Nonequilibrium Statistical Mechanics and Stochastic Thermodynamics

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Abstract

This is for the group seminar on the Introduction to Stochastic Thermodynamics at MIT, presented by Yulong Dong. This lecture follows a logistical order rather than historical order. To make the introduction clear, I simplify the math as much as I can and try to write this lecture in a more physical way.

1 Introduction

As we known, all motions in microscopic, driven by Hamiltonian dynamics or Langevin dynamics, are inverse because of the inversity of those PDEs. However, in macro world, time evolution have a certain direction.

2 Basic of Nonequilibrium Statistic

2.1 Two Requirements

1. temperature is constant in dynamics;
2. micro dynamics obeys Markov process.

2.2 Four Essential PDEs in MD

1. **Definition 1 (Chapman Kolmogorov equation)** *This equation marks the Markov property of a Markovian chain, which means only adjacent two steps have correlation and equilavent to*

$$P(C_N|C_{N-1},...,C_1,C_0) = P(C_N|C_{N-1}) \tag{1}$$

2. **Definition 2 (Master equation)** *As for probability in Markov process, if we denote the transient probability in unit time as $\mathcal{W}(x \to x')$, the master equation of probability is*

$$\frac{\partial P(x,t)}{\partial t} = \int dx'(\mathcal{W}(x' \to x)P(x',t) - \mathcal{W}(x \to x')P(x,t)) \tag{2}$$

This equation represents the evolution of the quantity P in a jump process, like the chemical system. The matrix A defines the topological interaction.

$$\frac{dP(t)}{dt} = \mathbf{A}(t)P(t)$$

3. **Definition 3 (Langevin equation)** *This equaution describes the evolution of coordinates and velocities of Brownian particles.*

$$m\ddot{x} = -\gamma\dot{x} + \partial_x U(x) + \xi \tag{3}$$

where $\langle\xi(t)\rangle = 0 \quad \langle\xi(t)\xi(s)\rangle = 2\gamma kT\delta(t-s)$

4. **Definition 4 (Fokker-Planck equation)** *This equation corresponds to the Langevin equation and represents the evolution of P.D.F. of coordinates and velocities.*
If the Stochatic PDE has the form of $dX(t) = F(X)dt + dW(t)$, where W(t) is a Winner process and we denotes the noise $dW(t) = \xi(t)dt$ with $\langle\xi(t)\rangle = 0$, $\langle\xi_i(t)\xi_j(s)\rangle = g_{ij}\delta(t-s)$, the corresponding F-P equation is

$$\partial_t P(X,t) = -\partial_X \cdot (F(X)P(X,t) + \frac{1}{2}\partial_X \cdot \mathbf{g} \cdot \partial_X P(X,t) \tag{4}$$

2.3 Detailed Balanced Condition

Because we consider dynamics here instead of static properities, we should use sochastic process to describe it.

Definition 5 (Detailed Balance Condition) *If a process satisfies*

$$\frac{\mathcal{W}(C \to C')}{\mathcal{W}(C' \to C)} = \frac{P^{eq}(C')}{P^{eq}(C)} \tag{5}$$

, this process is time-inverse stationary process.

2.4 Given Trajectory Probability

Definition 6 (Trajectory) *Forward Trajectory: $\Gamma = \{C_0, C_1, C_2, ..., C_N\}$; Corresponding Backward Trajectory: $\Gamma^* = \{C_N, C_{N-1}, ..., C_0\}$*

Definition 7 (Given Trajectory Probability) *For a given trajectory, the probability of it is*

$$\begin{aligned}
\mathcal{P}_F(\Gamma) &= P(C_1, C_2, ..., C_N|C_0) \\
&= P(C_1|C_0)P(C_2|C_1, C_0)\cdots P(C_N|C_0, C_1, ..., C_{N-1}) \\
&= P(C_1|C_0)P(C_2|C_1)\cdots P(C_N|C_{N_1}) \\
&= \prod_{i=0}^{N-1} \mathcal{W}_i(C_i \to C_{i+1})
\end{aligned} \tag{6}$$

Similarly,

$$\begin{aligned}\mathcal{P}_R(\Gamma^*) &= \prod_{i=0}^{N-1} \mathcal{W}_{i,R}(C_{N-i} \to C_{N-i-1}) \\ &= \prod_{i=0}^{N-1} \mathcal{W}_i(C_{i+1} \to C_i)\end{aligned} \tag{7}$$

where the parameter $\lambda_{i,R} = \lambda_{N-i-1,F}$

3 Entropy, Fluctuation Theorem

3.1 Entropy in Nonequilibrium System

Definition 8 (Trajectory Entropy) *For a given trajectory* Γ*, we define the entropy production of the system as*

$$\begin{aligned}\frac{\mathcal{P}_F(\Gamma)}{\mathcal{P}_R(\Gamma)} &= \prod_{i=0}^{N-1} \frac{\mathcal{W}_i(C_i \to C_{i+1})}{\mathcal{W}_i(C_{i+1} \to C_i)} \\ &= \prod_{i=0}^{N-1} \frac{P_i^{eq}(C_{i+1})}{P_i^{eq}(C_i)} \\ &= e^{S_p(\Gamma)}\end{aligned} \tag{8}$$

Definition 9 (Boundary Entropy) *The boundary term represents the contributions of the begining and end of a stochatic process.*

$$B(\Gamma) = \ln P_0^{eq}(C_0) - \ln b(N) \tag{9}$$

where $b(N)$ *is an arbitrary density function such that* $\sum_{C_N} b(C_N) = 1$.

Definition 10 (Total Entropy – Dissipation Function) *The total entropy of a stochatic process is*

$$\begin{aligned}S(\Gamma) &= S_p(\Gamma) + B(\Gamma) \\ &= \sum_{i=0}^{N-1} \ln \frac{P_i^{eq}(C_{i+1})}{P_i^{eq}(C_i)} + \ln P_0^{eq}(C_0) - \ln b(N)\end{aligned} \tag{10}$$

We choose the form $b(N) = P_N^{eq}(C_N)$ *such that*

$$P_0^{eq}(C_0) e^{S_p(\Gamma)} = P_N^{eq}(C_N) e^{S(\Gamma)}$$

and the total entropy can be antisymmetric under time reversal, i.e. $S(\Gamma) = -S(\Gamma^*)$.

Proposition 3.1

$$\langle \exp(-S(\Gamma)) \rangle_\Gamma = \sum_\Gamma \exp(-S(\Gamma)) P(\Gamma) = 1 \tag{11}$$

Proof 3.1 *According to equation 10,*

$$\exp(-S(\Gamma)) = \frac{b(N)}{P_0^{eq}(C_0)} \prod_{i=0}^{N-1} \frac{P_i^{eq}(C_i)}{P_i^{eq}(C_{i+1})}$$

Therefore,

$$\begin{aligned}
\langle \exp(-S(\Gamma)) \rangle_\Gamma &= \sum_\Gamma \exp(-S(\Gamma)) P(\Gamma) \\
&= \sum_\Gamma \frac{b(N)}{P_0^{eq}(C_0)} \prod_{i=0}^{N-1} \frac{P_i^{eq}(C_i)}{P_i^{eq}(C_{i+1})} P_0^{eq}(C_0) \prod_{i=0}^{N-1} \mathcal{W}_i(C_i \to C_{i+1}) \\
&= \sum_\Gamma b(N) \prod_{i=0}^{N-1} \frac{P_i^{eq}(C_i)}{P_i^{eq}(C_{i+1})} \mathcal{W}_i(C_i \to C_{i+1}) \\
&= \sum_\Gamma b(N) \prod_{i=0}^{N-1} \mathcal{W}_i(C_{i+1} \to C_i) \\
&= \sum_\Gamma P_R(\Gamma^*) \\
&= 1
\end{aligned} \tag{12}$$

3.2 Probability of Total Entropy of System

Definition 11 (Probability of Total Entropy of System)

$$P_F(S) = \sum_\Gamma P_0^{eq}(C_0) \mathcal{P}_F(\Gamma) \delta(S(\Gamma) - S) \tag{13}$$

$$P_R(S) = \sum_{\Gamma^*} P_N^{eq}(C_N) \mathcal{P}_R(\Gamma^*) \delta(S(\Gamma^*) - S) \tag{14}$$

3.3 Fluctuation Theorem

Theorem 1 (Fluctuation Theorem) *For a given trajectory, we denote the total entropy of it as $S(\Gamma) = S$, the fluctuation theorem is*

$$\frac{P_F(S)}{P_R(-S)} = e^S \tag{15}$$

Proof 3.2

$$
\begin{aligned}
P_F(S) &= \sum_{\Gamma} P_0^{eq}(C_0)\mathcal{P}_F(\Gamma)\delta(S(\Gamma)-S) \\
&= \sum_{\Gamma} P_0^{eq} e^{S_p(\Gamma)}\mathcal{P}_R(\Gamma^*)\delta(S(\Gamma)-S) \\
&= \sum_{\Gamma} P_N^{eq}(C_N) e^{S(\Gamma)}\mathcal{P}_R(\Gamma^*)\delta(S(\Gamma)-S) \\
&= e^S \sum_{\Gamma^*} P_N^{eq}(C_N)\mathcal{P}_R(\Gamma^*)\delta(S(\Gamma^*+S)) \\
&= e^S P_R(-S)
\end{aligned}
\tag{16}
$$

Corollary 1

$$
\langle e^{-S}\rangle_{F(R)} = 1 \tag{17}
$$

Proof 3.3

$$
\begin{aligned}
\langle e^{-S}\rangle_R &= \int dS e^{-S} P_R(S) = \int dS P_F(-S) = 1 \\
\langle e^{-S}\rangle_F &= \int dS e^{-S} P_F(S) = \int dS P_R(-S) = 1
\end{aligned}
\tag{18}
$$

Corollary 2 (Second Law of Thermodynamics)

$$
\langle S\rangle \geqslant 0 \tag{19}
$$

Proof 3.4 *By applying Jensen's inequality,*

$$
\phi(\mathbb{E}X) \leqslant \mathbb{E}(\phi(X))
$$

where ϕ is an arbitrary convex function, to Cor 17, we can get the proof of this Cor, Here we choose $\phi(x) = -\ln x$ as the convex function.

$$
\langle S\rangle \geqslant -\ln\langle e^{-S}\rangle = 0 \tag{20}
$$

3.4 Nonequilibrium Transient State (NETS)

We consider a system whose initial state is equilibrium and is transiently brought to a nonequilibrium state. To simplify, we just consider carnonical ensemble.

Theorem 2 (Crook's Fluctuation Theorem) *If the difference of free energy is ΔF and the work of a trajectory is W, the formula*

$$
\frac{P_F(W)}{P_R(-W)} = \exp(\frac{W-\Delta F}{T}) \tag{21}
$$

holds.

Proof 3.5 *In carnonical ensemble,* $P_\lambda^{eq}(C) = \exp(\frac{\Delta F - E_\lambda(C)}{T})$. *Therefore,*

$$
\begin{aligned}
S(\Gamma) &= \sum_{i=0}^{N-1} \frac{E_{\lambda_i}(C_i) - E_{\lambda_i}(C_i+1)}{T} + \frac{E_{\lambda_N}(C_N) - E_{\lambda_0}(C_0) - \Delta F}{T} \\
\Delta E &= E_{\lambda_N}(C_N) - E_{\lambda_0}(C_0) = TS(\Gamma) + \Delta F - TS_p(\Gamma)
\end{aligned}
\tag{22}
$$

Comparing with first law of thermodynamics, we can obtain

$$
\begin{aligned}
\Delta E &= W(\Gamma) - Q(\Gamma) \\
W(\Gamma) &= TS(\Gamma) + \Delta F = \sum_{i=0}^{N-1} E_{\lambda_{i+1}}(C_{i+1}) - E_{\lambda_{i+1}}(C_{i+1}) \\
Q(\Gamma) &= TS_p(\Gamma) = \sum_{i=0}^{N-1} E_{\lambda_i}(C_i) - E_{\lambda_i}(C_{i+1})
\end{aligned}
\tag{23}
$$

Work is the difference of energy to keep the configuration when the external force changes. Heat of the object, $-Q(\Gamma)$*, is caused by changing configuration with relatively constant external force.*

Therefore, the total entropy represents the difference between the mechanical work and reversible work,

$$S(\Gamma) = \frac{W - \Delta F}{T}$$

Using theorem 15, we convert the r.v. from S *to* W*,*

$$\frac{P_F(\frac{W-\Delta F}{T})}{P_R(-\frac{W-\Delta F}{T})} = \frac{P_F(W)}{P_R(-W)} = \exp(\frac{W-\Delta F}{T})$$

Theorem 3 (Jarzynski equality)

$$\langle \exp(-\frac{W}{T}) \rangle = \exp(-\frac{\Delta F}{T}) \tag{24}$$

Proof 3.6 *Using equation 11, JE can be proved.*

4 Applications

4.1 A Bead in an Optical Trap

In NETS situation, the position of laser trap is $x^*(t)$ with force field $f_{x^*}(x) = -\partial_x U(x - x^*)$. A bead is traped by laser in viscous fluid, driven by overdamped Langevin equation.

$$\gamma \dot{x} = f_{x^*}(x) + \xi(t) \tag{25}$$

where $\langle \xi(t)\xi(s) \rangle = 2\gamma k T \delta(t-s)$.

We choose trajectory $\Gamma = \{x(t) : 0 \leqslant t \leqslant s\}$, controling parameter $\Lambda = \{x^*(t) : 0 \leqslant t \leqslant s\}$.

4.1.1 P.D.F.

Firstly, we find the expression of probability. According to master eqaution, we apply the stationnary condition to it and obtain the detailed balanced condition. By discreting Langevin equation, we get

$$x' = x + \frac{f(x - x^*)}{\gamma}\Delta t + \sqrt{\frac{2kT\Delta t}{\gamma}}r + O(\Delta t) \tag{26}$$

where r is standard gaussian ranndom number.

For given x, the distribution of x' only relates to that of r, i.e. gaussian distribution with

$$\begin{aligned}\langle x' \rangle &= x + \frac{f(x - x^*)}{\gamma}\Delta t + O(\Delta t)\\ \langle (\delta x')^2 \rangle &= \frac{2kT\Delta t}{\gamma} + O((\Delta t)^2)\end{aligned} \tag{27}$$

Therefore, the transient probability

$$\mathcal{W}_{x^*}(x \to x') = P_{x^*}(x'|x) = (2\pi\langle(\delta x')^2\rangle)^{-\frac{1}{2}} \exp(-\frac{x' - x - \frac{f(x-x^*)}{\gamma}\Delta t}{2\langle(\delta x')^2\rangle}) \tag{28}$$

Using Taylor expansion, we can get

$$\begin{aligned}U(x' - x^*) = U(x - x^*) + f(x - x^*)(x' - x) + O((x' - x)^2)\\ U(x - x^*) = U(x' - x^*) + f(x' - x^*)(x - x') + O((x' - x)^2)\end{aligned} \tag{29}$$

Therefore, we get

$$\begin{aligned}(x' - x)(f(x - x^*) + f(x' - x^*)) &= 2(U(x' - x^*) - U(x - x^*))\\ \frac{\mathcal{W}_{x^*}(x \to x')}{\mathcal{W}_{x^*}(x' \to x)} &= \exp(-\frac{(x' - x)(f(x - x^*) + f(x' + x^*))}{2T})\\ &= \exp(-\frac{U(x' - x^*) - U(x - x^*)}{T})\\ &= \frac{P_{x^*}(x')}{P_{x^*}(x)}\end{aligned} \tag{30}$$

Therefore, the distribution is canonical, i.e. $P_{x^*}(x) = \exp(\frac{F - U(x - x^*)}{T})$.

4.1.2 Entropy

1. Trajectory Entropy Production:

$$
\begin{aligned}
S_p(\Gamma) &= \sum_t (\ln P^{eq}_{x^*}(x(t+\Delta t)) - \ln P^{eq}_{x^*}(x(t))) \\
&= \sum_t \frac{\ln P^{eq}_{x^*}(x(t+\Delta t)) - \ln P^{eq}_{x^*}(x(t))}{\Delta x} \frac{\Delta x}{\Delta t} \Delta t \\
&\to \int_0^t ds \dot{x}(s) \partial_x \ln P_{x^*(s)}(x(s)) \\
&= \frac{1}{T} \int_0^t ds \dot{x}(s) f(x(s) - x^*(s)) \\
let\ x(t) = y(t) + x^*(t) \ &= \frac{1}{T} \int_0^t ds (\dot{y} + \dot{x}^*) f(y) \\
&= \frac{1}{T} (\int_{y(0)}^{y(t)} dy f(y) + \int_0^t dx^*(s) f(y(s))) \\
\int dy(-\partial_y U(y)) = -\Delta U \ &= \frac{-\Delta U + W(\Gamma)}{T} \\
1st\ law \ &= \frac{Q(\Gamma)}{T}
\end{aligned}
\tag{31}
$$

2. Boundary Entropy:

$$
B(\Gamma) = \ln P^{eq}_0(x_0) - \ln P^{eq}_t(x_t) = \frac{U_t - U_0}{T} = \frac{\Delta U}{T} \tag{32}
$$

3. Total Entropy:

$$
S(\Gamma) = S_p(\Gamma) + B(\Gamma) = \frac{W(\Gamma)}{T} \tag{33}
$$

4.2 Active Brownian Particle

4.2.1 Langevin equation

In this situation, we add the self-propelled force $F(v)$ on the active particles and denote the external force field as $f(t)$.

$$
\begin{aligned}
&\dot{x} = v \\
&m\dot{v} = -\gamma v + F(v) - \partial_x U(x) + \xi + f(t) \\
&\langle \xi(t) \rangle = 0 \quad \langle \xi(t)\xi(s) \rangle = 2kT\gamma\delta(t-s)
\end{aligned}
\tag{34}
$$

4.2.2 1st Law

$$
\begin{aligned}
E &= \frac{1}{2}mv^2 + U(x) \\
\Delta E &= \Delta W + \Delta q \\
\Delta W &= \int ds f(t) = \int_t dt v f(t) \\
\Delta q &= \Delta Q + \Delta Q_m
\end{aligned} \tag{35}
$$

The heat flux to thermal bath is $\Delta Q = \int_t dt v(-\gamma v + \xi(t))$ and the heat flux of self-propulsion is $\Delta Q_m = \int_t dt v F(v)$.

4.2.3 2nd Law

We know the P.D.F. of noise, i.e.

$$
P(\xi) \propto \exp(-\frac{\int_0^t ds \xi^2(s)}{4kT\gamma})
$$

We use the vector $X = \{x(t), v(t), f(t)\}$ to represent the trajectory. With the conditions of Langevin equation, we can convert the P.D.F. of noise to a given trajectory through Jacobi transform

$$
\begin{aligned}
\mathcal{P}_F(X) &= \hat{J}P(\xi) \\
&\propto \delta(\dot{x} - v)\exp(-\frac{1}{4kT\gamma}\int_0^t ds(m\dot{v} + \gamma v - F(v) + \partial_x U(x) - f(t))^2) \\
&\exp(-\frac{1}{2}\int_0^t ds \partial_v(-\gamma v + F(v)))
\end{aligned}
$$

Assuming $F(v)$ is odd, by inversional transform, we can also get the reverse P.D.F.

$$
\begin{aligned}
\mathcal{P}_R(X) &\propto \delta(\dot{x} - v)\exp(-\frac{1}{4kT\gamma}\int_0^t ds(m\dot{v} - \gamma v + F(v) + \partial_x U(x) - f(t))^2) \\
&\exp(-\frac{1}{2}\int_0^t ds \partial_v(-\gamma v + F(v)))
\end{aligned}
$$

According to the definition of entropy, the entropy production is

$$
\begin{aligned}
S_p(\Gamma) &= k \ln \frac{\mathcal{P}_F}{\mathcal{P}_R} \\
&= -\frac{1}{T\gamma}\int_0^t ds(m\dot{v} + \partial_x U(x) - f(t)(-\gamma v + F(v))) \\
&= -\beta(\Delta q + \Delta Q_{em} + \frac{1}{\gamma}\Delta\Phi)
\end{aligned} \tag{36}
$$

where $\Delta Q_{em} = \frac{1}{\gamma}\int_0^t dsF(v)(f(s) - \partial_x U)$ represents the couple of mechanical force and self-propulsion and $\Phi = -\int_v dvF(v)$ is the efficient potential of self-propulsion.

We treat the boundary term as the entropy flux. Therefore, the entropy of the system is

$$\Delta S_{sys} = k \ln \frac{P_0(C_0)}{P_t(C_t)}$$

The total entropy is

$$S(\Gamma) = k \ln \frac{P_F(\Gamma)}{P_R(\Gamma)} = \Delta S_{sys} - \frac{1}{T}(\Delta q + \Delta Q_{em} + \frac{1}{\gamma}\Delta\Phi) \tag{37}$$

4.2.4 Fluctuation Theorem and Jarzynski Equality

The fluctuation theorem is

$$\langle \exp(-\Delta S/k) \rangle = 1 \tag{38}$$

The Jarzynski equality is

$$\langle \exp(-\beta \Delta W) \rangle = \exp(-\beta \Delta F) \langle \exp(-\beta(\Delta Q_{em} + \frac{1}{\gamma}\Delta\Phi)) \rangle \tag{39}$$

4.2.5 Approximate Solution of F-P Equation

If the potential is relatively smaller than the kinetic energy, the F-P equation can be approximately solved.

Firstly, we rewrite the Langevin equation

$$\begin{aligned} &mvdv = -\gamma v^2 dt + vF(v)dt - \partial_x U(x)dx + \xi dt \\ &d(\frac{1}{2}mv^2 + U(x)) = (-\gamma v + F(v) + \xi)vdt \\ &\partial_t H = g(H) + \sqrt{\frac{2H}{m}}\xi \end{aligned} \tag{40}$$

The cooresponding F-P equation is

$$\partial_t P(H,t) = -\partial_H(g(H)P(H,t)) + \frac{2kT\gamma}{m}\partial_H(H\partial_H P(H,t)) \tag{41}$$