Theoretical test of Jarzynski's equality for reversible volume-switching processes of an ideal gas system

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We present an exact theoretical test of Jarzynski's equality (JE) for reversible volume-switching processes of an ideal gas system. The exact analysis shows that the prediction of JE for the free energy difference is the same as the work done on the gas system during the reversible process that is dependent on the shape of path of the reversible volume-switching process.

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As free energy is one of central concepts in thermodynamics by which we can predict the direction of a spontaneous change between thermodynamic states and equilibrium subpopulation among various states of a system, quantification of the free energy is one of the key issues in many problems of science. In conventional thermodynamics, it is well established that the free energy change of a system is equal to the amount of work done on the system during an isothermal reversible process. However, in practice, it is not easy to perform a reversible process that should be infinitely slow, and not feasible to measure a reversible work directly from any finite time measurement.

Jarzynski's equality (JE) is an equation in modern statistical thermodynamics that offers another method for measuring the free energy difference. It relates the free energy difference ΔF_{BA} between two equilibrium states, A and B, of a system to statistical distribution $P_{A\to B}(W)$ of work W done on the system for an *arbitrary* process connecting the two states [1],

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

with β being the inverse temperature. According to Jarzynski, Eq. (1) has such a wide range of application that it holds irrespective of the shape of the transition path from one state to the other and the rate at which the change occurs along the transition path. As such, JE has drawn much attention since its first derivation. JE was rederived for a variety of model systems [2–6], and verified experimentally for a single RNA stretching process [7,8]. Although difficulty or inefficiency of its practical application has been noted [9–11], currently JE seems accepted as a general thermodynamic equation that holds for a system undergoing an arbitrary process [1–15].

On the other hand, Cohen and Mauzerall recently raised a question about the correctness of JE for a general process, during which distribution of a system can deviate from the Boltzmann distribution and the temperature is not well defined [16,17]. In response to the latter, Jarzynski presented an alternative derivation of Eq. (1) to keep 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 for reversible ones, even though the temperature of the system is not even well defined or deviates from the initial temperature β^{-1} during the parameter switching process [18].

To shed some light on the controversy over the validity of JE, we present an exact theoretical test of Eq. (1) for a reversible volume-switching process of an ideal gas system. The reversible process under our consideration here is a nonadiabatic process distinct from any adiabatic volume switching process in which distribution of the system deviates from the Boltzmann distribution [19]. At any moment of the reversible volume-switching process, the statistical distribution of the system obeys the Boltzmann distribution. In the latter case, there is not an entropy production due to an irreversible relaxation of the system to the equilibrium state and the entropy change dS of the system is equal to $\delta q/T$, with δq being the heat absorbed by the system during an infinitesimal volume change at any temperature T [20].

We find that the predictions of JE for the free energy difference are dependent on the shape of the path of the reversible volume-switching process as shown in Fig. 1. That is to say, the result predicted by JE for the free energy difference is not actually a difference of a state function such as the Helmholtz free energy.

For a typical ideal gas system composed of a number N of

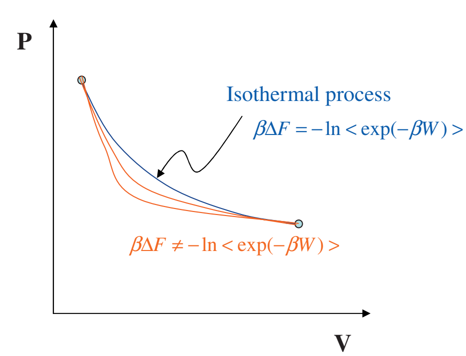

FIG. 1. (Color) Validity of JE for a reversible ideal gas expansion process. ΔF denotes the Helmholtz free energy. The prediction $\Delta F_J[=-\beta^{-1}\ln\langle\exp(-\beta W)\rangle]$ of JE for the Helmholtz free energy difference turns out to be the same as the work, $-\int dVP(V)$, done on the gas system during the reversible volume-switching process. Therefore, ΔF_J is not a difference of a state function such as Helmholtz free energy for the reversible volume-switching process. JE may break down for a nonisothermal reversible volume-switching process.

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noninteracting particles confined in a cylinder by a moving piston, let (T,V) denote the equilibrium thermodynamic state of the system identified by temperature T and the volume V of the system, in which the probability density of a microscopic state of the system obeys the Boltzmann distribution. In conventional statistical thermodynamics, Helmholtz free energy difference $\Delta F(V_1,V_0)[=F(T,V_1)-F(T,V_0)]$ between state (T,V_0) and state (T,V_1) is well known to be $\Delta F(V_1,V_0)=-\beta^{-1}N\ln(V_1/V_0)$, which is the same as the work $W_{rev}(V_1,V_0)$ done on the system during *the isothermal reversible* volume-switching process connecting state (T,V_0) and state (T,V_1).

In comparison, prediction $\Delta F_J(V_1,V_0)$ of JE for the free energy difference between state (T,V_0) and state (T,V_1) is given by $\Delta F_J(V_1,V_0)=-kT\ln\int dW\exp(-W/kT)P_{V_0\to V_1}(W)$, where $P_{V_0\to V_1}(W)$ is the statistical distribution of work W done on the system during an *arbitrary* process in which the value of V is switched from V_0 to V_1. The question we address here is whether $\Delta F_J(V_1,V_0)$ is the same as $\Delta F(V_1,V_0)$ for the reversible volume-switching process of an ideal gas system, irrespective of the shape of the reversible volume-switching path. For the reversible volume-switching process, an exact expression for $\Delta F_J(V_1,V_0)$ can be obtained based on the kinetic theory of gas as follows.

We consider a system of ideal gas particles confined in a cylinder-piston system in three-dimensional space. The direction of the piston motion is set to be the direction of the x axis in a laboratory-fixed Cartesian coordinate. The cylinder head is fixed and its position is chosen to be zero in the x axis. The position l of the piston along the x axis changes from L_0 to L_1 during the reversible volume switching process. Throughout the piston motion, the surface of the piston is in parallel with the yz plane in the laboratory fixed Cartesian coordinate.

According to the kinetic theory of gas, the force F exerted on the piston by the gas particles is given by $F=\Sigma_{j=1}^{N}\frac{mv_{x,j}^2}{l}=\frac{m}{l}\xi$ with $\xi\equiv\Sigma_{j=1}^{N}v_{x,j}^2$, where $v_{x,j}$ denotes the x component of the velocity vector of the j-th gas particle. During the reversible volume-switching process, the probability distribution of $v_{x,j}$ is given by Gaussian $G(v_{x,j})=\left(\frac{1}{2\pi\sigma_l^2}\right)^{1/2}\exp\left(-\frac{v_{x,j}^2}{2\sigma_l^2}\right)$, with $\sigma_l^2=k_BT(l)/m$. Here, k_B and $T(l)$ denote, respectively, the Boltzmann constant and the temperature of the gas system with the piston being at l. As ξ is a stochastic variable, so is the force F on the piston exerted by the gas particles. The probability distribution $P(\xi)$ of ξ, which is the sum of identically distributed independent squared Gaussian variables, is well known to be the gamma distribution [21],

$$P(\xi)=\frac{\xi^{N/2-1}\exp\left(-\frac{\xi}{2\sigma_l^2}\right)}{\Gamma(N/2)(2\sigma_l^2)^{N/2}}. \tag{2}$$

Note that $P(\xi)$ depends on the position l of the piston as σ_l^2 or the temperature $T(l)$ of the gas system does.

To calculate $\langle\exp(-\beta W)\rangle[\equiv\int dW\exp(-W/kT)P_{V_0\to V_1}^{\mathrm{rev}}\times(W)]$, we divide interval (L_0,L_1) into a large number M of small subinterval $(l_k,l_k+\Delta l)$, where l_k is given by $l_k=L_0+k\Delta l$ with $\Delta l=(L_1-L_0)/M$. The amount of work done $-W_k$ by the system during the expansion from $L=l_k$ to $L=l_k+\Delta l$ is given by

$$-W_k=\int_{l_k}^{l_k+\Delta l}F(l)dl=m\ln\left(1+\frac{\Delta l}{l_k}\right)\xi_k$$
$$=\xi_k\frac{m}{l_k}\Delta l+O\left[\left(\frac{\Delta l}{l_k}\right)^2\right], \tag{3}$$

given that the value of stochastic variable ξ is given by $\xi=\xi_k$ during the infinitesimal volume-switching process. Therefore, in the small $\Delta l/l_k$ limit, the total work W done on the system during the expansion from $L=L_0$ to $L=L_1$ is given by $W=\Sigma_{k=0}^{M-1}W_k=-m\Delta l\Sigma_{k=0}^{M-1}\xi_k/l_k$, given that $\xi=\xi_k$ during the infinitesimal volume is switching from $L=l_k$ to $L=l_k+\Delta l$ $(1\leq k\leq M-1)$. As we know the probability distribution of ξ_k, we can calculate $\langle\exp(-\beta W)\rangle$ as

$$\langle\exp(-\beta W)\rangle=\lim_{\Delta l\to 0+}\int_0^\infty d\xi_0 d\xi_1\cdots d\xi_{M-1}\times\exp\left(\beta m\Delta l\sum_{k=0}^{M-1}\frac{\xi_k}{l_k}\right)\prod_{k=0}^{M-1}P_k(\xi_k)$$
$$=\lim_{\Delta l\to 0+}\prod_{k=0}^{M-1}\left[\int_0^\infty d\xi P_k(\xi)\exp\left(\frac{\beta m\Delta l}{l_k}\xi\right)\right], \tag{4}$$

where $M=(L_1-L_0)/\Delta l$ and $P_k(\xi)$ denotes the probability distribution given by Eq. (2) with $\sigma_l^2=k_BT(l_k)/m$. The characteristic function of $P_k(\xi)$ appearing in the bracket of Eq. (4) can be obtained exactly, and, from Eq. (4), we obtain

$$\ln\langle\exp(-\beta W)\rangle=\lim_{\Delta l\to 0+}N\sum_{k=0}^{M-1}\frac{\Delta l}{l_k}\frac{T(l_k)}{T_0}=N\int_{L_0}^{L_1}\frac{dl}{l}\frac{T(l)}{T_0}. \tag{5}$$

Changing the integration variable from l to $V(=Al)$ with A being the area of the piston, one can rewrite Eq. (5) as

$$\ln\langle\exp(-\beta W)\rangle=\frac{1}{kT_0}\int_{V_0}^{V_1}dVP(V), \tag{6}$$

where $P(V)$ denotes the pressure of the ideal gas system with volume V, i.e., $P(V)=NkT(l)/V$. Equation (6) directly leads to

$$\Delta F_J(V_1,V_0)\equiv-kT_0\ln\langle\exp(-\beta W)\rangle=-\int_{V_0}^{V_1}dVP(V). \tag{7}$$

Equation (7) tells us that $\Delta F_J(V_1,V_0)$ for the reversible volume-switching process is nothing but the average work done on the system during the reversible volume-switching process. Therefore, $\Delta F_J(V_1,V_0)$ is dependent on a shape of the path of the volume-switching process or a functional form of $P(V)$. This is illustrated in Fig. 1.

In the present work, we present an exact theoretical test of

JE for the reversible volume-switching processes of an ideal gas system. We find that the prediction $\Delta F_J(V_1, V_0)$ of JE for the free energy difference is nothing but the average work done on the system during the reversible volume-switching process. Since $\Delta F_J(V_1, V_0)$ is dependent on the functional form of $P(V)$ or the shape of the volume-switching path, $\Delta F_J(V_1, V_0)$ is not the difference of a state function such as Helmholtz free energy for the reversible volume-switching process of an ideal gas. We finish this work by noting that this is not the singular example for the breakdown of JE, which will be published elsewhere.

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