The Formulation Of Thermodynamical Path Integral

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Abstract

In a non-equilibrium thermodynamical physics, there has been almost no universal theory for representing the far from equilibrium systems. In this work, I formulated the thermodynamical path integral from macroscopic view, using the analogy of optimal transport and large deviations to calculate the non-equilibrium indicators quantitatively. As a result, I derived Jarzynski equality, fluctuation theorem, and second law of thermodynamics as its corollaries of this formula. In addition, the latter result implies the connection between non-equilibrium thermodynamics and Riemannian geometry via entropic flow.

1 Continuous time thermodynamical path integral

1.1 Optimal transport

First, we consider transport of a distribution. This concept has been already discussed for a long time [Vil09], and bears many fruits in probability theory, mathematical statistics, and machine learning. To begin with, the minimum distance which includes the concept of "cost" between start and goal distributions is defined by Wasserstein distance.

Definition 1.1 (Wasserstein distance)**.** *Let* $\mathcal{P}_2(\mathbb{R}^d) := \{\rho \in \mathcal{P}(\mathbb{R}^d) : \int |x|^2 \rho(dx) < \infty\}$ *be the associated Wasserstein space of order 2, so* L^2-*Wasserstein distance between* $\rho_0, \rho_1 \in \mathcal{P}_2(\mathbb{R}^d)$ *is defined by*

$$W_2^2(\rho_0, \rho_1) = \inf_{\pi \in \Pi(\rho_0,\rho_1)} \{ \int_{\mathbb{R}^d \times \mathbb{R}^d} d^2(x,y) d\pi(x,y) \}, \tag{1}$$

where $d(\cdot,\cdot)$ *is the cost function and* $\pi \in \mathcal{P}(\mathbb{R}^d \times \mathbb{R}^d)$ *is coupling which satisfies* $\pi(\cdot \times \mathbb{R}^d) = \rho_0(\cdot),\ \pi(\mathbb{R}^d \times \cdot) = \rho_1(\cdot)$*.*

Intuitively, when the particle which mass is $d\pi(x,y)$ transferred, the corresponding cost $d^2(x,y)$ is required to be paid. The infimum is taken all over the $\pi(x, y)$ to minimize the cost, then we have the optimal transport plan $\Pi(\rho_0, \rho_1)$. Equivalently, this metric will be translated into dynamical characterized one with the language of gradient flow.

Formula 1.2 (The Benamou-Brenier formula [BB00]). *Wasserstein distance is also defined as follows;*

$$W_2^2(\rho_0, \rho_1) = \inf_{(\rho_t)_t \in \mathrm{AC}^2(\rho_0, \rho_1)} \{ \int_0^1 \| \partial_t \rho_t \|_{\rho_t}^2 dt \}, \tag{2}$$

where the norm $\|\partial_t \rho_t\|_{\rho_t}$ about the infinitesimal variation $\partial_t \rho_t$ of the measure ρ_t is defined by

$$\|\partial_t \rho_t\|_{\rho_t} := \inf_{v \in L^2(\rho_t; \mathbb{R}^d)} \{ \int_{\mathbb{R}^d} |v(x)|^2 d\rho(x); \qquad \partial_t \rho_t + \nabla \cdot (\rho_t v) = 0 \}, \tag{3}$$

and $\mathrm{AC}^2(\rho_0, \rho_1)$ denotes the set of 2-absolutely continuous curve $(\rho_t)_{t \in [0,1]}$ in $(\mathcal{P}_2(\mathbb{R}^d), W_2)$.

1.2 Thermodynamical path integral

Next, the analogy of Feynman path integral formula [Kac49] is applied to thermodynamical statistics. At first, we define the Wasserstein distance as follows:

$$W_2^2(\rho_0, \rho_1) = \inf \int_{\gamma_0}^{\gamma_1} d\gamma \int_0^1 \mathcal{L}(\gamma_t, \dot{\gamma}_t, t) dt. \tag{4}$$

Here a cost function is

$$c(x, y) = \{ \int_0^1 \mathcal{L}(\gamma_t, \dot{\gamma}_t, t) dt; \ \gamma_0 = x, \gamma_1 = y; \ \gamma \in \mathcal{C} \}, \tag{5}$$

where $\mathcal{C}$ is a certain class of continuous curves and we can regard this cost function as an action. Taking the infimum of the cost function means a least action in the classical physics sense. Then, the cost function is applied to the path integral formula, deriving

$$\rho_1 \propto \int_{\gamma_0}^{\gamma_1} \rho_0 \exp[- \int_0^1 \mathcal{L}(\gamma_t, \dot{\gamma}_t, t) dt] d\gamma. \tag{6}$$

This expression makes the connection between optimal transport and thermodynamics through Lagrangian. In the thermodynamical sense, the normalization factor is associated with the difference of the free-energy, and the entropy constraint term requires to be added. Then we define the thermodynamical cost function as follows.

Definition 1.3 (Thermodynamical Lagrangian). *Let $w(\gamma_t, \dot{\gamma}_t, t)$ be continuous non-equilibrium external work time density, and $S(\cdot)$ entropy function that is only defined in the equilibrium states ($t = 0, 1$). Besides Lagrangian $L(\gamma) = \int \mathcal{L}(\gamma_t, \dot{\gamma}_t, t)dt$ is the sum of work and constraints force, thus we define Lagrangian time density to satisfy them;*

$$\mathcal{L}(\gamma_t, \dot{\gamma}_t, t) = w(\gamma_t, \dot{\gamma}_t, t) + \sigma(\rho_t), \tag{7}$$

where $\sigma(\rho_t)$ denotes the entropy generation rate.

From path integral analogy, the propagator is written by

$$\exp[-\int_0^1 \mathcal{L}(\gamma_t, \dot{\gamma}_t, t)dt] = \exp[-W(\gamma) - \{S(\rho_1) - S(\rho_0)\}]. \tag{8}$$

Then, we get next formula.

Formula 1.4 (Thermodynamical path integral). *Let $(\rho_t)_{t\in[0,t]} \in (\mathcal{P}_2(\mathbb{R}^d), W_2)$ denote the Boltzmann distributions, and quasi-static isothermal process is conducted. Then we can write an arbitrary equilibrium states ρ_t as*

$$\rho_t = \frac{1}{Z_{0\to t}} \int_{\gamma_0}^{\gamma_t} \rho_0 \exp[-\inf_{(\rho_t)_t} \int_0^t \mathcal{L}(\gamma_t, \dot{\gamma}_t, t)dt]d\gamma, \tag{9}$$

where the relative partition function satisfies $Z_{0\to t} = Z_t/Z_0$.

In this manner, we will proof the famous theorem as a corollary.

Corollary 1.5 (Jarzynski equality [Jar97]). *Under the assumptions that (i) the work is isothermal process and (ii) the system follows Liouville's theorem, the conducted non-equilibrium work and the difference of free-energy have the relation that,*

$$\overline{\exp[-W(\gamma)]} = \exp[-\Delta F]. \tag{10}$$

where an overline means path ensemble average.

Proof. According to the TOT,

$$\begin{aligned}\rho_1 &= \frac{1}{Z_{0\to 1}} \int \rho_0 \exp[-\int_0^1 \mathcal{L}(\gamma_t, \dot{\gamma}_t, t)dt]d\gamma \\ &= \frac{\rho_0 \exp[-\Delta S]}{Z_{0\to 1}} \int \exp[-W(\gamma)]d\gamma,\end{aligned}$$

because the difference of entropy ΔS and initial state ρ_0 does not depend on the path γ. Then, the averaged work is

$$\begin{aligned}\therefore \overline{\exp[-W(\gamma)]} &= \frac{\rho_1}{\rho_0} Z_{0\to 1} \exp[\Delta S] \\ &= \exp[-\Delta F],\end{aligned}$$

which completes the proof. □

However, this equality is trivial because the assumption (ii) is too strong. If there are no quantity that change dynamically in the non-equilibrium situations, the result of non-equilibrium work would be the same as the equilibrium. As a matter of fact, the cause that makes the system complex is none other than the dynamical entropy flow which is derived from Boltzmann equation. Thus, considering Liouville's theorem is equivalent to require a system being under an adiabatic process without entropic flow. Therefore this assumption collapses, but the result is invariant due to the heat bath and the relaxation. These details are discussed in my parallel work. On the other hand, the proposed method is able to explain this dynamical factor explicitly.

Next, a situation of an infinitesimal time variation is considered.

Corollary 1.6 (Fluctuation inequality). *About the forward and backward time evolution, the following relation consists.*

$$\frac{\rho(t=-\epsilon)}{\rho(t=+\epsilon)} \leq \exp[2\epsilon\Delta\sigma], \tag{11}$$

where this equality holds for a minimum time step size $|t| = 1$ $(\epsilon \geq 1)$*, and* Δf, $\Delta\sigma$ *are unit generation rates of free-energy and entropy.*

Proof. Using TOT and the approximation $\int_{-\epsilon}^{\epsilon} \mathcal{L}(\gamma_t, \dot{\gamma}_t, t)dt \simeq 2\epsilon\mathcal{L}(\gamma)$, we have,

$$\begin{aligned}
\frac{\rho(t=\epsilon)}{\rho(t=-\epsilon)} &= \frac{1}{Z_{-\epsilon\to\epsilon}} \int \exp[-\int_{-\epsilon}^{\epsilon} \mathcal{L}(\gamma_t, \dot{\gamma}_t, t)dt]d\gamma \\
&= \exp[2\epsilon\Delta f]\exp[-2\epsilon\Delta\sigma] \int \exp[-w(\gamma)]^{2\epsilon} d\gamma \\
&\geq \exp[2\epsilon\Delta f]\exp[-2\epsilon\Delta\sigma]\overline{\exp[-w(\gamma)]}^{2\epsilon} \\
&= \exp[-2\epsilon\Delta\sigma].
\end{aligned}$$

The inequality of third line is due to Hölder's inequality. □

This result denotes the realization probability of time reversal events. The same as the last corollary, this inequality can be explained by the dynamical entropy flux and distortion effects. However, enough small ϵ will not cause them explicitly.

2 Discrete time thermodynamical path integral

2.1 Large-deviation principles

To consider discretization of thermodynamic processes and deviation from quasi-static processes, we introduce the large deviations rate functional.

This functional does not only represent the realization probabilities of rare events, but also calculates the deviance between the optimal path and the actually operated path.

Definition 2.1 (Large deviations rate)**.** *Let $\rho_0 \in \mathcal{P}_2(\mathbb{R}^d)$ fixed, the functional $I_\tau(\cdot|\rho_0) : \mathcal{P}_2(\mathbb{R}^d) \to [0, +\infty]$ is defined by*

$$I_\tau(\bar{\rho}|\rho_0) := \inf_{(\rho_t)_t \in \mathrm{AC}^2(\rho_0, \bar{\rho})} \frac{1}{4\tau} \int_0^{\bar{t}} \|\partial_t \rho_t - \tau \Delta \rho_t\|_{\rho_t}^2 dt, \tag{12}$$

where $\mathrm{AC}^2(\rho_0, \bar{\rho})$ denotes the set of 2-absolutely continuous curve $(\rho_t)_{t \in [0, \bar{t}]}$ in $(\mathcal{P}_2(\mathbb{R}^d), W_2)$, and $\tau \in (0, 1]$ is the time constant of the heat equation.

$$\partial_t \rho_t = \tau \Delta \rho_t \tag{13}$$

In this theory, the quasi-static process is comparable to $\tau = 0$ (because of keeping equilibrium, $\partial_t \rho_t = 0$), and requires infinity number of iteration from ρ_0 to ρ_1. On the other hand, the case of $\tau = 1$ requires only one step to attain the target state. Then, the general non quasi-static case $\tau \in (0, 1]$ is considered.

From this definition, we will find the next representation

$$\begin{aligned} 2I_\tau(\bar{\rho}|\rho_0) &= \frac{1}{2\tau} \int dt \|\partial_t \rho_t\|_{\rho_t}^2 - \int dt \langle \partial_t \rho_t, \Delta \rho_t \rangle + \frac{\tau}{2} \int dt \|\Delta \rho_t\|_{\rho_t}^2 \\ &= \frac{1}{2\tau} W_2^2(\rho_0, \rho_1) + \{S(\rho_1) - S(\rho_0)\} + \frac{\tau}{2} \int dt \mathcal{G}(\rho_t), \end{aligned} \tag{14}$$

where the first term is derived from Benamou-Brenier formula, and the second term is given by [DLR13],

$$\frac{d}{dt} S(\rho_t) = \sigma(\rho_t) = -\langle \partial_t \rho_t, \Delta \rho_t \rangle_{\rho_t}. \tag{15}$$

Specifically, if ρ_t satisfies the heat equation, we have

$$-\frac{d}{dt} H(\rho_t) = \|\Delta \rho_t\|_{\rho_t}^2 = \mathcal{G}(\rho_t), \tag{16}$$

where $H(\rho_t) = \int \rho_t \ln \rho_t$ is Boltzmann's H-functional and $\mathcal{G}(\rho_t)$ is Fisher information metric.

Next, the convergence theorem of I_τ is given.

Theorem 2.2 ([EMR15])**.** *For every $\rho_0 \in \mathcal{P}_2(\mathbb{R}^d)$ such that $0 \le \mathcal{G}(\rho_0) < \infty$, we have*

$$I_\tau(\cdot|\rho_0) - \frac{1}{4\tau} W_2^2(\rho_0, \cdot) \xrightarrow[\tau \to 0]{\Gamma} \frac{1}{2}\{S(\cdot) - S(\rho_0)\}. \tag{17}$$

in the sense of $\Gamma-$convergence.

Unrigorously speaking, this theorem implies

$$2I_\tau \simeq \frac{1}{2\tau} W_2^2(\rho_0, \rho_1) + \{S(\rho_1) - S(\rho_0)\} \ as \ \tau \to 0, \tag{18}$$

for the fixed (ρ_0, ρ_1).

2.2 Deviation from a quasi-static process

In order to calculate the discrete path integral, we introduce the large deviations density functional sequence $(\mathcal{I}_i^\tau)_{i\in[0,\frac{1}{\tau}-1]}$ which is equivalent to $\int_0^1 \mathcal{L}(\gamma_t, \dot{\gamma}_t, t)dt$ in the continuous time limit, where we cut the path with length τ and the index of vertices i to fulfill $\rho_{1/\tau} = \rho_1$. Moreover, we require the system to relax to equilibrium state at each vertex because of the definition of entropy. Then we have the large deviations rate density at each step as follows:

$$2\mathcal{I}_i^\tau = \frac{1}{2\tau}W_2^2(\rho_i^\tau, \rho_{i+1}^\tau) + \{S(\rho_{i+1}^\tau) - S(\rho_i^\tau)\} + \frac{\tau^2}{2}\mathcal{G}(\rho_i^\tau) \tag{19}$$

$$= W_i^\tau + \{S(\rho_{i+1}^\tau) - S(\rho_i^\tau)\} + \frac{\tau^2}{2}\mathcal{G}(\rho_i^\tau), \tag{20}$$

where we defined a non-equilibrium work $W_i^\tau := \frac{1}{2\tau}W_2^2(\rho_i^\tau, \rho_{i+1}^\tau)$. Then, we apply this as a cost function to the thermodynamical path integral formula,

$$\rho_1 = \frac{1}{Z_{0\to1}}\prod_i \rho_0 \exp[-2\mathcal{I}_i^\tau]\delta x(\rho_i^\tau, \rho_{i+1}^\tau) \tag{21}$$

$$= \frac{\rho_0}{Z_{0\to1}}\prod_i \exp[-W_i^\tau - \{S(\rho_{i+1}^\tau) - S(\rho_i^\tau)\} - \frac{\tau^2}{2}\mathcal{G}(\rho_i^\tau)]\delta x(\rho_i^\tau, \rho_{i+1}^\tau) \tag{22}$$

$$= \frac{\rho_0 \exp[-\Delta S]}{Z_{0\to1}}\prod_i \exp[-W_i^\tau]\exp[-\frac{\tau^2}{2}\mathcal{G}(\rho_i^\tau)]\delta x(\rho_i^\tau, \rho_{i+1}^\tau). \tag{23}$$

Here, $\exp[-\frac{\tau^2}{2}\mathcal{G}(\rho_i^\tau)]$ is the exponential map in Riemannian geometry, and $\tau^2\mathcal{G}(\rho_i^\tau)$ denotes the squared discrete distance along $\delta x(\rho_i^\tau, \rho_{i+1}^\tau)$ in the tangent space on the information geometric manifold [Ama16]. So, this map $\exp[\tau^2\mathcal{G}(\rho_i^\tau)]$ denotes the squared distance $\delta\gamma^2(\rho_i^\tau, \rho_{i+1}^\tau)$ between ρ_i and ρ_{i+1} on the Riemannian manifold. Therefore, we assume the conservation law of work in the each space, such that $\exp[-W_i^\tau]\delta x(\rho_i^\tau, \rho_{i+1}^\tau) = \exp[-\mathcal{W}_i^\tau]\delta\gamma(\rho_i^\tau, \rho_{i+1}^\tau)$. Thus, the total work including the dynamical factor is derived in the next form:

$$\prod_i \exp[-W_i^\tau]\frac{\delta x(\rho_i^\tau, \rho_{i+1}^\tau)}{\delta\gamma(\rho_i^\tau, \rho_{i+1}^\tau)} = \prod_i \exp[-\mathcal{W}_i^\tau] \tag{24}$$

$$= \exp[-\mathcal{W}_{tot}^\tau]. \tag{25}$$

Therefore, the non-equilibrium work is conducted on the curved manifold without the concept of dissipation in this manner. According to the condition of $\tau \in (0, 1]$ or the relation of Boltzmann H-functional and Fisher metric such that $-\mathcal{G}(\rho_t) = \frac{dH(\rho_t)}{dt} \leq 0$, we have

$$\prod_i \exp[-W_i^\tau]\frac{\delta x(\rho_i^\tau, \rho_{i+1}^\tau)}{\delta\gamma(\rho_i^\tau, \rho_{i+1}^\tau)} \leq \int \exp[-W(\gamma)]d\gamma, \tag{26}$$

this equality is true in the case of $\tau = 0$ or under the assumption of the system following Liouville's equation with no entropic flow. Finally due to Jarzynski equality, we find

$$\exp[-\mathcal{W}_{tot}^{\tau}] \leq \overline{\exp[-W(\gamma)]} = \exp[-\Delta F] \tag{27}$$

Then, the next famous law is proved from this geometrical viewpoint.

Theorem 2.3 (The extension second law of thermodynamics)**.** *Let $\mathcal{W}^{\tau}$ external work on a Riemannian manifold, and ΔF difference of Helmholtz free energy, we have*

$$\mathcal{W}^{\tau} \geq \Delta F, \tag{28}$$

where this equality holds for $\tau = 0$ or under an adiabatic process.

The relation of the thermodynamic process and the entropy flow is discussed in my another work.

3 Discussion

The explanation of non-equilibrium work succeeds by introducing a curved path, and intrinsically non-equilibrium phenomenas happen on Riemannian manifolds. There is one possible story that high energy scale phenomenas would distort our real space through entropy flow, and the identity of the Arrow of Time be the curvature of the universe. When the curvature gets flat with Ricci flow or something, the universe will be in the state of Helmholtz's heat death. Finally, I am seeking a mentor and a Ph.D. via this theme.

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