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Jarzynski equality for the transitions between nonequilibrium steady states

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Jarzynski equality [Phys. Rev. E **56**, 5018 (1997)], which has been considered to be valid for the transitions between equilibrium states, is found to be applicable to the transitions between nonequilibrium stationary states satisfying certain conditions. Also numerical results confirm its validity. Its relevance for nonequilibrium thermodynamics of the operational formalism is discussed. [S1063-651X(99)51211-7]

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The framework of nonequilibrium thermodynamics has been sought by many authors [1] in order to treat various nonequilibrium systems such as chemical reactions, transport processes in solids, moleculer motors, etc. So far, all these attempts seem to be based on the fluid-dynamical approaches, which mostly have the assumption of local equilibrium at its starting point. Recently, Oono and Paniconi [2] present a different type of nonequilibrium thermodynamics whose framework corresponds to equilibrium thermodynamics. The unique feature of their work lies in the fact that it is a set of laws concerning operation from the outside, as well as equilibrium thermodynamics. We refer to their theory as the operational formalism. This formalism is so important that the concept of entropy in equilibrium thermodynamics is introduced concerning with the adiabatic operation [3]. The relation between dynamical entropy and thermodynamic entropy is also discussed from this viewpoint [4]. Hence, it is interesting to construct nonequilibrium thermodynamics from the operational point of view, apart from the existing fluid-dynamical approach.

Operation from the outside can cause an energy exchange between the system and the external operator. In equilibrium thermodynamics, there is a principle of the minimum work for the system in the isothermal environment:

$$\Delta F \leqslant \langle W \rangle, \tag{1}$$

where ΔF denotes the free energy difference between the initial state and the final state of the system, and W denotes the work done by the external operator. The average of a physical quantity f is written as $\langle f \rangle$, as usual. Note that the sign of W is positive when the work is performed on the system. The equality holds when and only when the process is reversible. Jarzynski recently proposed the intriguing equality for the finite time transition between the equilibrium states [5],

$$\exp(-\beta\Delta F) = \langle \exp(-\beta W) \rangle, \tag{2}$$

where β denotes the inverse temperature. Crooks [6] gives another intriguing derivation of Eq. (2) using the fluctuation theorem [7]. This equality is confirmed to be valid in the finite time transition between equilibrium states. In this Rapid Communication, however, we show that Eq. (2) is indeed applicable to the finite time transition between nonequilibrium steady states which satisfy certain conditions. The derivation is given below by roughly following Ref. [5].

Consider the system with the following Hamiltonian:

$$\mathcal{H} = H_0(p) + H(x;\alpha) - xF(t), \tag{3}$$

where α is a parameter and $F(t)$ denotes the perturbative driving force which may be responsible for the nonequilibrium situation, and $H_0(p)$ is independent of time. The external agent manipulates the system by varying the parameter α. The system may be in contact with a heat bath or several heat baths of different temperatures. In any case, we describe the dynamics of the system by the stochastic process in the phase space spanned by x and p. We introduce the probability distribution function $f(\Gamma,t)$ and the transition probability $P(\Gamma,t|\Gamma',t')$, where Γ denotes both x and p, to get

$$f(\Gamma,t) = \int d\Gamma' P(\Gamma,t|\Gamma',t') f(\Gamma',t'). \tag{4}$$

This leads to

$$\frac{\partial f(\Gamma,t)}{\partial t} = \int d\Gamma' R(\Gamma|\Gamma';t) f(\Gamma',t), \tag{5}$$

where

$$R(\Gamma|\Gamma';t) = \lim_{\Delta t \to +0} \frac{P(\Gamma,t+\Delta t|\Gamma',t) - P(\Gamma,t|\Gamma',t)}{\Delta t}. \tag{6}$$

The dynamics of our nonequilibrium system is described by Eq. (5) together with the initial condition. Then we make an important assumption that the steady state of our system is characterized by the following distribution function:

$$f_{steady}(\Gamma;\alpha) \propto \Phi(x,p)\exp[-\bar{\beta}H(x;\alpha)], \tag{7}$$

where $\Phi(x,p)$ is an arbitrary function of x and p, and $\bar{\beta}$ is a parameter that should be regarded as the effective inverse temperature. In other words, we confine the theory to the systems whose stationary distribution functions are represented by Eq. (7). By the definition of the stationary state, Eq. (5) leads to

$$\frac{\partial f_{steady}}{\partial t} = \int d\Gamma' R(\Gamma|\Gamma';t)\Phi(x',p')\exp[-\bar{\beta}H(x';\alpha)] = 0. \tag{8}$$

Our goal is to obtain the steady state version of Eq. (2),

$$\langle \exp(-\bar{\beta}W)\rangle = \exp(-\bar{\beta}\Delta F), \tag{9}$$

while the meaning of ΔF is unclear at this point. Note that $\bar{\beta}$ is identical to the one appearing in the distribution function Eq. (7). Adopting the path-integral expression, we write

$$\langle \exp(-\bar{\beta}W)\rangle = \int \mathcal{D}\Gamma(t)\exp(-\bar{\beta}W)\mathcal{P}[\Gamma(t)], \tag{10}$$

where $\mathcal{P}[\Gamma(t)]$ is a probability distribution functional of the path $\Gamma(t)$ in the phase space. The work done to the system is defined as [8]

$$W = \int dt\dot{\alpha}\frac{\partial H(x;\alpha)}{\partial \alpha}. \tag{11}$$

We manipulate the system by changing the value of α from $\alpha(0)$ to $\alpha(\mathcal{T})$.

Then we discretize time duration of the operation $[0,\mathcal{T}]$ as $(t_0,t_1,\ldots,t_N)$, and write $\Gamma(t_i)$ as Γ_i and $\mathcal{T}/N$ as Δt, respectively. As a result of the discretization, the distribution functional $\mathcal{P}[\Gamma(t)]$ is represented in terms of transition probability as follows:

$$\mathcal{P}[\Gamma(t)] = P_N(\Gamma_N|\Gamma_{N-1})\cdots P_1(\Gamma_1|\Gamma_0)f_0(\Gamma_0), \tag{12}$$

where $f_0(\Gamma_0)$ denotes the initial probability distribution function. Similarly, Eq. (11) becomes

$$W = \sum_{i=0}^{N-1} \delta H_{i+1}(x_i), \tag{13}$$

where

$$\delta H_{i+1}(x_i) = H(x_i;\alpha_{i+1}) - H(x_i;\alpha_i). \tag{14}$$

Due to Eqs. (12) and (13), Eq. (10) is rewritten as

$$\langle \exp(-\bar{\beta}W)\rangle = \left[\prod_{i=0}^{N}\int d\Gamma_i\right] P_N(\Gamma_N|\Gamma_{N-1}) \times e^{-\bar{\beta}\delta H_N(x_{N-1})}\cdots P_1(\Gamma_1|\Gamma_0) \times e^{-\bar{\beta}\delta H_1(x_0)} f_0(\Gamma_0). \tag{15}$$

The integrals on the right-hand side of Eq. (15) are represented by the following iteration:

$$g_{i+1}(\Gamma) = \int d\Gamma_i P_{i+1}(\Gamma|\Gamma_i)e^{-\bar{\beta}\delta H_{i+1}(x_i)}g_i(\Gamma_i), \tag{16}$$

where

$$g_0(\Gamma) = f_0(\Gamma), \tag{17}$$

$$\langle \exp(-\bar{\beta}W)\rangle = \int g_N(\Gamma)d\Gamma. \tag{18}$$

By taking the first order terms of Δt, we have

$$P_{i+1}(\Gamma|\Gamma_i) = \delta(\Gamma-\Gamma_i) + \Delta t R_i(\Gamma|\Gamma_i), \tag{19}$$

$$e^{-\bar{\beta}\delta H_{i+1}(x_i)} = 1 - \bar{\beta}\delta H_{i+1}(x_i). \tag{20}$$

Substituting Eqs. (19) and (20) into the recursive relation Eq. (16), and taking the limit $\Delta t \to 0$, we get

$$\frac{\partial g(\Gamma,t)}{\partial t} = -\bar{\beta}\dot{\alpha}\frac{\partial H(x;\alpha)}{\partial \alpha}g(\Gamma,t) + \int d\Gamma' R(\Gamma|\Gamma';t)g(\Gamma',t). \tag{21}$$

This equation gives

$$g(\Gamma,t) \propto \Phi(x,p)\exp[-\bar{\beta}H(x;\alpha(t))], \tag{22}$$

noting that the second term of the right-hand side of Eq. (21) vanishes by Eq. (8). Since Eq. (17) tells us that $g(\Gamma,0)$ is identical to the initial probability distribution function $f_0(\Gamma)$, the right-side of Eq. (22) must have an appropriate normalization factor,

$$g(\Gamma,t) = \frac{\Phi(x,p)}{Z_0}\exp[-\bar{\beta}H(x;\alpha(t))], \tag{23}$$

where

$$Z_0 = \int d\Gamma\Phi(x,p)\exp[-\bar{\beta}H(x;\alpha(0))]. \tag{24}$$

From Eq. (18), we finally obtain the desired quantity,

$$\langle \exp(-\bar{\beta}W)\rangle = \int d\Gamma g(\Gamma,\mathcal{T}) = \frac{Z_\mathcal{T}}{Z_0}, \tag{25}$$

where

$$Z_\mathcal{T} = \int d\Gamma\Phi(x,p)\exp[-\bar{\beta}H(x;\alpha(\mathcal{T}))]. \tag{26}$$

Note that Z_0 and $Z_\mathcal{T}$ depend only on the value of $\alpha(0)$ and $\alpha(\mathcal{T})$, respectively, so that they are the state variables. Namely, the quantity $\langle \exp(-\bar{\beta}W)\rangle$ does not depend on the transition process but only on the initial and final states. Furthermore, if we define the free energy by

$$F = -\bar{\beta}^{-1}\log Z, \tag{27}$$

Eq. (25) gives our goal Eq. (9), which is rewritten as

$$\Delta F = -\bar{\beta}^{-1}\log[\langle \exp(-\bar{\beta}W)\rangle]. \tag{28}$$

This completes the derivations of the steady state version of the Jarzynski equality Eq. (9). In this derivation, the restriction on the stationary distribution function, Eq. (7), is imposed. It is quite unknown at this point if the Jarzynski equality holds for the system whose stationary distribution function does not satisfy the condition. Hereafter, we check the validity of the results by numerical simulations on some concrete models.

We consider two examples. First we treat the uniform temperature system whose Hamiltonian is given by

$$\mathcal{H} = \frac{p^2}{2} + \frac{k(t)}{2}x^2 - xA\sin(\omega t). \tag{29}$$

This is one of the simplest models of the nonequilibrium steady state driven by external force. By changing $k(t)$, we can contribute work to the nonequilibrium system. Although the sinusoidal force contributes work to the system, its contribution is a stationary dissipation which characterizes nonequilibrium states; following Ref. [2], we call the work which stationarily dissipates ''housekeeping work.'' We do not count its contribution to the work.

We employ the Langevin dynamics as a model of the heat bath,

$$\ddot{x}+\gamma\dot{x}+k(t)x=A\sin(\omega t)+\xi(t), \tag{30}$$

where $\xi(t)$ is the Gaussian white noise satisfying

$$\langle\xi(t)\rangle=0, \quad \langle\xi(t)\xi(t')\rangle=2\gamma\beta^{-1}\delta(t-t'). \tag{31}$$

The control parameter $k(t)$ is changed from 1/4 to 1 as

$$k(t)=\frac{1}{4}\left(1+\frac{3t}{\mathcal{T}}\right), \tag{32}$$

where $\mathcal{T}$ denotes the time duration of the operation.

Let us discuss the statistical property of the stationary state. The model Eq. (30) leads to a time-dependent Kramers equation which yields time-dependent distributions, if the forcing period $2\pi/\omega$ is longer than the relaxation time of the system. However, since the operation process is much slower than the forcing period, we average out the sinusoidal motion to get the stationary distribution. If the forcing period becomes comparable to the relaxation time, the response of the system cannot follow the forcing so that the distribution functions become Gibbsian in the high-frequency limit $1/\omega\to 0$. Here we choose the parameter such that the relaxation time of the position $\tau_x\sim\gamma$ is longer than the forcing period, and that of the momentum $\tau_p\sim\gamma^{-1}$ is shorter than the forcing period, i.e., $\gamma^{-1}\leqslant 2\pi/\omega\leqslant\gamma$. We can expect that the distribution of the position $\chi(x)$ becomes Gibbsian and that of the momentum $\pi(p)$ is non-Gibbsian in this parameter range. The obtained $\chi(x)$ and $\pi(p)$ are shown in Fig. 1, where we can see that our expectation is realized,

$$f(\Gamma;k)\propto\exp\left(-\beta k\frac{x^2}{2}\right)\pi_0(p). \tag{33}$$

Note that this satisfies the condition of Eq. (7). Following Eq. (27), ΔF is calculated as $\bar{\beta}^{-1}\log 2$ for this process. Then we check if Eq. (28) holds. Since the distribution function is given by Eq. (33), $\bar{\beta}$ in Eq. (28) corresponds to β. The quantity to be focused on here, $-\bar{\beta}^{-1}\log\langle\exp[-\bar{\beta}W]\rangle$, is shown in Fig. 2 together with $\langle W\rangle$. As is clearly seen, while $\langle W\rangle$ changes its value depending on $\mathcal{T}$, $-\bar{\beta}^{-1}\log\langle\exp[-\bar{\beta}W]\rangle$ is an invariant with respect to the operation time $\mathcal{T}$, which has been proved to be a state variable. As $\mathcal{T}$ gets larger, $\langle W\rangle$ seems to converge to a finite value, which is identical to $-\bar{\beta}^{-1}\log\langle\exp[-\bar{\beta}W]\rangle$; we can regard this quantity as ΔF. These facts clearly indicate the validity of our main result.

On the other hand, by tuning parameters, we can get different steady states whose distribution functions do not satisfy Eq. (7). In those cases, we found that our equality no longer holds. However, the principle of the minimum work still seems to be valid.

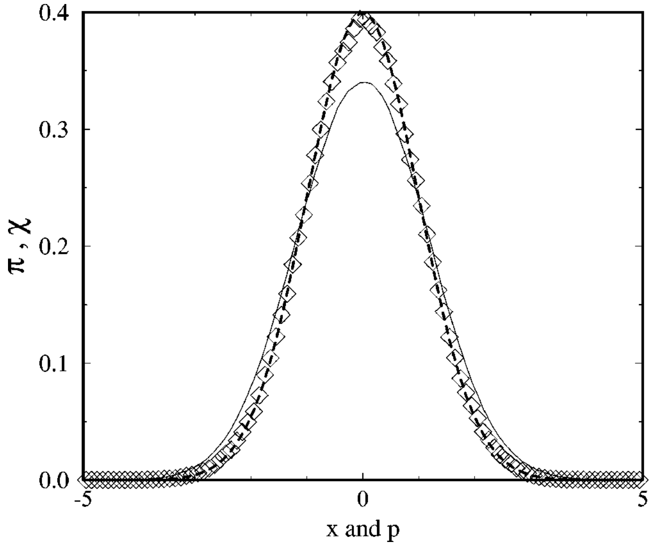

FIG. 1. The steady state distribution functions in the configuration space $\chi(x)$ (diamonds) and in the momentum space $\pi(p)$ (solid line). Dashed line represents the Gaussian distribution corresponding to $\exp[-\beta kx^2/2]$. Parameters are set as $k=1$, $\beta=1$, $\gamma=2$, $A=2$, and $\omega=3$.

Second, we consider the system in contact with two heat baths of different temperatures. The model we treat here is two Brownian particles coupled via the linear interacting potential. The Hamiltonian of the systems is

$$\mathcal{H}=\frac{p_1^2}{2}+\frac{p_2^2}{2}+\frac{k}{2}(x-y)^2. \tag{34}$$

And the dynamics is written as

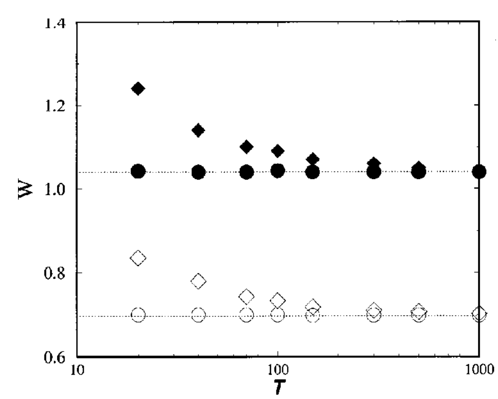

FIG. 2. Averaged work and the free energy of the two examples in the text. Plots on the down side are for the sine forcing system. Open diamonds and circles denote $\langle W\rangle$ and $-\bar{\beta}^{-1}\log\langle\exp[-\bar{\beta}W]\rangle$, respectively. All the parameters are the same as Fig. 1. Plots on the up side are for the heat conducting system. Closed diamonds and circles denote $\langle W\rangle$ and $-\bar{\beta}^{-1}\log\langle\exp[-\bar{\beta}W]\rangle$, respectively. We set the parameters to be $\gamma_1=\gamma_2=1$, $\beta_1=0.5$, and $\beta_2=1$. Dashed lines denote the free energy difference calculated from the stationary distribution functions.

$$\ddot{x}+\gamma_1\dot{x}+k(t)(x-y)=\xi_1(t), \tag{35}$$

$$\ddot{y}+\gamma_2\dot{y}+k(t)(y-x)=\xi_2(t). \tag{36}$$

Again $\xi_1(t)$ and $\xi_2(t)$ are the Gaussian white noise,

$$\langle \xi_i(t)\rangle =0, \quad \langle \xi_i(t)\xi_j(t')\rangle =2\gamma_i\beta_i\delta_{ij}\delta(t-t'). \tag{37}$$

where

$$\delta_{ij}=\begin{cases}1, & (i=j)\\ 0, & (i\neq j).\end{cases} \tag{38}$$

This may be the simplest heat conduction system, which is of course in nonequilibrium. This system has been intensively studied by Sekimoto [9], and was found to have the following distribution:

$$f_{steady}(\Gamma;k)\propto \exp\left(-\bar{\beta}k\frac{(x-y)^2}{2}\right)\exp\left(-\bar{\beta}\frac{p_1^2+p_2^2}{2}\right), \tag{39}$$

where

$$\bar{\beta}=\frac{\gamma_1+\gamma_2}{\gamma_1\beta_1+\gamma_2\beta_2}\beta_1\beta_2. \tag{40}$$

The steady state of the system hence satisfies the condition of Eq. (7). We again control the parameter $k(t)$ as given in Eq. (32) and check if the Jarzynski equality holds. With the knowledge on the distribution function, ΔF is calculated to be $\bar{\beta}^{-1}\log 2$ again. The numerical result using $\bar{\beta}$ of Eq. (40) is shown in Fig. 2. It is clear if the Jarzynski equality is also valid in this heat conducting systems.

In this Rapid Communication, we derive the steady state version of the Jarzynski equality and reconfirm its validity by numerical simulations. The condition in which the equality holds is that the stationary distribution function is given by Eq. (7). Note that the principle of minimum work immediately follows Eq. (28). Namely, the principle of minimum work is also valid for the transition between nonequilibrium steady states.

However, the equality has clear limitations on its application. The condition Eq. (7) is rather crucial in that it cannot describe the steady state of the system where the temperature depends on position; e.g. the Brownian particle in the nonuniform temperature environment [10]. It is unclear to what extent Eq. (7) is satisfied in various nonequilibrium systems.

Another open question is the definition of the free energy in nonequilibrium systems. As we have seen in the numerical simulations above, Eq. (27) seems to be valid in the system satisfying Eq. (7) regardless of the statistical property of the momentum space. However, in more general systems, the definition of the nonequilibrium free energy as well as entropy is still unclear, although it may appear as the minimum work as is stated in Eq. (1). Broader application and further development of the framework stated in Ref. [2] should be fruitful for nonequilibrium thermodynamics and should be the main focus of future investigation of the problem.

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