Nonequilibrium work relation in a macroscopic system

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Abstract. We reconsider a well-known relationship between the fluctuation theorem and the second law of thermodynamics by evaluating stochastic evolution of the density field (probability measure valued process). In order to establish a bridge between microscopic and macroscopic behaviors, we must take the thermodynamic limit of a stochastic dynamical system following the standard procedure in statistical mechanics. The thermodynamic path characterizing a dynamical behavior in the macroscopic scale can be formulated as an infimum of the action functional for the stochastic evolution of the density field. In our formulation, the second law of thermodynamics can be derived only by symmetry of the action functional without recourse to the Jarzynski equality. Our formulation leads to a nontrivial nonequilibrium work relation for metastable (quasi-stationary) states, which are peculiar in the macroscopic system. We propose a prescription for computing the free energy for metastable states based on the resultant work relation.

Keywords: driven diffusive systems (theory), stochastic particle dynamics (theory), metastable states, large deviations in non-equilibrium systems
1. Introduction

The Jarzynski equality [1] \( \langle e^{-\beta W} \rangle_{\text{eq}} = e^{-\beta \Delta \Phi_{\text{eq}}} \), where \( \Delta \Phi_{\text{eq}} \) and \( W \) are a free-energy difference and a performed work respectively, plays the role of a bridge between the symmetry of microscopic dynamics as given by the fluctuation theorem [2]–[8] and the fundamental limitation on time evolution of macroscopic quantities, which is described as the second law of thermodynamics. The brackets \( \langle \cdots \rangle_{\text{eq}} \) denote the average over all the realizations during the dynamics starting from the initial equilibrium state. The fluctuation theorem implies that the microscopic stochastic dynamics satisfies the following symmetry,

\[
P[\lambda, \Gamma|x_0] e^{\beta Q[\lambda, \Gamma]} = P[\hat{\lambda}, \hat{\Gamma}|x_T],
\]

where \( \lambda, \Gamma, \) and \( Q \) denote an external protocol, a microscopic time evolution of the system with the initial condition \( x_0 \), and a heat flow from the surrounding heat bath to the system, respectively. In addition, \( \hat{\cdot} \) stands for the time-reversal operation. We usually term the Jarzynski equality as a generalization of the second law of thermodynamics since the Jarzynski equality yields \( \langle W \rangle_{\text{eq}} \geq \Delta \Phi_{\text{eq}} \) by use of Jensen’s inequality. Although the present study does not aim at giving any objection against the validity of the Jarzynski equality, we would like to ask the following fundamental question on the above ordinary understanding of the relationship between the Jarzynski equality and the second law of thermodynamics. Does \( \langle W \rangle_{\text{eq}} \) express the performed work in thermodynamics?

The reasons for asking this question are as follows. Let us go back to a starting point of statistical mechanics and its connection with thermodynamics. To elucidate macroscopic properties from a microscopic description of the system, we consider an infinite-number limit of the sample mean, which is a coarse-grained picture of the system.

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On the other hand, the performed work given in the Jarzynski equality $\langle W \rangle_{\text{eq}}$ has not been confirmed yet through this ordinary procedure. Within a framework of the large deviation theory [9, 10], which underlies statistical mechanics, the observed physical quantity in the thermodynamics is characterized by a global minimum of the rate function. The performed work used in the Jarzynski equality is not yet confirmed as being expressed by the global minimum of the rate function. In addition, the rate function can possess not only the global minimum but also several local minima, which represent the existence of so-called metastable (quasi-stationary) states. The system with metastable states does not always relax towards the equilibrium state within a moderate time scale in a practical experiment. From the above considerations, we cannot readily regard the performed work $\langle W \rangle_{\text{eq}}$ in methods with the Jarzynski equality as that in thermodynamics. This problem motivates us to compute the performed work in thermodynamics by directly evaluating the dynamics for the coarse-grained quantity, which can be described by stochastic evolution of the density field (probability measure valued process [11, 12]).

We analyze the stochastic evolution of the density field by employing the following strategy. First, we evaluate the entropy production of the system from the action functional [10, 12, 13], which is the rate function for the stochastic evolution of the density field and describes contributions around the most probable path of time evolution of the density fields. As one of our main results in the present study, the second law of thermodynamics can be rederived from the symmetry of this action functional, which is generated from the fluctuation theorem. This formalism is the confirmed route towards thermodynamics using the rate function, which is different from the ordinary way through the Jarzynski equality as in the literature [3], [5]–[8]. These analyses provide a deep understanding of the connection between the fluctuation theorem and the second law of thermodynamics and bring us another nontrivial result that is relevant for macroscopic behavior in a system with metastable states. The further analysis of the action functional leads to the form of the rate function for the metastable states, which enables us to establish a nontrivial nonequilibrium work relation for metastable states. This work relation can be expressed in the same form as the Jarzynski equality in the special condition related to relaxation processes towards the preselected metastable state denoted by an index $i$.

$$\langle e^{-N\beta w} \rangle_i = e^{-N/\beta \{\phi_{\text{eq}}(\beta, \lambda_T) - \phi_i(\beta, \lambda_0)\}},$$

where $N$ is the number of degrees of freedom in the system we deal with, $w$ is the performed work per degree of freedom through the external protocol characterized by $\lambda$. The quantity $\phi_{\text{eq}}$ is the free energy per degree of freedom for the last equilibrium state at $\lambda_T$, while $\phi_i$ is that for the initial metastable state identified by an index $i$ among several metastable states at $\lambda_0$. Using our nonequilibrium work relation (2), we can compute the free energy for the metastable state due to the same form as the Jarzynski equality. The existence of metastable states is considered to be related to peculiar relaxation dynamics, as in the glassy systems. Our result would provide a significant insight for the understanding of the special behavior observed in such complicated systems.

We organize the present paper as follows. Before going to the detailed analysis, in section 2, we explain our motivation for the present study in more detail by showing a gap in the understanding of the fluctuation theorem from the description of the thermodynamic system. In section 3, we demonstrate the detailed analysis on the action
functional, which characterizes the rate function for the stochastic evolution of the density field. The description of the second law of thermodynamics, by our presentation, is shown in section 4. In section 5, we assess the Jarzynski equality for the system with metastable states. In section 6, we conclude our study.

2. Large deviation property and its importance

In order to evaluate the most probable event in the stochastic system, we often evaluate the rate function. In our study, we focus on the performed work in the thermodynamic system. The Crooks fluctuation theorem [3, 4] shows the symmetry of the path probability for the forward process and backward process with the performed work. The Jarzynski equality can be obtained as a consequence of the Crooks fluctuation theorem. One might think that all we have to do is to consider the limit of large-number degrees of freedom as $N \to \infty$ (in [14], the Crooks fluctuation theorem in the context of the large deviation theory is presented). It is, however, not always true. The simple limitation is validated under a specific assumption that the large deviation property holds for the path probability associated with the performed work. In other words, we assume the existence of a rate function with a convex form for the performed work as

$$P(w) \sim \exp(-NI(w)), \quad (3)$$

where $P(w)$ is the probability for the performed work and $I(w)$ is its rate function. The assumption is quite natural, but often gives rise to a misunderstanding of the correct description of the macroscopic system. For instance, the phase transition in an equilibrium system can be explained in the context of the rate function as a breakdown of convexity. The form of the rate function should be discussed in detail to correctly understand thermodynamic behavior.

In the present study, we analyze the rate function without any assumption on its form for a mean-field model. In equilibrium statistical mechanics, the mean-field model, such as the Curie–Weiss model, plays a role in providing the essential understanding on the macroscopic behavior including the phase transition by describing various forms of the rate function of the order parameter. We show the detailed analysis of the rate function in section 3. After that, we point out the possibility that a different nonequilibrium equality holds for the peculiar dynamics in a system with metastable states.

3. Action functional for mean-field dynamics

Let us consider that the system consists of $N$ degrees of freedom $\{x_i\} (i = 1 \ldots N)$ and is attached to a heat bath with an inverse temperature $\beta$. Work is performed on the system through an external protocol $\lambda$. Let us make two additional assumptions for the system in our study. First, the dynamics is governed by the diffusion process [15]. Second, the Hamiltonian is written by two-body interactions with all the components (i.e. mean field). Under this assumption, the stochastic process satisfying the fluctuation theorem (1) is described as

$$\mathrm{d}x_i = \left[ -\frac{\partial}{\partial x_i} H_N (\{x_i\}, \lambda_t) \right] \mathrm{d}t + \sqrt{\frac{2}{\beta}} \mathrm{d}\xi, \quad (4)$$

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where $\xi_i$ denotes the Wiener process and $H_N(\{x_i\}, \lambda)$ is the Hamiltonian of the system. The Hamiltonian is written by

$$H_N(\{x_i\}, \lambda) = -\sum_i F(\lambda) - \frac{1}{2N} \sum_{ij} G(x_i, x_j),$$

(5)

where $F(\lambda)$ stands for the potential trap, $G$ is the two-body interaction term, which is symmetric such that $G(x, y) = G(y, x)$. In this dynamical system, we analyze stochastic evolution of the density field (empirical measure) $\mu(x, t) = (1/N)\sum_i \delta(x_i - x)$ [11, 12, 16, 17]. By employing equation (4) and the Ito formula, we evaluate the derivative of $\mu$ as

$$d\mu(x, t) = \sum_j \frac{\partial}{\partial x_j} \left\{ \frac{1}{N} \sum_i \delta(x_i - x) \right\} dx_j + \frac{1}{2} \sum_{k,l} \frac{\partial^2}{\partial x_k \partial x_l} \left\{ \frac{1}{N} \sum_i \delta(x_i - x) \right\} dx_k dx_l$$

$$= \frac{1}{N} \sum_i \frac{\partial \delta(x_i - x)}{\partial x_i} dx_i + \frac{1}{N\beta} \sum_i \frac{\partial^2 \delta(x_i - x)}{\partial x_i^2} dt$$

$$= \frac{1}{N} \sum_i \frac{\partial \delta(x_i - x)}{\partial x_i} \left\{ F(\lambda) + \frac{1}{N} \sum_j g(x_i, x_j) \right\} dt$$

$$+ \frac{1}{N\beta} \sum_i \frac{\partial^2 \delta(x_i - x)}{\partial x_i^2} dt + \frac{1}{N} \sqrt{\frac{2}{\beta}} \sum_i \frac{\partial \delta(x_i - x)}{\partial x_i} d\xi_i,$$

(6)

where we use abbreviations $f(\lambda) = \partial F(\lambda)/\partial x$, $g(x, y) = \partial G(x, y)/\partial x$ and the property of the Wiener process $d\xi_k d\xi_l = \delta_{k,l} dt$, where $\delta_{k,l}$ denotes Kronecker delta. We substitute properties of the density field,

$$\frac{\partial^2 \mu(x, t)}{\partial x^2} = \frac{1}{N} \sum_i \frac{\partial^2 \delta(x_i - x)}{\partial x_i^2},$$

(7)

$$\frac{\partial}{\partial x} \left\{ A(x) \mu(x, t) \right\} = -\frac{1}{N} \sum_i A(x_i) \frac{\partial \delta(x_i - x)}{\partial x_i},$$

(8)

$$\int A(x) \mu(x, t) dx = \frac{1}{N} \sum_i A(x_i),$$

(9)

where $A(x)$ is an arbitrary function, into equation (6). Then, we obtain the stochastic evolution of the density field as

$$d\mu(x, t) = D_{\mu, \lambda}(x) dt + \frac{1}{N} \sqrt{\frac{2}{\beta}} \sum_i \frac{\partial \delta(x_i - x)}{\partial x_i} d\xi_i,$$

(10)

where

$$D_{\mu, \lambda}(x) = -\frac{\partial}{\partial x} \left\{ f(\lambda) \mu(x, t) \right\} - \frac{\partial}{\partial x} \left\{ \mu(x, t) \int g(x, y) \mu(y, t) dy \right\} + \frac{1}{\beta} \frac{\partial^2 \mu(x, t)}{\partial x^2}.$$

(11)

By employing equation (10), we derive the functional Fokker–Planck equation, following doi:10.1088/1742-5468/2013/04/P04012
the ordinary procedure [15] (see also appendix A), as
\[
\frac{\partial}{\partial t} \text{Prob}_t[\mu] = \int dx \frac{\delta}{\delta \mu(x)} \{-D_{\mu,\lambda}(x)\text{Prob}_t[\mu] \}
\]
\[
+ \frac{1}{2N} \int dx \int dy \frac{\delta^2}{\delta \mu(x) \delta \mu(y)} \{R_{\mu}(x,y)\text{Prob}_t[\mu] \},
\]
(12)
where \( \text{Prob}_t[\mu] \) is the probability for the density field and \( R_{\mu}(x,y) \) denotes a diffusion matrix of the functional Fokker–Planck equation (12) as
\[
R_{\mu}(x,y) = \frac{2}{\beta} \int dz \frac{\partial \delta(x - z)}{\partial z} \frac{\partial \delta(y - z)}{\partial z} \mu(z).
\]
(13)

Let us consider the thermodynamic limit \((N \rightarrow \infty)\) on equation (10) to elucidate the macroscopic behavior of the system. We reach a nonlinear diffusion equation for the density field \( \mu(x,t) \), which represents thermodynamic time evolution of the system,
\[
\frac{\partial \mu(x,t)}{\partial t} = D_{\mu,\lambda}(x).
\]
(14)

Next let us consider deriving the second law of thermodynamics through the fluctuation theorem. In order to examine the fluctuation of the density field from the solution of the nonlinear diffusion equation (14) in a sufficient large \( N \), we analyze the conditional path probability for the stochastic dynamics governed by the functional Fokker–Planck equation (12). In the present case, we can express the conditional path probability during the time interval \([0,T]\) by the exponential form as \( \text{Prob}[\lambda,\mu|\mu_0] = e^{-NJ_{[0,T]}[\lambda,\mu]} \). In other words, we find the rate function without assumption on its form. Here, \( J_{[0,T]}[\lambda,\mu] \) is called the action functional, given as
\[
J_{[0,T]}[\lambda,\mu] = \int_0^T dt L_{\lambda_t}[\dot{\mu}_t,\mu_t],
\]
(15)
where \( L_{\lambda_t}[\dot{\mu}_t,\mu_t] \) is obtained by using equation (12) as [10, 13, 18]
\[
L_{\lambda_t}[\dot{\mu}_t,\mu_t] = \frac{1}{2} \int dx \int dy R_{\mu_t}^{-1}(x,y) \{ \dot{\mu}(x,t) - D_{\mu,\lambda_t}(x) \} \{ \dot{\mu}(y,t) - D_{\mu,\lambda_t}(y) \}.
\]
(16)

Here, \( R_{\mu_t}^{-1}(x,y) \) denotes the inverse of the diffusion matrix, which satisfies the identity
\[
\int d\alpha R_{\mu_t}(x,\alpha)R_{\mu_t}^{-1}(\alpha,y) = \delta(x - y).
\]
(17)

For subsequent calculations, we transform equation (17) to a useful form. By substituting equation (13) into equation (17), we obtain
\[
\delta(x - y) = \frac{2}{\beta} \int d\alpha \int dz \frac{\partial \delta(z - x)}{\partial z} \frac{\partial \delta(z - \alpha)}{\partial z} \mu(z,t)R_{\mu_t}^{-1}(\alpha,y)
\]
\[
= - \frac{2}{\beta} \int d\alpha \int dz \delta(z - \alpha)R_{\mu_t}^{-1}(\alpha,y) \frac{\partial}{\partial z} \left\{ \mu(z,t) \frac{\partial \delta(z - x)}{\partial z} \right\}
\]
\[
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\]
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Thus, we find that the inverse of the diffusion matrix $R_{\mu t}^{-1}$ satisfies the following equation,

$$\frac{\partial}{\partial x} \left\{ \mu(x, t) \frac{\partial R_{\mu t}^{-1}(x, y)}{\partial x} \right\} = -\frac{\beta}{2} \delta(x - y).$$

(19)

Owing to this property, we can reveal the symmetry of the action functional corresponding to the fluctuation theorem given by the ratio of the time-forward path probability written by $L_{\lambda t}[\mu_t, \mu_t]$ to the time-backward path probability by $L_{\hat{\lambda}_t}[\hat{\mu}_t, \hat{\mu}_t]$. Here, $\hat{\cdot}$ stands for the time-reversal operation: $\hat{\mu}_t = \mu_t, \hat{\lambda}_t = \lambda_t, \hat{t} = T - t$. In particular, the time derivation of $\hat{\mu}_t$ is $\hat{\mu}_t = -\mu_t$, where we use $\partial/\partial \hat{t} = -\partial/\partial t$. This ratio is indeed evaluated as

$$L_{\lambda_t}[\mu_t, \mu_t] = \frac{1}{2} \int \int dx \, dy R_{\mu t}^{-1}(x, y) \left\{ -\hat{\mu}(x, \hat{t}) - D_{\mu_t, \lambda_t}(x) \right\} \left\{ -\hat{\mu}(y, \hat{t}) - D_{\mu_t, \lambda_t}(y) \right\}$$

$$= \frac{1}{2} \int \int dx \, dy R_{\mu t}^{-1}(x, y) \left\{ \hat{\mu}(x, \hat{t}) - D_{\hat{\mu}_t, \hat{\lambda}_t}(x) \right\} \left\{ \hat{\mu}(y, \hat{t}) - D_{\hat{\mu}_t, \hat{\lambda}_t}(y) \right\}$$

$$- \int \int dx \, dy R_{\mu t}^{-1}(x, y) \hat{\mu}(x, \hat{t}) \left\{ \hat{\mu}(y, \hat{t}) - D_{\hat{\mu}_t, \hat{\lambda}_t}(y) \right\}$$

$$- \int \int dx \, dy R_{\mu t}^{-1}(x, y) \hat{\mu}(x, \hat{t}) \left\{ \hat{\mu}(y, \hat{t}) - D_{\hat{\mu}_t, \hat{\lambda}_t}(x) \right\} \hat{\mu}(y, \hat{t})$$

$$+ 2 \int \int dx \, dy R_{\mu t}^{-1}(x, y) \hat{\mu}(x, \hat{t}) \hat{\mu}(y, \hat{t})$$

$$= L_{\hat{\lambda}_t}[\hat{\mu}_t, \hat{\mu}_t] + 2 \int \int dx \, dy R_{\mu t}^{-1}(x, y) D_{\mu_t, \lambda_t}(x) \hat{\mu}(y, \hat{t}),$$

(20)

where we use the symmetric property $R_{\mu t}^{-1}(x, y) = R_{\mu t}^{-1}(y, x)$. Thus, we obtain

$$L_{\lambda_t}[\hat{\mu}_t, \mu_t] = L_{\hat{\lambda}_t}[\hat{\mu}_t, \hat{\mu}_t] - 2 \int \int dx \, dy R_{\mu t}^{-1}(x, y) D_{\mu_t, \lambda_t}(x) \hat{\mu}(y, \hat{t}).$$

(21)

The explicit form of $D_{\mu_t, \lambda_t}$ (see equation (11)) enables us to calculate the second term of the right hand side in equation (21) by use of integration by parts as

$$\int \int dx \, dy R_{\mu t}^{-1}(x, y) D_{\mu_t, \lambda_t}(x) \hat{\mu}(y, \hat{t}) = -\int \int dx \, dy \frac{\partial R_{\mu t}^{-1}(x, y)}{\partial x} \hat{\mu}(y, \hat{t})$$

$$\times \left\{ -f_{\lambda_t}(x) \mu(x, t) - \mu(x, t) \int g(x, z) \mu(z, t) \, dz + \frac{1}{\beta} \frac{\partial \mu(x, t)}{\partial x} \right\} \hat{\mu}(y, \hat{t})$$

$$= -\int \int dx \, dy \frac{\partial R_{\mu t}^{-1}(x, y)}{\partial x} \mu(x, t)$$

$$\times \left\{ -\frac{\partial F_{\lambda_t}(x)}{\partial x} - \frac{\partial}{\partial x} \int G(x, z) \mu(z, t) \, dz + \frac{1}{\beta} \frac{\partial \mu(x, t)}{\partial x} \right\} \hat{\mu}(y, \hat{t})$$

where $F_{\lambda_t}(x) = -\int_0^x \frac{1}{\beta} \frac{\partial \mu(z, t)}{\partial x} \, dz$ and $G(x, z) = \delta(x - z)$.
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\[
\begin{align*}
&= \int \int dx\, dy \frac{\partial}{\partial x} \left\{ \mu(x, t) \frac{\partial R_{\mu}^{-1}(x, y)}{\partial x} \right\} \\
&\times \left\{ -F_\lambda(x) - \int G(x, z) \mu(z, t) \, dz + \frac{1}{\beta} \log \mu(x, t) \right\} \frac{\partial}{\partial y} (y, t). \\
&= -\frac{1}{2} \int dx \left\{ -\beta F_\lambda(x) - \beta \int G(x, z) \mu(z, t) \, dz + \log \mu(x, t) \right\} \frac{\partial}{\partial y} (y, t). \\
\end{align*}
\]

In addition, by employing the property of the inverse diffusion matrix (19), we obtain

\[
\int \int dx\, dy R_{\mu}^{-1}(x, y) D_{\mu, \lambda}(x) \frac{\partial}{\partial y} (y, t) = -\frac{\beta}{2} \int \int dx\, dy \delta(x - y) \\
\times \left\{ -F_\lambda(x) - \int G(x, z) \mu(z, t) \, dz + \frac{1}{\beta} \log \mu(x, t) \right\} \frac{\partial}{\partial y} (y, t)
\]

On the other hand, we evaluate the variation of the rate function for the canonical distribution \( \exp(-\beta H_N)/Z_N \) with the external parameter \( \lambda_t \), which is \( I_{\text{eq}, \lambda_t} [\mu_t] = \beta \epsilon_\lambda [\mu_t] - s[\mu_t] - \beta \phi_{\text{eq}}(\beta, \lambda_t) \), where \( \epsilon_\lambda \), \( s \) and \( \phi_{\text{eq}} \) represent the energy per degree of freedom, the same form as the Shannon entropy and the free energy per degree of freedom, respectively [10] (see also appendix B). Then, we obtain

\[
\frac{\delta I_{\text{eq}, \lambda_t} [\mu_t]}{\delta \mu(x, t)} = -\beta F_\lambda(x) - \beta \int G(x, z) \mu(z, t) \, dz + \log \mu(x, t) + 1
\]

where we use the explicit form of \( \epsilon_\lambda \) and \( s 

\[
\epsilon_\lambda [\mu] = -\int F_\lambda(x) \mu(x) \, dx + \frac{\beta}{2} \int (\mu(x) G(x, y) \mu(y)) \, dx \, dy,
\]

\[
s[\mu] = -\int \mu(x) \log \mu(x) \, dx.
\]

By multiplying both sides in equation (24) by \( \frac{\partial}{\partial y} (y, t) \) and integrating them, we find

\[
\int dx \frac{\delta I_{\text{eq}, \lambda_t} [\mu_t]}{\delta \mu(x, t)} \frac{\partial}{\partial y} (y, t) = \int dx \left\{ -\beta F_\lambda(x) - \beta \int G(x, z) \mu(z, t) \, dz + \log \mu(x, t) \right\} \frac{\partial}{\partial y} (y, t)
\]

where we use the normalization condition \( \int \frac{\partial}{\partial y} (y, t) \, dx = 0 \). Comparison of equation (23) with equation (27) enables us to evaluate equation (21) as

\[
L_{\lambda_t} [\hat{\mu}_t, \mu_t] = L_{\lambda_t} \left[ \hat{\mu}_t, \hat{\mu}_t \right] + \int dx \frac{\delta I_{\text{eq}, \lambda_t} [\mu_t]}{\delta \mu(x, t)} \frac{\partial}{\partial y} (y, t).
\]

By substituting equation (28) into the action functional (15), we obtain that the symmetry of action functional \( J_{[0, T]} [\lambda, \mu] \) can be written as

\[
J_{[0, T]} [\lambda, \mu] = J_{[0, T]} [\hat{\lambda}, \hat{\mu}] + \int_0^T dt \left( \frac{\delta I_{\text{eq}, \lambda_t} [\mu_t]}{\delta \mu_t} \right) \hat{\mu}_t.
\]

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Here, we note that the second term of the right hand side in equation (29) is represented as:

\[
\int_0^T dt \left( \frac{dI_{eq,\lambda_t}[\mu_t]}{dt} - \frac{\partial I_{eq,\lambda_t}[\mu_t]}{\partial \lambda_t} \dot{\lambda}_t \right) = I_{eq,\lambda_T}[\mu_T] - I_{eq,\lambda_0}[\mu_0] - \beta \int_0^T dt \frac{\partial \epsilon_{\lambda_t}[\mu_t]}{\partial \lambda_t} \dot{\lambda}_t + \beta \{ \phi_{eq}(\beta, \lambda_T) - \phi_{eq}(\beta, \lambda_0) \},
\]

and the work per degree of freedom performed by the external protocol \( \lambda \) during the time interval \([0, T]\) is written as:

\[
w_{[0,T]}[\lambda, \mu] = \int_0^T dt \frac{\partial \epsilon_{\lambda_t}[\mu_t]}{\partial \lambda_t} \lambda_t.
\]

Taking these facts into account, we find that the symmetry of action functional (29) is represented as:

\[
I_{eq,\lambda_0}[\mu_0] + J_{[0,T]}[\lambda, \mu] + \beta w_{[0,T]}[\lambda, \mu] = I_{eq,\lambda_0}[\tilde{\mu}_0] + J_{[0,T]}[\lambda, \tilde{\mu}] + \beta \{ \phi_{eq}(\beta, \lambda) - \phi_{eq}(\beta, \lambda_0) \}.
\]

Equation (32) stands for the fluctuation theorem described by the action functional and allows us to formulate the second law of thermodynamics in terms of the work as usually observed in thermodynamics.

4. The second law of thermodynamics

Now we are in a position to end the discussion on the second law of thermodynamics, starting from the coarse-grained picture of the system. In terms of the action functional, the thermodynamic path \( \mu^* \), which denotes a solution of the nonlinear diffusion equation (14), must satisfy \( J_{[0,T]}[\lambda, \mu^*] = \inf_{\mu} J_{[0,T]}[\lambda, \mu] \), i.e. \( J_{[0,T]}[\lambda, \mu^*] = 0 \). The second law of thermodynamics is written in the inequality form, which connects the performed work and the free-energy difference between two different equilibrium states. We thus choose the initial condition of equation (14) as the equilibrium state \( \mu_{eq,\lambda_0} \), for which \( I_{eq,\lambda_0}[\mu_{eq,\lambda_0}] = 0 \) holds. The thermodynamic path launched from the equilibrium state, \( \mu^*[\lambda; \mu_{eq,\lambda_0}] \), which means the most probable path, satisfies

\[
I_{eq,\lambda_0}[\mu_{eq,\lambda_0}] + J_{[0,T]}[\lambda, \mu^*[\lambda; \mu_{eq,\lambda_0}]] = 0.
\]

Substituting equation (33) into the symmetry (32), we obtain

\[
\beta w_{[0,T]}[\lambda, \mu^*[\lambda; \mu_{eq,\lambda_0}]] = I_{eq,\lambda_0}[\tilde{\mu}_0^*[\lambda; \mu_{eq,\lambda_0}]] + J_{[0,T]}[\lambda, \tilde{\mu}^*[\lambda; \mu_{eq,\lambda_0}]] + \beta \{ \phi_{eq}(\beta, \lambda_T) - \phi_{eq}(\beta, \lambda_0) \},
\]

where \( \tilde{\mu}^*[\lambda; \mu_{eq,\lambda_0}] \) denotes the time-reversal most probable path, \( \tilde{\mu}_0^*[\lambda; \mu_{eq,\lambda_0}] \) is its initial condition and \( w[\lambda, \mu^*[\lambda; \mu_{eq,\lambda_0}] \) stands for the work performed on the system which is termed in thermodynamics. Since the action functional \( J_{[0,T]}[\lambda, \mu] \) and the rate function \( I_{eq,\lambda}[\mu] \) always take a non-negative value, \( I_{eq,\lambda_0}[\tilde{\mu}_0^*[\lambda; \mu_{eq,\lambda_0}]] + J_{[0,T]}[\lambda, \tilde{\mu}^*[\lambda; \mu_{eq,\lambda_0}]] \geq 0 \), we find the second law of thermodynamics \( w_{[0,T]}[\lambda, \mu^*[\lambda; \mu_{eq,\lambda_0}]] \geq \phi_{eq}(\beta, \lambda_T) - \phi_{eq}(\beta, \lambda_0) \). The entropy production \( \sigma[\lambda] = \beta \{ w_{[0,T]}[\lambda, \mu^*[\lambda; \mu_{eq,\lambda_0}]] - \Delta \phi_{eq} \} \) can also be written in terms

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of the action functional and the rate function as
\[ \sigma[\lambda] = I_{eq,\lambda} [\hat{\mu}_0 [\lambda; \mu_{eq,\lambda}]] + J_{[0,T]} [\hat{\lambda}, \hat{\mu} [\lambda; \mu_{eq,\lambda}]]. \] (35)

Before closing this section, we show the derivation of the ordinary Jarzynski equality from the symmetry (32). Suppose that the system is set in an initial equilibrium state. Then, the rate function for the time evolution of the density field is given by 
\[ I_{eq,\lambda} [\mu_0] + J_{[0,T]} [\lambda, \mu]. \]
We can evaluate the expectation of the exponentiated work in a sufficient large \( N \) (i.e. \( N \to \infty \)), by employing Varadhan’s theorem [19] (also see equation (60) in section 3.5.4 of [10]), as
\[ -\frac{1}{N} \log \langle e^{-N\beta w}\rangle_{eq} = \inf_{\mu} \left( I_{eq,\lambda} [\mu_0] + J_{[0,T]} [\lambda, \mu] + \beta w_{[0,T]} [\lambda, \mu] \right). \] (36)

Here, using the symmetry (32), we obtain
\[ -\frac{1}{N} \log \langle e^{-N\beta w}\rangle_{eq} = \beta \Delta \phi_{eq} + \inf_{\mu} \left( I_{eq,\lambda} [\mu_0] + J_{[0,T]} [\hat{\lambda}, \hat{\mu}] \right) = \beta \Delta \phi_{eq}, \] (37)
where \( \Delta \phi_{eq} = \phi_{eq}(\beta, \lambda_T) - \phi_{eq}(\beta, \lambda_0) \) and we use the property of the rate function, \( \inf_{\mu} (I_{eq,\lambda} [\mu_0] + J_{[0,T]} [\hat{\lambda}, \hat{\mu}]) = 0 \). Accordingly, we find the ordinary Jarzynski equality
\[ \langle e^{-N\beta w}\rangle_{eq} = e^{-N\beta \Delta \phi_{eq}}. \]

5. Nonequilibrium work relation for metastable states

We now comment on several properties of metastable states. First, we show how metastable states emerge in the relaxation process. Suppose that the system is not perturbed during the relaxation process. We choose the external parameter \( \lambda \) as a constant \( c \). The thermodynamic time evolution is given by the nonlinear diffusion equation (14). Thus, metastable states and equilibrium state are given as fixed points of this equation. In order to obtain the fixed points of equation (14), we examine the Lyapunov function [15]. We find that the rate function \( I_{eq,c} [\mu] \) plays the role of the Lyapunov function as follows. First, the rate function \( I_{eq,c} [\mu] \) satisfies \( I_{eq,c} [\mu] \geq 0 \) for all \( \mu \). Second, the derivative of \( I_{eq,c} [\mu] \) with respect to \( t \) is represented as
\[ \frac{dI_{eq,c} [\mu]}{dt} = \int dx \frac{\delta I_{eq,c} [\mu]}{\delta \mu(x, t)} \hat{\mu}(x, t) = -\beta \int dx \mu(x, t) \times \{ f_c(x) + \int g(x, y) \mu(y, t) dy - \frac{1}{\beta} \partial \log \mu(x, t) \partial x \}^2 \leq 0, \] (38)
where we use equation (27) with equations (11) and (14). Thus, we can regard the rate function \( I_{eq,c} [\mu] \) as the Lyapunov function of the nonlinear diffusion equation (14). From this fact, the metastable states and equilibrium state are given as the local minima and the global minimum of \( I_{eq,c} [\mu] \), respectively (see figure 1). Second, let us show the rate function for metastable states. Suppose that the system has \( n \) metastable states. We then focus on the \( i \)th metastable state, denoted by \( \mu_{i,c} \). The rate function for this metastable state can be represented as [10, 12, 13]
\[ V_{i,c} [\nu] = \inf_{\mu: \mu_0 = \mu_{i,c}, \mu_\infty = \nu} J_{[0,\infty]} [\nu]. \] (39)

\[ \text{doi:10.1088/1742-5468/2013/04/P04012} \]
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\[ I_{eq,c} \left[ \mu_0 \right] + J_{[0,T]}^c \left[ \mu \right] = I_{eq,c} \left[ \hat{\mu}_0 \right] + J_{[0,T]}^c \left[ \hat{\mu} \right]. \] (40)

Then, we obtain the rate function for the metastable state as [12, 18] (see also figure 1),

\[ V_{i,c} [\nu] = \inf_{\mu: \mu_0 = \mu_{i,c}, \mu_{\infty} = \nu} J_{[0,\infty]}^c [\mu] \]
\[ = \inf_{\mu: \mu_0 = \nu, \mu_{\infty} = \mu_{i,c}} \left( I_{eq,c} [\hat{\mu}_0] + J_{[0,\infty]}^c [\hat{\mu}] - I_{eq,c} [\hat{\mu}_{\infty}] \right) \]
\[ = I_{eq,c} [\nu] - I_{eq,c} [\mu_{i,c}] + A_{i,c} [\nu], \] (41)

where \( A_{i,c} [\nu] \) denotes a functional,

\[ A_{i,c} [\nu] = \begin{cases} 0 & \text{if } \nu \text{ in basin of } \mu_{i,c} \\ \text{positive} & \text{others.} \end{cases} \] (42)

Notice that we do not need to reveal the explicit form of \( A_{i,c} [\nu] \) to obtain the final result.

Let us give a nontrivial nonequilibrium work relation for metastable states by use of the above functionals. Suppose that the system is initially set in the \( i \)th metastable state, which differs from the initial condition of the ordinary Jarzynski equality. The expectation of the exponentiated work is then evaluated, by using the same procedure as the above

\[ \text{Figure 1. The blue curve represents the Lyapunov function of the nonlinear diffusion equation (the rate function for equilibrium state), } I_{eq,c}. \text{ The red dashed curve denotes the rate function for the } i \text{th metastable state, } V_{i,c}. \text{ The black circles represent the metastable states, while the white circle denotes the equilibrium state. The black arrow represents the downward parallel translation by } I_{eq,c} [\mu_{i,c}] \text{ as the blue dashed curve. The white arrows describe the modification by } A_{i,c} \text{ of the blue dashed curve into the red dashed curve } V_{i,c}. \]
case for the Jarzynski equality, as

\[- \frac{1}{N} \log \langle e^{-N\beta w} \rangle_i = \inf_{\mu} (V_{i,\lambda_0}[\mu_0] + J_{[0,T]}[\lambda, \mu] + \beta w_{[0,T]}[\lambda, \mu]). \quad (43)\]

By the symmetry (32) and equation (41), we reach

\[- \frac{1}{N} \log \langle e^{-N\beta w} \rangle_i = \inf_{\mu} \{ I_{\text{eq},\lambda_0}[\mu_0] + J_{[0,T]}[\lambda, \mu] + \beta w_{[0,T]}[\lambda, \mu] + A_{i,\lambda_0}[\mu_0] - I_{\text{eq},\lambda_0}[\mu_i,\lambda_0] \}
\]

\[= \{ \beta (\phi_{\text{eq}}(\beta, \lambda_T) - \phi_{\text{eq}}(\beta, \lambda_0)) - I_{\text{eq},\lambda_0}[\mu_i,\lambda_0] \}
\]

\[+ \inf_{\mu} \{ I_{\text{eq},\lambda_0}[\hat{\mu}_0] + J_{[0,T]}[\hat{\lambda}, \hat{\mu}] + A_{i,\lambda_T}[\hat{\mu}_T] \} = \beta \{ \phi_{\text{eq}}(\beta, \lambda_T) - \phi_i(\beta, \lambda_0) \}
\]

\[+ \inf_{\mu} \{ I_{\text{eq},\lambda_0}[\hat{\mu}_0] + J_{[0,T]}[\hat{\lambda}, \hat{\mu}] + A_{i,\lambda_T}[\hat{\mu}_T] \}, \quad (44)\]

where we employ the fact that the free energy per degree of freedom of the ith metastable state [10, 12] can be represented, by use of the rate function $I_{\text{eq},\lambda}$ (see equation (B.11) in appendix B), as

\[\phi_i(\beta, \lambda) = \epsilon_x[\mu_i] - (1/\beta)s[\mu_i] = (1/\beta)I_{\text{eq},\lambda}[\mu_i,\lambda] + \phi_{\text{eq}}(\beta, \lambda). \quad (45)\]

Notice that the infimum in equation (44), $\inf_{\hat{\mu}} (I_{\text{eq},\lambda_0}[\hat{\mu}_0] + J_{[0,T]}[\hat{\lambda}, \hat{\mu}] + A_{i,\lambda_T}[\hat{\mu}_T])$, cannot be always equal to zero for any $\lambda$, in contrast with the case of the ordinary Jarzynski equality. However, due to the fact that each term in the infimum has a minimum which is zero separately, we can make the value of the infimum vanish by choosing the external protocol $\lambda$ appropriately. Taking into account the form of the functional $A_{i,c}[\nu]$ as in equation (42), we find that the infimum can vanish without any additional information of the functional $A_{i,c}[\nu]$ if the time-reversal external protocol $\hat{\lambda}$ expresses the protocol which leads the system to the ith metastable state $\mu_{i,\lambda_T}$ from the equilibrium state $\mu_{\text{eq},\lambda_0}$ in thermodynamic limit. To be more precise, we explain this situation as follows.

Consider a solution of the nonlinear diffusion equation (14) with the initial condition $\mu_{\text{eq},\lambda_0}$ under the protocol $\hat{\lambda}$. Here, we denote this solution as $\mu^*_T[\hat{\lambda}, \mu_{\text{eq},\lambda_0}]$. If the solution at time $T$, $\mu^*_T[\hat{\lambda}, \mu_{\text{eq},\lambda_0}]$, is in the basin of the ith metastable state $\mu_{i,\lambda_T}$, the infimum $\inf_{\hat{\mu}} (I_{\text{eq},\lambda_0}[\hat{\mu}_0] + J_{[0,T]}[\hat{\lambda}, \hat{\mu}] + A_{i,\lambda_T}[\hat{\mu}_T])$ vanishes. Accordingly, in the restricted case as mentioned above, we establish the nonequilibrium work relation for metastable states in the same form as the Jarzynski equality, which is equation (2).

Before going to the conclusion, we provide a method to compute the free energy for the metastable state in the actual experiment by employing the nonequilibrium work relation obtained in the above discussion. We first prepare an initial equilibrium state as depicted by I in figure 2. Suppose that we drive the system towards a specific metastable state (ith state) we are interested in by controlling the external protocol $\lambda$ as II in figure 2. The measurement protocol starts from its metastable state. We again drive the system by inversely controlling the external protocol $\lambda$, while measuring the performed work during II and III. The final state denoted by III is not necessarily in equilibrium. We then compute the free energy for the metastable state from the exponentiated work following equation (2).
Figure 2. The lower parabolic curve denotes the trivial rate function for the initial condition. The upper curve with many valleys represents the nontrivial rate function characterizing the interesting system with the metastable states. The preparation of the experiment is as follows. I. We prepare an initial equilibrium state. II. We find a metastable state. We record the protocol $\lambda$, which can lead to the metastable state we are interested in. The main part of the experiment is from II to III. III. We drive the system from the metastable state by the inverse protocol $\hat{\lambda}$, while we measure the performed work from II (red arrow).

6. Conclusion

We have provided the correct understanding of the connection between the fluctuation theorem and the second law of thermodynamics, by employing the symmetry of the action functional. This argument succeeds in describing the behavior of the performed work in the thermodynamic limit. In addition, we have derived the nonequilibrium work relation for metastable states. As a result, this work relation can be expressed in the same form as the Jarzynski equality by the particular external protocol, enabling us to compute the free energy for preselected metastable states by observing the performed work. Our result would serve as an important insight for the understanding of the peculiar relaxation observed as in glassy systems.

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Appendix A

In this appendix, we derive the functional Fokker–Planck equation (12) from the stochastic evolution of the density field, equation (10). As an ordinary procedure to derive the Fokker–Planck equation from the Ito process, we consider the derivative of the test functional $\psi[\mu]$ as

$$d\psi[\mu] = \int dx \frac{\delta \psi[\mu]}{\delta \mu(x)} d\mu(x) + \frac{1}{2} \int dx dy \frac{\delta^2 \psi[\mu]}{\delta \mu(x) \delta \mu(y)} d\mu(x) d\mu(y).$$

(A.1)
By substituting equation (10) into equation (A.1), we evaluate the expectation of the test functional as
\[
\langle d\psi[\mu] \rangle = \int dx \left\langle \frac{\delta \psi[\mu]}{\delta \mu(x)} D_{\mu,\lambda}(x) \right\rangle dt + \frac{1}{2N} \int dxdy \left\langle \frac{\delta^2 \psi[\mu]}{\delta \mu(x) \delta \mu(y)} R_{\mu}(x,y) \right\rangle dt
\]
\[
= \int dx \int \mathcal{D}\mu \frac{\delta \psi[\mu]}{\delta \mu(x)} D_{\mu,\lambda}(x) \text{Prob}_{t}[\mu] dt + \frac{1}{2N} \int dxdy \int \mathcal{D}\mu \frac{\delta^2 \psi[\mu]}{\delta \mu(x) \delta \mu(y)} R_{\mu}(x,y) \text{Prob}_{t}[\mu] dt,
\]
where Prob_{t}[\mu] denotes the probability for the density field. By integration by parts, equation (A.2) is calculated as
\[
\frac{\partial}{\partial t} \int \mathcal{D}\mu \psi[\mu] \text{Prob}_{t}[\mu] = \int \mathcal{D}\mu \psi[\mu] \int dx \frac{\delta}{\delta \mu(x)} \left\{ D_{\mu,\lambda}(x) \text{Prob}_{t}[\mu] \right\}
\]
\[
+ \int \mathcal{D}\mu \psi[\mu] \frac{1}{2N} \int dxdy \frac{\delta^2}{\delta \mu(x) \delta \mu(y)} \left\{ R_{\mu}(x,y) \text{Prob}_{t}[\mu] \right\}.
\]
Accordingly, we obtain the functional Fokker–Planck equation,
\[
\frac{\partial}{\partial t} \text{Prob}_{t}[\mu] = \int dx \frac{\delta}{\delta \mu(x)} \left\{ -D_{\mu,\lambda}(x) \text{Prob}_{t}[\mu] \right\}
\]
\[
+ \frac{1}{2N} \int dxdy \frac{\delta^2}{\delta \mu(x) \delta \mu(y)} \left\{ R_{\mu}(x,y) \text{Prob}_{t}[\mu] \right\}.
\]

Appendix B

In this appendix, we show that the rate function for the canonical distribution can be represented as \( I_{\text{eq,}\lambda}[\mu] = \beta \epsilon_{\lambda}[\mu] - s[\mu] - \beta \phi_{\text{eq}}(\beta, \lambda) \) in the case where the Hamiltonian of the system is described as equation (5). Here, \( \epsilon_{\lambda} \), \( s \) and \( \phi_{\text{eq}} \) are denoted as follows.

\[
\epsilon_{\lambda}[\mu] = -\int F_{\lambda}(x) \mu(x) dx - \frac{1}{2} \int \mu(x) G(x,y) \mu(y) dx dy,
\]
\[
s[\mu] = -\int \mu(x) \log \mu(x) dx,
\]
\[
\phi_{\text{eq}}(\beta, \lambda) = -\frac{1}{N\beta} \log Z_{\beta,\lambda,N},
\]
where \( Z_{\beta,\lambda,N} \) denotes the partition function. Let us consider the coarse-grained picture of the canonical distribution by the density field \( \mu \). The canonical distribution is represented as
\[
\rho_{\beta,\lambda,N}(\{x_i\}) \prod_{i} dx_i = \frac{1}{Z_{\beta,\lambda,N}} e^{-\beta H_{\lambda}(\{x_i\}, \lambda)} \prod_{i} dx_i.
\]
We then obtain the coarse-grained distribution of \( \mu \) as
\[
\text{Prob}_{\beta,\lambda}[\mu|\mathcal{D}\mu] = \frac{1}{Z_{\beta,\lambda,N}} e^{-N \left\{ -\beta \int F_{\lambda}(x) \mu(x) dx - (\beta/2) \int \mu(x) G(x,y) \mu(y) dx dy \right\}} W[\mu|\mathcal{D}\mu].
\]
Here, $W[\mu]$ denotes the state density satisfying $\Pi_i \, d x_i = W[\mu] \, d \mu$ and we employed the fact that the Hamiltonian was described by use of $\mu$ as

$$H_N[\mu] = -N \int F_\lambda(x) \mu(x) \, d x - \frac{N}{2} \int \mu(x) G(x, y) \mu(y) \, d x \, d y.$$  \hspace{1cm} (B.6)

According to Sanov’s theorem [10], the rate function of the density field for IID random variables with a common probability density $\rho(x)$ is given as

$$I[\mu] = \int d x \mu(x) \log(\mu(x) / \rho(x)).$$

On the other hand, by using the state density, we can express $\text{Prob}[\mu]$ as

$$\text{Prob}[\mu] = W[\mu] / \Lambda^N.$$  \hspace{1cm} (B.8)

By comparing equation (B.7) to equation (B.8), we can evaluate the state density for a sufficiently large $N$ as

$$W[\mu] = e^{-N \int \mu(x) \log \mu(x) \, d x}. \hspace{1cm} (B.9)$$

By substituting equation (B.9) into equation (B.5) and taking equations (B.1), (B.2) and (B.3) into account, we obtain

$$\text{Prob}_{\beta, \lambda}[\mu] = e^{-N \{\beta \epsilon_\lambda[\mu] - s[\mu] - \beta \phi_{eq}(\beta, \lambda)}.$$  \hspace{1cm} (B.10)

Accordingly, we find the rate function of the canonical distribution as

$$I_{eq, \lambda}[\mu] = \beta \epsilon_\lambda[\mu] - s[\mu] - \beta \phi_{eq}(\beta, \lambda).$$  \hspace{1cm} (B.11)

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