Liouville's theorem

equation for $f(q, p, t)$

PDF for an ensemble in phase space.

Density function for many phase points.

$$\frac{\partial f}{\partial t} + \sum_i \dot{q}_i \frac{\partial f}{\partial q_i} + \dot{p}_i \frac{\partial f}{\partial p_i} = 0$$

If we follow $(q(t), p(t))$, the phase trajectory, then $\frac{d}{dt} f = 0$

$$f(q(t+\Delta t), p(t+\Delta t), t+\Delta t) = f(q(t), p(t), t)$$

Equilibrium system → equilibrium ensemble. $\frac{\partial f}{\partial t} = 0$,

Stationary distribution.

$$\sum_i \dot{q}_i \frac{\partial f}{\partial q_i} + \dot{p}_i \frac{\partial f}{\partial p_i} = 0$$

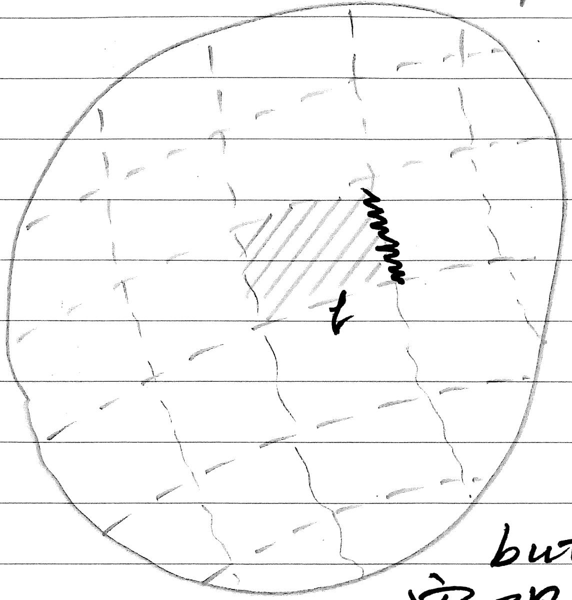
$f(q, p)$ itself is a mechanical invariant.

$f(q, p)$ is associated with $H(q, p)$ because

$$\sum_i \dot{q}_i \frac{\partial H}{\partial q_i} + \dot{p}_i \frac{\partial H}{\partial p_i} = 0, \quad H \text{ is a mech. invariant.}$$

$$f = f(H(q, p)) \rightarrow \sum_i \dot{q}_i \frac{\partial f}{\partial q_i} + \dot{p}_i \frac{\partial f}{\partial p_i} = 0.$$

Statistical independence



Quasi-closed subsystems

近独立子系，

Each subsystem is still macroscopic.

Macroscopically small, but microscopically large

宏观小

微观大.

Surface to volume ratio $\frac{l^2}{l^3} \sim \frac{1}{l} \to 0$.

Interactions through the boundary. Short range.

l >> short-range of interaction

Very weak interaction between subsystems.

$\downarrow$

Quasi-closed.

Statistical independence. 近独立.

X, Y. $\qquad f_{XY}(x,y) = f_X(x) f_Y(y)$

Macroscopic system divided into many quasi-closed subsystems.

$$f = f_1 \cdot f_2 \cdot f_3 \cdots$$

to label the subsystems.

$$\log_e f = \log f_1 + \log f_2 + \log f_3 + \cdots$$

$\log f$ is additive. (可加的)
is an extensive quantity.

① f is a mechanical invariant.
so that f is a stationary solution to Liouville equation.

$$\frac{df}{dt} = 0, \quad \frac{\partial f}{\partial t} = 0 \Rightarrow \frac{d}{dt} f(q(t), p(t)) = 0$$

$$\sum_i \dot{q}_i \frac{\partial f}{\partial q_i} + \dot{p}_i \frac{\partial f}{\partial p_i} = 0.$$

② $\ln f$ is additive.

① & ② : $\log f$ is an additive mechanical invariant.
→ Energy.

$$E = E_1 + E_2 + \cdots$$

$$\log f_i = -\alpha_i - \beta E_i \quad , \quad i: \text{ith subsystem.}$$

α_i: a normalization const.
β: same for different subsystems

$$\log f = \sum_j (-\alpha_j - \beta E_j) = \sum_j \log f_j$$

$$= -\sum_j \alpha_j - \beta \sum_j E_j = -\alpha - \beta E.$$

β: same for different subsystems. temperature

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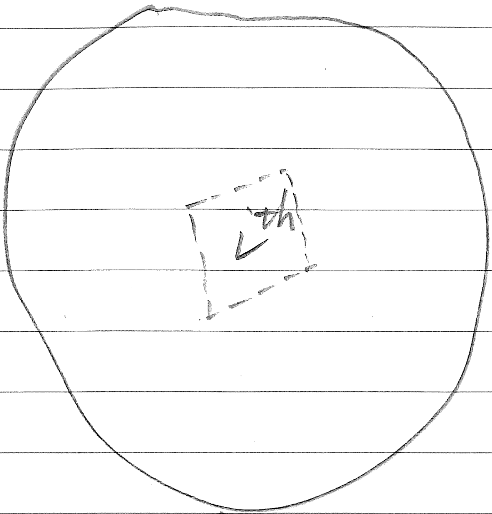

i^{th} subsystem

$$f_i = e^{-\alpha_i - \beta E_i}$$

$$\log f_i = -\alpha_i - \beta E_i$$

α_i for normalization.
β is related to temperature.
β is the same for all the subsystems in equilibrium.

$$\sum_j -\beta E_j = -\beta \sum_j E_j$$

$$\beta = \frac{1}{k_B T} \quad , \ T, \text{ absolute temperature}$$

$$f_i = e^{-\alpha_i - \beta E_i}$$

$$f \propto e^{-\beta E} = e^{-\frac{E(q,p)}{k_B T}}$$

$E(q,p) \rightarrow H(q,p)$

$T \to 0^+$, only low-energy states are occupied with significant probabilities.
$T \to \infty$, all the energy states are equally occupied.

$$f \propto e^{-\frac{E}{k_B T}}$$ Gibbs distribution.

for a macrascopic system in thermal contact with the environment.

$E \uparrow$, $f \downarrow$

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The Gibbs ensemble, the canonical ensemble $f \propto e^{-\beta E}$

$$f(q,p) = e^{-\alpha - \beta E(q,p)}$$

$$\int f(q,p)\, dq\, dp = \int dq\, dp\; e^{-\alpha - \beta E(q,p)}$$

吉布斯.

Entropy. S to be expressed through a distribution $f(q,p)$: q & p are continuous variables.

$$S = \int dq\, dp\; f \log f$$

For the sake of clarity in expression, I switch to summation over discrete states.

Quantum physics.

$$f(q,p) \longrightarrow W_n$$

$$\int dq\, dp\, f = 1 \qquad \sum_n W_n = 1$$

$$\int dq\, dp\; f \log f \rightarrow \sum_n W_n \log W_n = S$$

W_n: probabilities of discrete states.

S: additive.

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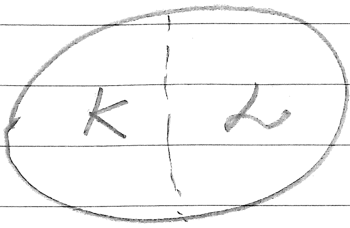

$$f = f_K \cdot f_L$$

$$W = W_K \cdot W_L$$

$$S = S_K + S_L \quad \text{additive.}$$

$$S = \sum_n W_n \log W_n \quad , \quad n = (n_K, n_L)$$

$$= \sum_{n_K, n_L} (W_{n_K} W_{n_L}) (\log W_{n_K} + \log W_{n_L})$$

$$W_n = W_{n_K} W_{n_L}$$

$$= \sum_{n_K, n_L} W_{n_K} \underline{W_{n_L}} \log W_{n_K} + \sum_{n_K, n_L} \underline{W_{n_K}} W_{n_L} \log W_{n_L}$$

$$= \sum_{n_K} W_{n_K} \log W_{n_K} + \sum_{n_L} W_{n_L} \log W_{n_L}$$

$$\left\{ \begin{array}{l} \sum_{n_L} W_{n_L} = 1 \\ \sum_{n_K} W_{n_K} = 1 \end{array} \right.$$

$$= S_K + S_L$$

Entropy additive
广延量.

Meaning of S for the Gibbs ensemble.

$$W_n = \frac{e^{-\beta E_n}}{\sum_m e^{-\beta E_m}} \quad , \quad \sum_n W_n = 1$$

$$S = - \sum_n W_n \log W_n$$

"$-$" just added, additivity not changed by adding "$-$".

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$$S = -\sum_n W_n \log W_n , \qquad W_n = \frac{e^{-\beta E_n}}{\sum_m e^{-\beta E_m}} = \frac{e^{-\beta E_n}}{Z(\beta)}$$

partition function.

$$= -\sum_n W_n (-\beta E_n - \log Z)$$

$$= -(-\beta\langle E\rangle) - (-\log Z)$$

$$= \beta\langle E\rangle + \log Z$$

mean energy $\langle E\rangle$

$$\sum_n W_n E_n = \langle E\rangle$$

$$= -\log e^{-\beta\langle E\rangle - \log Z}$$

$$a = \log e^{a} = -\log e^{-a}$$

$$= -\log \frac{e^{-\beta\langle E\rangle}}{Z}$$

$$W_n = \frac{e^{-\beta E_n}}{Z}$$

$$= -\log W(\langle E\rangle)$$

$$W(\langle E\rangle) = \frac{e^{-\beta\langle E\rangle}}{Z}$$

Probability for a state with ~~its~~ energy equal to $\langle E\rangle$.

$W(\langle E\rangle) = W_n$ with $E_n = \langle E\rangle$.

Because energy E is additive, its variance scales with the system size linearly.

$E = \sum_{i=1}^{N} \varepsilon_i$, sum over N subsystems.

$\mathrm{Var}(E) \sim N$, statistical independence.

LLN.

$$\frac{\sqrt{\mathrm{Var}(E)}}{E} \sim \frac{\sqrt{N}}{N} \sim N^{-\frac{1}{2}} \to 0$$ for macroscopic system.

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for macroscopic system, E's fluctuation is approaching zero relative to energy itself.

$\sqrt{N}$ vs N.

Variance $\sim N$

S.D. $\sim \sqrt{N}$, $E \sim N$.

Energy at $\langle E \rangle$ is representative. Distribution in energy is very concentrated near $\langle E \rangle$.

$\frac{\sqrt{N}}{N} \sim \frac{1}{\sqrt{N}} \to 0$. Peaked distribution.

$W(\langle E \rangle)$: Probability for a representative state.

$\sum_n W_n = 1$

Important states : E_n close to $\langle E \rangle$.

Number of important states $\frac{1}{W(\langle E \rangle)}$

$$\frac{1}{W(\langle E \rangle)} W(\langle E \rangle) = 1 = \sum_n W_n$$

↳ sum over states with $E_n \sim \langle E \rangle$.

↳ over all states.

$$S = -\log W(\langle E \rangle) = \log \frac{1}{W(\langle E \rangle)}$$

$= \log$ (Number of important states)

Meaning of S.

Tombstone formula.

Boltzmann.

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$$f \sim e^{-\frac{1}{k_B T} E(q,p)}$$ in phase space.

$$\langle Q(q,p) \rangle = \int dq\,dp\; Q(q,p)\, f(q,p)$$

Computationally, mission impossible
(q,p) space $\sim 6N$ ↳ Number of particles

Monte Carlo method.

Effectively, only a very small part of phase space contributes to the integral.
M.C. → capture this small & effective part.
↳ high distribution density.

① Integral to compute for $\langle Q \rangle$
② Phase space is high-dimensional.
③ ✱ $f(q,p)$ is very singular.

Markov chain:
A sequence of microscopic states

$S_1 \to S_2 \to S_3 \to S_4 \to \cdots$

using random "walker" in phase space.

S_{n+1} depends on S_n only.
No memory.

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$$I = \int_{-\infty}^{\infty} Q(x) f(x)\, dx = \langle Q \rangle_f$$

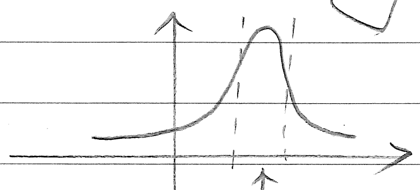
$$\int_{-\infty}^{\infty} f(x)\, dx = 1 \quad \text{. PDF .}$$

X : $x_1 \to x_2 \to x_3 \to x_4 \to x_5 \cdots$

A markov chain (x_{n+1} from x_n only), say, x_4 by x_3 ONLY.

A sequence of values for x : PDF $f(x)$

Histogram of $x_i \to$ PDF of x.



x_i in this interval will appear with large frequency.

More probable x would appear in the Markov Chain more frequently.

$$\langle Q \rangle = \int Q(x) f(x)\, dx = \frac{1}{N} \sum_{i=1}^{N} Q(x_i)$$

N ↳ length of the chain.

Number of x_i values in $(x, x+dx)$ $\sim f(x)\, dx$

Key : How to generate a Markov Chain according to $f(x)$?

frequency of $x \sim f(x)$.

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Metropolis importance sampling.

to let x appear with a frequency $\sim f(x)$.

Algorithm for simulation.

No memory S_{n+1} determined from S_n only.

Initial state S_1 given,
Make a trial move from S_1:
$S_1 \dashrightarrow S_c$
Candidate state.

Compute $E(S_c)$ & $E(S_1)$
If $E(S_c) \le E(S_1)$, downhill $S_1 \dashrightarrow S_c$,
then S_c is accepted as S_2.
Else (Othewise), $E(S_c) > E(S_1)$,
uphill $S_1 \dashrightarrow S_c$,
S_c is to be accepted as S_2
with $r = e^{-(E(S_c)-E(S_1))/k_BT}$
< 1.

In short, candidate state is surely accepted if downhill,
or is accepted with $r < 1$
(if uphill).

$r = e^{-\Delta E/k_BT}$ for $\Delta E > 0$.
< 1.

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Given S_1, trial move $\rightarrow S_c$.

If $E(S_c) \leq E(S_1)$, then $S_2 = S_c$,
i.e., S_c becomes S_2.

Else $(E(S_c) > E(S_1))$ S_c is accepted to be S_2 with a probability r,

$$r = e^{-(E(S_c)-E(S_1))/k_BT} < 1$$

How to accept S_c as S_2 with probability $r<1$?

Generate a random number $\xi \in [0, 1]$

if $\xi \leq r$, then acceptance: $S_2 = S_c$.
$\hookrightarrow$ probability $= r$

Otherwise, if $\xi > r$, $S_2 = S_1$
probability $= 1-r$ $\downarrow$ S_1 re-used as S_2.

$P \sim r$ $P \sim 1-r$

$0 \quad \xi \quad r \quad \xi \quad 1$

How to grow the Markov chain using the importance sampling.

Consider a system with two energy states only: H & L
$\hookrightarrow$ high energy $\hookrightarrow$ low energy

How to generate a Markov chain that shows the Gibbs distribution by using Importance Sampling.

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$$E_H - E_L = \Delta > 0$$
$$W = e^{-\Delta/k_B T} < 1$$

$H \rightarrow S_c = L$: Every trial move
$L \rightarrow S_c = H$: will change the state.

According to the algorithm, in the M.C. H is always followed by L (downhill), while L is followed by H with probability $W < 1$ (uphill).

HLH, W
$HLLH$, $(1-W)W$
$HLLLH$, $(1-W)^2 W$
$HLLLLH$, $(1-W)^3 W$.

Segments in M.C.

$$\sum \text{probabilities} = W + (1-W)W + (1-W)^2 W + (1-W)^3 W + \cdots$$
$$= W\left(1 + (1-W) + (1-W)^2 + (1-W)^3 + \cdots\right)$$
$$= W \frac{1}{1-(1-W)} = W \cdot \frac{1}{W} = 1 \qquad 1-W<1$$

Normalized.

Let's count the number of L's following H:

$$n = W + 2(1-W)W + 3(1-W)^2 W + 4(1-W)^3 W + \cdots$$

mean

$$= W\left(1 + 2(1-W) + 3(1-W)^2 + 4(1-W)^3 + \cdots\right)$$
$$= W \frac{1}{\cancel{1+(1-W)}\,(1-(1-W))^2} = W \cdot \frac{1}{W^2} = \frac{1}{W}.$$

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Every H is followed by $n = \frac{1}{w}$ L's on average.

$$\rho_H : \rho_L = 1 : \frac{1}{w} = 1 : e^{+\Delta/k_BT} = w : 1$$

desired distribution

$$\rho_H \sim e^{-E_H/k_BT}$$

$$\rho_L \sim e^{-E_L/k_BT}$$

$$\frac{\rho_H}{\rho_L} = e^{-(E_H - E_L)/k_BT} = e^{-\Delta/k_BT}$$

$$= w < 1$$

High energy H is less populated than lower energy L.

M.C.

HLLHLLLLHLHLLH ....

Averaging over this M.C.,

we can compute the average according to the Gibbs distribution

$$\frac{\rho_H}{\rho_L} = w < 1 \qquad \begin{cases} \rho_H = \frac{w}{1+w} \\ \rho_L = \frac{1}{1+w} \end{cases}$$