_1\} = Q(f,f)$$

with:

$$Q(f,f) = \int d\vec{\sigma} \int d\vec{p}_* \, d\vec{p}_*' \, d\vec{p}' \; \chi(\sigma; \vec{p}', p_*' \to p_* p) \; \{ f(\vec{p}', q) f(p_*', q) - f(p_*, q) f(p, q) \}$$

f : p-space distribution: $(p,q) \in \mathbb{R}^3$.

H_1 : one particle Hamiltonian; $H_1 = \dfrac{\vec{p}_1^{\,2}}{2m} + V_1[\vec{q}_1]$.

$\chi(\sigma; \vec{p}', \vec{p}_*' \to p_* p)$: elastic $\left[\begin{array}{l}\text{collision} \\ \text{scattering}\end{array}\right]$ scale. (Homogeneous)

Satisfying:

$$\chi(\sigma; p_* p \to p_*' p') = \chi(\sigma; p_*' p' \to p_* p)$$

Non-zero only for $\{p_*' \, p', \, p_*'' \, p''\}$

such that $\left[\begin{array}{l} p_* + p = p' + p_*' \\ p_*^2 + p^2 = p_*'^2 + p'^2 \end{array}\right.$

Obs: Except from the non zero rhs, BE resemble a lot a Liouville equation. [with the obvious observation that it is defined on p-space rather than Γ-space].

One could fear that the presence of non-zero rhs may greatly alter the conservation laws of the original equation. This is apparently not the case, as almost by construction, the (BE) preserves:

(Conservation laws)

- $E = \int_p f_1 H_1(\vec{p}_1 \vec{q}_1)$ (Energy)
- $N = \int_p f_1(\vec{p}_1, \vec{q}_1, t)$ (Number of particles)
- $P = \int_p f_1 \vec{p}_1$ (Momentum)

where conservation for the momentum depends on the Liouville equation also preserving momentum (no box or translation-invariance of H_1)

~~For all this, we again go back to~~

These conservation laws emerge from the highly symmetric nature of $\chi(\sigma)$

Indeed: Consider an observable $G(p_1, q_1)$.

Then $\frac{d}{dt}\langle G\rangle_{f,p} = \int_p dp_1 dq_1 (\partial_t f) G = \langle\{O_1, H_1\}\rangle_p + \underbrace{\int dp\, dq\, (\bigcirc\, \varphi)}_{\text{collision contribution}}$.

The collision term can be evaluated as:

$$\int_p \mathcal{O}(q,p)\, Q(f,f) = \int d\sigma \int dq \int dp' dp'_* dp\, dp_*\, \chi(\sigma) \left[f' f'_* - f f_* \right] \mathcal{O}(q,p)$$

$$= \underline{\qquad\qquad} \sim \underline{\qquad\qquad\qquad} \; \mathcal{O}(q,p_*)$$

$$= \underline{\qquad\qquad} \sim \underline{\qquad\qquad\qquad} \; \mathcal{O}(q,p'_*)(-$$

$$= \underline{\qquad\qquad} \sim \underline{\qquad\qquad\qquad} \; \mathcal{O}(q,p')($$

$$\Rightarrow_{(*)} \boxed{\int_p \mathcal{O}\, Q(f,f) = \frac{1}{4} \int d\sigma \int dq \int dp' dp'_* dp\, dp_*\, \chi(\sigma) \left(f' f'_* - f f_* \right) \left[\mathcal{O}_* + \mathcal{O} - \mathcal{O}'_* - \mathcal{O}' \right]}$$

where $\chi(\sigma) \doteq \chi(\sigma, p'p'_* \to p p_*) = \chi(\sigma, p p_* \to p' p'_*) = \dots$

and obvious shorthand notations.

<u>This implies:</u> $\int \mathcal{O} Q = 0$ for $\mathcal{O} = \begin{cases} 1, \\ \frac{p^2}{2m}, p \\ \varphi(q) \quad \forall \varphi. \end{cases}$ (<u>global collisional invaria</u>

The latter implies $\int \mathcal{O} H_1 = 0$. $\uparrow$ for .

<u>Hence</u> Conservation of energy momentum and number of particles relies on streaming term!

For such <u>global</u> collisional invariants,

Evolution equation is $\frac{d}{dt}\langle \mathcal{O} \rangle = \langle \{\mathcal{O}, H_1\} \rangle + 0$

- 0 if $\mathcal{O} = H_1$ or 1.
- 0 if $\mathcal{O} = p$ and H_1 has translational <u>symmetry</u>.

<u>Obs</u>: Conservation of global invariants relies heavily on the symmetry wrt to time reversal of the collision scattering rate!!

② H-theorem

In spite of conservation law, the symmetry of the collision scattering rate is a central ingredient of irreversibility of S.M. In particular it yields the

H-Thm:

$$\frac{d}{dt} H \leq 0,$$

where $H[f] = \int_{\mu} dp\,dq\, f \log f$.

with strict inequality unless f is ^locally Maxwellian.

Obs [Bad notation alert!].

The H of the H-thm is radically different than the Hamiltonian.

It resembles the Gibbs entropy ... (but in μ-space) - We will comment on that point later.

2/ The "proof" of the H-thm relies essentially on the same trick as the derivation of the previous conservation laws.

Using the same string of calculation that was previously employed yields.

$$\underbrace{\frac{d}{dt} H[f]}_{\text{H-function}} = \frac{d}{dt} \langle \log f \rangle_{\mu} = \langle \underbrace{\{ \log f, H_1 \}}_{=0} \rangle + \int_{\mu} \mathcal{C} \log f$$

Hamiltonian

$$= \int f \{\log f, H\} = \int \{f, \log f\} H = 0.$$

This implies:

$$\frac{d}{dt} H[f] = \frac{1}{4} \int d\sigma \int dq \int dp' dp'_* dp\, dp_*\ \chi[\sigma] \left[f' f'_* - f f_* \right] \left[\log f + \log f_* - \log f' - \log f'_* \right]$$

$$= \underline{\qquad\qquad} \sim \underbrace{\chi[\sigma]}_{>0} \left[f' f'_* - f f_* \right] \log \frac{f f_*}{f' f'_*} \leq 0$$

two quantities of opposite sign!

This shows the <u>H-Thm.</u>

The case of equality:

$$\log f' + \log f'_* = \log f + \log f_* \qquad \text{(Detailed Balance)}$$

For all pairs $p'_1 p'_* \to p\, p_*$ such that $\chi(\sigma) \neq 0$. (*)

This implies that $\log f$ is a <u>collisional invariant</u>. [cf previous discussion].

ie $\log f = A(q) + B(q) \vec{p}^{\,2}/2m + \gamma(q) \vec{P}_0$ (*)

with normalization: $\int f_0\, dp\, dq = N$.

The solution to (*) is a local Maxwellian:

$$f_{loc}(\vec{q}, \vec{p}) = f(\vec{q}) \sqrt{\frac{\beta(q)}{2m\pi}}^{\,3} e^{-\beta(q)(\vec{p} - \vec{p}_0)^2/2m}.$$

$$\int f_{loc}(q,p)\, d\vec{p} = f(\vec{q}) \qquad \text{(local density)}$$

$\int f(q)\, d\vec{q} = N$. (<u>number of particles</u>).

Obs: The conditions $H(t) \searrow$ ⊕ $H \geq H_B$

guarantee convergence of H towards a limit as $t \to \infty$.

Rigorous proof that this limit is indeed the global M.B distribution requires finer (very fine!) mathematical approach.

eg, See Discussion in Cercignani (Theory of dilute gas)
References in Villani's (H-theorem and beyond)

Example of results (Villani & Desvillettes, 2005)

If f very regular: $\int f |v|^k < \infty$. + bounded derivatives.
f strictly positive $\geq K e^{-a|v|^q}$

then $f(t) \xrightarrow[t\to\infty]{} f_{eq}$ with convergence faster than any power law.

This goes beyond the scope of the present course
(and technical ability of the lecturer!)

③ _ global equilibrium:

- Observe that the H-function is bounded below:

$$H[f] \geq H[f_\beta].$$

where f_β solves:

(Non-Homogeneous) $H[f] \longrightarrow \inf$; $E = \int_\mu f_1 H_1 := \int_\mu f_1 \left[\frac{p_1^2}{2m} + V_1(q)\right]$
$N = \int_\mu f_1$

(Homogeneous) $H[f] \longrightarrow \inf$; $E = \int_\mu \frac{p_1^2}{2m}$; $N \int_\mu f_1$; $\vec{P} = \int_\mu f_1 \vec{p}$

For simplicity consider the first case. ~~[illegible]~~
(In the case with V models a hard wall) Maxwell-Boltzmann statistics:
the solution to those optimization problems are

$$f_1(q,p,t) = \frac{N}{V}\left(\frac{\beta}{2m\pi}\right)^{3/2} e^{-\beta\frac{\vec{p}^2}{2m}} \mathbb{1}_{\vec{q}\in\mathcal{D}}. \qquad (MB)$$

$|\mathcal{D}| = V$.

$\Longrightarrow$ Maxwell-Boltzmann "Canonical" distribution has just emerged naturally!!!...

One can check that MB is indeed a stationary solution to (BE) as $\left|\begin{array}{l}\{f_1, H_1\} = 0, \quad \int Q f = 0. \text{ (from Detailed Balance)} \\ \partial_t f_1 = 0.\end{array}\right.$

MB is the unique global equilibrium of the Boltzmann Equation.

(4) Thermodynamics.

- The H-thm has a clear second law flavor, but is now formulated in μ-space and is a dynamical statement about convergence to equilibrium.
- Upon adding the appropriate constant to H_β, one will retrieve ideal gas expression previously found for the entropy:

Recall: $f_\beta = \underset{\frac{N}{V}}{n} \left(\frac{\beta}{2m\pi}\right)^{3/2} e^{-\beta \vec{p}^2/2m} \quad \mathbb{1}_{\vec{q} \in V}. \qquad p, q \in \mathbb{R}^3 \quad$ (μ-space)

Compute: $H_\beta = \int_\mu f_\beta \log f_\beta = H_{\mu,\beta}.$

$$= \int_\mu f_\beta \log n\left(\frac{\beta}{2m\pi}\right)^{3/2} - \int_\mu f_\beta \frac{\vec{p}^2}{2m}\beta.$$

$$= N \log n\lambda^3 - N\log h^3 - \underset{\frac{3}{2}N}{E\beta} \qquad E = \frac{3}{2}N/\beta.$$

$$= -N\left(\log\frac{V}{N\lambda^3} + \frac{3}{2}\right) - N\log h^3.$$

$$= -S_{G,\mu} + N(1 - \log h^3) \implies \boxed{S_{G,\mu} = \int_\mu f(1 - \log h^3 f)}$$

(Ideal gas).

$H \uparrow \implies S_{G,\mu} \downarrow$ (obviously)

Obs: $S_{G\Gamma} \neq S_{G,\mu}$.

$\hookrightarrow$ Gibbs Entropy defined in Γ-space.

To see this,

Define $$H_{\Gamma,\beta} = - S_{G,\Gamma} + N(1-\log h^3)$$

with $$S_{G,\Gamma} = - \int_\Gamma \rho_\beta \log \rho_\beta N!\, h^{3N} \quad \text{(Recall Lecture 1)}$$

obtain

$$H_{\Gamma,\beta} = + \int \rho_\beta \log \rho_\beta + N\log N - \cancel{N} + \cancel{3N\log h} + \cancel{N} - \cancel{\log h^3}$$
$$= \int \rho_\beta \log \rho_\beta N^N$$

Now observe

$$H_{\mu,\beta} = N \int_\Gamma \rho_N \log \rho_1(z_1) N \; dz_1 \ldots dz_N \qquad \rho_1(z) = f_1/N$$
$$= N \int_\Gamma \rho_N \log \rho_1(z_2) N \; dz_1 \ldots dz_N$$
$$\text{———} \sim \rho_1(z_2) \text{———}$$
$$\vdots$$
$$\text{———} \sim \rho_1(z_N) \sim \text{———}$$
$$= \int_\Gamma \rho_N \log \rho_1(z_1) \cdots \rho_1(z_N)\, N^N$$

$$\Longrightarrow \quad H_{\mu,\beta} - H_{\Gamma,\beta} = \int_\Gamma \rho_{\beta,N} \log \frac{\prod_{i=1}^N \rho_1(z_i)\, N^N}{\rho_{\beta,N}\, N^N} \leq 0 \quad \text{(concavity)}$$

ie

$$\boxed{H_{\mu,\beta} \leq H_{\Gamma,\beta} \quad \text{, eg} \quad S_{\mu,\beta} \geq S_{\Gamma,\beta}^{*}}$$

with equality provided the n point probability factorizes. (ie independence of particles).

(*) cf Expression $S_{\Gamma,\beta}$ for weak correction to ideal gas obtained in the Van Der Waals gas (...)

Did we just prove the 2nd law? (re thermodynamics)

Apart from the discrepancy between T-p entropies, it looks close.

While the H-thm is valid (a priori) in so far as it concerns the BE equation, it is unclear whether it applies to a dilute gas. Is the H-thm a mere artefact of the chaotic hypothesis? $(f_2 = f_1 f_1)$.

(5) Two apparent objections to the H-Thm:

A Loschmidt

(I) Prepare the gas in a state of molecular chaos $\Rightarrow \frac{dH}{dt} \geq 0$ at $t+\varepsilon$

(II) Flip the initial velocities, evolve the gas $\Rightarrow \frac{dH}{dt} \geq 0$ at $t = t+\varepsilon$.

(if $\{p,q\}$ is in a molecular χ state so is $\{-p,q\}$

ie $f_1(p) f_1(p) = f_2(p,p)$ $\qquad f_2(-p,-p) = f_1(-p) f_1(-p)$

Since the pair of evolutions (1) is obviously the time-reversed evolution (II)

this should imply $\frac{dH}{dt} = 0$ for any state in molecular chaos.

A This is not a paradox.

- The correct statement of H-thm as applied to dilute gas is

Molecular chaos at $t=0 \Rightarrow \frac{dH}{dt}$ at $t = 0^+$ | Causality is embodied in the χ hypothesis.

at $t = \varepsilon \Rightarrow \frac{dH}{dt} \geq 0$ | cf Kac Ring Model

One cannot invoke the chaotic hypothesis for both future and past evolution!

- $\dfrac{dH}{dt}$ not C^0 due to molecular collisions

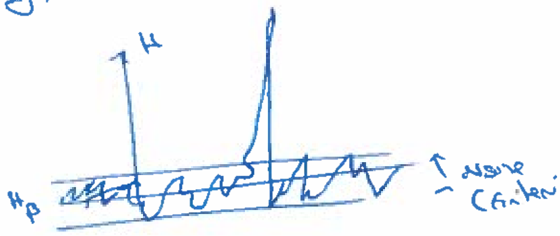
Exercise: Adapt Molecular dynamics program to see this behavior!

B Poincaré:

A system with finite energy confined to finite volume will after a sufficiently long time return to arbitrary neighborhood of the initial state.

Answer:
- OK for most of the time when H lies in the noise range.
  → this implies that small fluctuations repeat themselves.
- For large fluctuations, Poincaré cycle $\sim 10^N \sim 10^{10^{23}}$ cf Feller
- Results (Math) show damping of fluctuation is fast! (ie $O(t^{-1})$)

Typical rare fluctuation.



- cf again Kac Ring Model, where X hypothesis is relevant in the limit $N \to \infty$.

⟹ See Also discussion in Huang, Statistical Mechanics (Chapter 4).

Another proof of Poincaré thm Kac, probability in physics (Chapter ?)

Add-on: Distinguishability, Permutations and Liouville operator

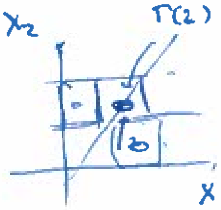
- Recall the definition of the Liouville density:

$$h^N \rho_N(z_1, \dots z_N, t) = P[\mathbf{X}_1 \in dz_1 \dots \mathbf{X}_N \in dz_N].$$

$$= P[\vec{\mathbf{X}} \in \Gamma(z)]$$

ordered

Γ cell centered around position



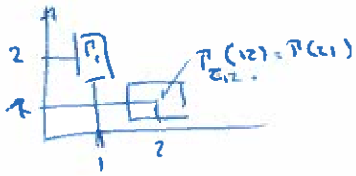
$\vec{X} = (x_1, \dots x_N)$ ~~position of the vector~~. Dynamical state of the gas.

ρ_N solves the Liouville equation:

$$\partial_t \rho_N + \{\rho_N, H\} = 0.$$

- Now define: $\rho_\sigma(z_1, \dots z_N, t) = \frac{1}{h^N} P[\vec{X} \in \Gamma_\sigma(z)]$.

with Γ_σ the Γ-cell centered around $[z_{\sigma(1)} \dots z_{\sigma(N)}]$.



Then ρ_σ solve the Liouville equation

$$\partial_t \rho_\sigma + \{\rho_\sigma, H\} = 0.$$

2/ Take $O_\sigma = \mathbb{1}_{z \in \Gamma_\sigma}$

From Liouville, one gets $\frac{d}{dt}\langle O_\sigma \rangle = \langle \{O_\sigma, H\} \rangle$. average with ρ.

$$= \int \rho \, d\vec{z} \, \mathbb{1}_{z \in \Gamma_\sigma} = \rho_\sigma |\Gamma|$$

$$= \int \{H, \rho\} \mathbb{1}_{z \in d\sigma}$$

$$= \{H_\sigma, \rho_\sigma\} |\Gamma| = \{H, \rho_\sigma\} |\Gamma|$$

Now a possible defining:

$$\tilde{\rho} = \frac{1}{N!} \sum_{\sigma \in \mathfrak{S}_N} \rho_\sigma \; ; \quad \tilde{\rho} \text{ solves } \partial_t \tilde{\rho} + \{\tilde{\rho}, H\} = 0$$

with $\int \tilde{\rho} \, dz_1 \dots dz_N = 1$ $\qquad$ $\tilde{\rho}$ is symmetric with to particles