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Application range of Jarzynski's equation for boundary-switching processes

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Jarzynski's equation (JE) has been known to relate free energy change of a system to statistical distribution of work done on the system for an arbitrary process. In the present work, we first establish the validity condition of JE for boundary switching processes. The validity condition of JE is examined for an example of spontaneous irreversible processes, for which, obviously, JE does not hold. We find that the free energy difference between two configurational states with different phase-space volume cannot be correctly estimated by JE for any adiabatic boundary switching process.

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Free energy is one of the central concepts in thermodynamics and statistical thermodynamics, whose quantification is of great interest in many problems of science. It is well established in conventional thermodynamics that free energy difference $F_B - F_A[\equiv \Delta F_{BA}]$ between two equilibrium states, A and B, of a system is equal to the work done on the system during the isothermal reversible transition process from state A to state B. However, for other transition processes, there had not been any quantitative relationship between free energy difference and work before Jarzynski proposed his equation a decade ago.

Jarzynski's equation (JE) relates the difference $\Delta F_{BA}[=F_B - F_A]$ of the free energy of state B from that of state A to statistical distribution $P_{A\to B}(W)$ of work W done on the system during an *arbitrary* transition process from state A to state B by

$$\exp(-\beta\Delta F_{BA}) = \int \exp(-\beta W) P_{A\to B}(W) dW, \qquad (1)$$

with β being the inverse temperature [1]. As Eq. (1) suggests that free energy difference could be measured from transition processes other than the reversible one, it has drawn much attention. JE was rederived for a variety of model systems [2–8], and verified experimentally for a single RNA stretching process [9,10].

An exception to this trend for JE was Cohen and Mauzerall's question about the correctness of JE for a general irreversible process, during which distribution of a system deviates from the Boltzmann distribution and temperature is not well defined [11,12]. In response to the criticism, Jarzynski presented another derivation of Eq. (1) and kept his assertion that, if an initial state A of the system is a thermal equilibrium state with temperature β^{-1}, Eq. (1) holds for irreversible processes as well as reversible ones even though the temperature of the system is not well defined or deviates from β^{-1} during the dynamics [13]. Afterward, while difficulty or inefficiency of its practical application has been noted [14–16], JE has seemed to be accepted as a general equation that holds for any system undergoing an arbitrary process [6–8,17–26].

However, recently, it was shown for an exactly solvable model that prediction of Eq. (1) for free energy difference is dependent on the shape of the transition path whereas free energy difference cannot be [27]. Therefore it is now an important issue to define the validity condition of JE. In this work, we first establish the validity condition of JE for an adiabatic boundary switching process. Recently, Presse and Silbey discussed important issues in practical applicability of JE to macroscopic systems for the case where JE is formally correct [16]. In comparison, the question we address here is under what condition JE is formally correct for a boundary switching process.

In Jarzynski's derivations of JE for a parameter switching process [1,13], it is implicitly assumed that boundary conditions imposed on a system remain intact from the parameter switching process. Nevertheless, defining the application range of JE for a boundary switching process seems necessary because we are often interested in free energy difference between two equilibrium states defined by different boundary conditions. When we identify the canonical equilibrium state of a system by temperature T and other state parameters R, the latter state parameters R often represent a boundary condition or a constraint imposed on microscopic variables of the system in the equilibrium state. For example, the canonical equilibrium state of a system of gas particles whose position vectors $\mathbf{r}_j$ satisfy the constraint $\mathbf{r}_j \in V$, with V being a volume confining the gas system, may be represented by (T, V). The equilibrium configurational state of a chain polymer composed of only those microscopic configurational states of the chain polymer satisfying constraint $|\mathbf{r}_i - \mathbf{r}_f| = R_{\mathrm{ETE}}$ with $\mathbf{r}_i$ and $\mathbf{r}_f$ being the position vectors of the initial and the final units of the chain polymer may be identified by $(T, R_{\mathrm{ETE}})_c$. Additional examples for equilibrium states identified by boundary conditions include equilibrium configurational states of a molecular pair identified by the pair separation, equilibrium configurational states of a biopolymer identified by its radius of gyration, and so on. In these examples, boundary conditions of systems are dependent on values of state parameters of the systems.

In the case where the system in state A is subject to a boundary condition different from that of the system in state B, the phase-space domain $\Omega_{\mathrm{eq}}(A)$ accessible to microscopic states of the system in state A is different from $\Omega_{\mathrm{eq}}(B)$ of the system in state B. We find that ΔF_{BA} predicted by Eq. (1) is correct for an adiabatic boundary switching process only if the latter transforms the phase-space domain $\Omega_{\mathrm{eq}}(A)$ of the

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initial equilibrium state A into $\Omega_{\mathrm{eq}}(B)$ of the final equilibrium state B at the very end of the adiabatic switching process. The validity condition is discussed for two adiabatic expansion processes of an ideal gas system. The Liouville theorem indicates that the validity condition cannot be satisfied for any adiabatic boundary switching process when JE is applied to estimate the free energy difference between configurational states with different phase-space volumes from each other.

Free energy difference ΔF_{10} between two equilibrium states, $(T,R=R_0)$ and $(T,R=R_1)$, is given by

$$\exp[-\beta\Delta F_{10}] = \frac{\int_{\Omega_{\mathrm{eq}}(R_1)} d\Gamma \exp[-\beta H_1(\Gamma)]}{\int_{\Omega_{\mathrm{eq}}(R_0)} d\Gamma_0 \exp[-\beta H_0(\Gamma_0)]}. \qquad (2)$$

Here the phase-space domain $\Omega_{\mathrm{eq}}(R_0)$ of state $(T,R=R_0)$ can be different from the phase-space domain $\Omega_{\mathrm{eq}}(R_1)$ of state $(T,R=R_1)$. $H_j(\Gamma)$ and $\int_{\Omega_{\mathrm{eq}}(R_j)} d\Gamma$, respectively, denote the Hamiltonian of the system at microscopic state Γ and the sum over all microscopic states composing the equilibrium phase-space domain of our system with state parameter R being equal to R_j.

In comparison, the prediction ΔF_{10}^J of Eq. (1) for free energy difference is given by

$$\Delta F_{10}^J = -\beta^{-1} \ln \int dW \; P_{R_0\to R_1}(W)\exp(-\beta W), \qquad (3)$$

where $P_{R_0\to R_1}(W)$ denotes the probability distribution of work done on the system during an arbitrary process in which the value of the state parameter R switches from R_0 to R_1. In this work, we will confine ourselves to the case where the parameter switching process is an adiabatic process, during which dynamics of the system obeys the Hamilton equation of motion. The system is initially in state (T,R_0) in thermal equilibrium with a heat bath, but is isolated from the heat bath during the parameter switching process in which state parameter $R(t)$ of the system is varied in a controlled manner from R_0 to R_1 in time interval $[0,t_S]$. Note here that the adiabatic process alone cannot transform the initial state (T,R_0) into the target equilibrium state (T,R_1). To reach the target equilibrium state, the system should be coupled again to the heat bath after the adiabatic process. However, prediction of Eq. (3) for the free energy difference has nothing to do with the thermal relaxation process necessary for the system to reach the final state (T,R_1) after the adiabatic process.

We will calculate ΔF_{10}^J in Eq. (3) and compare it to ΔF_{10} given in Eq. (2). Let us first consider the system whose microscopic state happens to be Γ_0 at time 0 at which the adiabatic process begins. During the adiabatic process in which we control the time evolution of state parameter R, the microscopic state Γ^* of the system evolves from Γ_0 according to classical dynamics. Because the dynamics of our system is deterministic throughout the adiabatic process with a given time evolution $R(t)$ of state parameter R, the phase-space trajectory of our system is unique for each initial microscopic state Γ_0. Let $\Gamma^*(t|\Gamma_0)$ denote the unique microscopic state of our system at time t evolved from initial microscopic state Γ_0 for the given adiabatic process. The work done on the system with initial state Γ_0 during the adiabatic process in time interval $[0,t_S]$ is given by

$$W(\Gamma_0) = H_1[\Gamma^*(t_S|\Gamma_0)] - H_0(\Gamma_0). \qquad (4)$$

As Eq. (4) indicates that work W done on the system during the adiabatic process is a function of Γ_0, $P_{R_0\to R_1}(W)$ is related to the initial equilibrium distribution $P_{\mathrm{eq}}(\Gamma_0)$ of Γ_0 by $P(W)=\int d\Gamma_0 \delta[W-W(\Gamma_0)]P_{\mathrm{eq}}(\Gamma_0)$ with $W(\Gamma_0)$ given by Eq. (4).

With this at hand one can rewrite the right-hand side of Eq. (3) as

$$\langle\exp(-\beta W)\rangle = \int_{\Omega_{\mathrm{eq}}(R_0)} d\Gamma_0 \exp[-\beta W(\Gamma_0)] \times \frac{\exp[-\beta H_0(\Gamma_0)]}{\int_{\Omega_{\mathrm{eq}}(R_0)} d\Gamma_0' \exp[-\beta H_0(\Gamma_0')]}. \qquad (5)$$

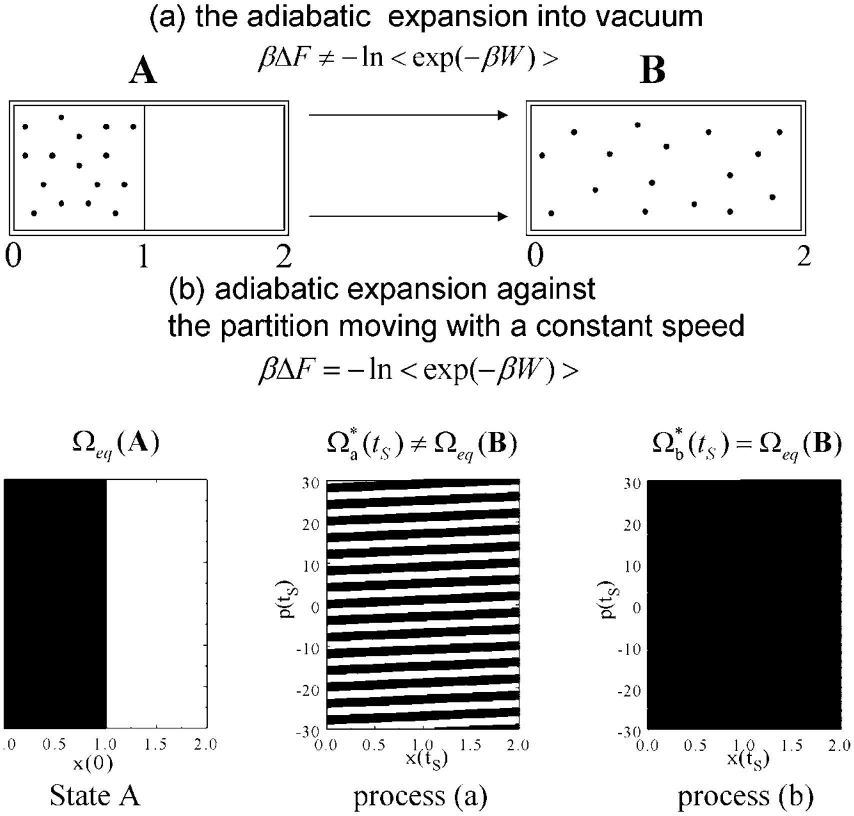
Substituting Eq. (4) into Eq. (5), we get

$$\langle\exp(-\beta W)\rangle = \frac{\int_{\Omega_0} d\Gamma_0 \exp\{-\beta H_1[\Gamma^*(t_s|\Gamma_0)]\}}{\int_{\Omega_0} d\Gamma_0' \exp[-\beta H_0(\Gamma_0')]}. \qquad (6)$$

Because of the uniqueness of mechanical motion we can think of the initial phase point Γ_0 as a function of the phase-space point Γ^* at time t_S, i.e., $\Gamma_0=\Gamma_0(t_S,\Gamma^*)$, and change the integration variable from Γ_0 to Γ^*: $\int_{\Omega_0} d\Gamma_0 = \int_{\Omega^*(t_S)} d\Gamma^* |\frac{\partial\Gamma_0}{\partial\Gamma^*}|$ in the integral in the denominator on the right-hand side of Eq. (6). Here, $|\frac{\partial\Gamma_0}{\partial\Gamma^*}|$ denotes the Jacobian determinant and $\int_{\Omega^*(t_S)} d\Gamma^*$ denotes the sum over the phase-space domain $\Omega^*(t_S)$ accessible to microscopic states of our system at time t_S or at the very end of the adiabatic process. In general, $\Omega^*(t_S)$ can be different from $\Omega_{\mathrm{eq}}(R_1)$ although the value of $R(t_1)$ is R_1. An example of the latter will be discussed shortly in this work. It is well established that as long as the dynamics of the system obeys the Hamilton equation of motion, we have $|\frac{\partial\Gamma_0}{\partial\Gamma^*}|=1$ [28]. Consequently, Eq. (6) becomes

$$\langle\exp(-\beta W)\rangle = \frac{\int_{\Omega^*(t_S)} d\Gamma \exp[-\beta H_1(\Gamma)]}{\int_{\Omega_{\mathrm{eq}}(R_0)} d\Gamma_0' \exp[-\beta H_0(\Gamma_0')]}. \qquad (7)$$

Comparing Eq. (7) with Eq. (2), one can see that JE holds if and only if



State A

process (a)

process (b)

FIG. 1. State A and state B represent the two states of a one-dimensional ideal gas system in thermal equilibrium with a heat bath. The phase-space domain $\Omega_{\mathrm{eq}}(A)$ of a single gas particle in the system at state A is given by $0 < x < 1$ and $-\infty < p < \infty$, and the phase-space domain $\Omega_{\mathrm{eq}}(B)$ of a single gas particle in the system at state B is given by $0 < x < 2$ and $-\infty < p < \infty$, where x and p denote the position and the momentum of the gas particle, respectively. $\Omega^*_{a(b)}(t_S)$ denotes the phase-space domain at time t_S transformed from $\Omega_{\mathrm{eq}}(A)$ by (a) the adiabatic expansion into vacuum and (b) the adiabatic expansion in which the position of the partition increases from 1 to 2 with a unit speed. The value of t_S is 1.

$$\frac{\displaystyle\int_{\Omega(t_s)} d\Gamma \exp[-\beta H_1(\Gamma)]}{\displaystyle\int_{\Omega_{\mathrm{eq}}(R_1)} d\Gamma \exp[-\beta H_1(\Gamma)]} = 1. \tag{8}$$

Equation (8) indicates that JE is correct for an adiabatic boundary switching process only if the phase-space extension $\Omega^*(t_S)$ of the system with $R = R_1$ at the very end of the adiabatic process coincides with the equilibrium phase-space extension $\Omega_{\mathrm{eq}}(R_1)$ of the system with $R = R_1$. In other words, *JE holds for an adiabatic boundary switching process if the adiabatic process transforms the phase-space domain of the initial equilibrium state to that of the final equilibrium state, at the end of the adiabatic process.*

The validity condition is trivially satisfied when the initial equilibrium state has the same boundary conditions as the final equilibrium state and the adiabatic process changes only the finite potential imposed on the system, not the boundary conditions. However, in many situations, we are interested in the free energy difference between two equilibrium states, one of which satisfies different boundary conditions from the other. In this case, to estimate the free energy difference based on Eq. (1), one has to perform processes that switch the boundary conditions imposed on the system, for which the validity condition of JE may not be always satisfied.

To present the concept of the validity condition of JE concretely, we examine the validity condition of JE for two adiabatic expansion processes of a one-dimensional ideal gas system. As depicted in Fig. 1, in state A, the gas particles of the system are confined in the left-hand side of the partition and the vacuum is in the right-hand side, being in thermal equilibrium with a heat bath. Let the position of the partition be the unit of our length scale. In comparison, state B designates the thermal equilibrium state of the ideal gas system confined in the box with length 2. The difference ΔF_{BA} of free energy of state B from that of state A is well known to be $-\beta^{-1}N \ln 2$ with N being the number of gas particles in the system.

The lower leftmost panel in Fig. 1 shows a part of the phase-space domain $\Omega_{\mathrm{eq}}(A)$ of a single gas particle of the system in state A, which represents every microscopic state of a gas particle satisfying $0 < x < 1$ and $-\infty < p < \infty$ with x and p being the position and the momentum of the gas particle. In comparison, the phase-space domain $\Omega_{\mathrm{eq}}(B)$ of a gas particle of the system in state B represents every microscopic state of the gas particle satisfying $0 < x < 2$ and $-\infty < v < \infty$. The lower middle panel shows how the initial phase-space extension $\Omega_{\mathrm{eq}}(A)$ is transformed at time t_S by the adiabatic expansion into vacuum initiated by removing the partition instantly at time 0 [29]. The mass of the gas particle is chosen to be the unit mass. The figure shows that the phase-space domain $\Omega_a^*(t_S)$ transformed from $\Omega_{\text{eq}}(A)$ by adiabatic expansion into vacuum does not coincide with $\Omega_{\text{eq}}(B)$, and the validity condition of JE is not satisfied for the adiabatic expansion into vacuum.

Recently, it was asserted that the initial state A in this example is not a thermal equilibrium state and this is the reason for the breakdown of JE for the adiabatic expansion into vacuum [30]. Nevertheless, it can be shown that, *for the same initial condition*, the validity condition of JE is satisfied for other adiabatic expansion processes. The figure in the lower rightmost panel shows the phase-space domain $\Omega_b^*(t_S)$ of a single gas particle at time t_S transformed from $\Omega_{\text{eq}}(A)$ by the adiabatic expansion process in which the position of the partition is controlled to increase in a constant speed [29]. One can see that $\Omega_b^*(t_S)$ coincides with $\Omega_{\text{eq}}(B)$; the validity condition of JE is satisfied for the latter adiabatic expansion process. In the model calculation, the speed of the partition is chosen to be the unit speed so that the value of t_S is 1 in the unit system. One can show that the prediction of JE is indeed correct for the latter adiabatic expansion process of an ideal gas system [15].

The adiabatic expansion into vacuum is an example of irreversible spontaneous processes initiated by changing boundary conditions imposed on systems for which, obviously, JE does not hold. Note that the breakdown of JE is not limited to the spontaneous processes. If $|\Omega_{\text{eq}}(X)|$ is the phase-space volume of state X defined by $\int_{\Omega_{\text{eq}}(X)} d\Gamma$, the validity condition of JE cannot be satisfied for any adiabatic process when $|\Omega_{\text{eq}}(A)|$ exists [31] and differs from $|\Omega_{\text{eq}}(B)|$ because of the Liouville theorem [28]. The latter validity condition of JE is useful when we are interested in free energy difference between two configurations of a system, of which phase-space volumes are well defined. Frequently encountered examples for such cases will be published elsewhere.

In this work, we first establish the validity condition of JE for adiabatic boundary switching processes. We illustrate the concept of the validity condition for two adiabatic expansion processes of an ideal gas system, and show that the validity condition of JE is not satisfied for an example of irreversible spontaneous processes. The validity condition of JE cannot be satisfied for any adiabatic boundary switching processes when the phase-space volume of the initial equilibrium state exists and differs from that of the final equilibrium state. That is to say, the free energy difference between two configurational states cannot be correctly estimated by JE for any adiabatic boundary switching process unless the two configurational states have the same phase-space volume.

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