A possible generalized form of Jarzynski equality

Z. C. Tu\textsuperscript{1} and Zicong Zhou\textsuperscript{1,2,*}

\textsuperscript{1}Department of Physics, Tamkang University, Tamsui 25137, Taiwan
\textsuperscript{2}Physics Division, National Center for Theoretical Sciences at Taipei, National Taiwan University, Taipei 10617, Taiwan

The crucial condition in the derivation of the Jarzynski equality (JE) from the fluctuation theorem is that the time integral of the phase space contraction factor can be exactly expressed as the entropy production resulting from the heat absorbed by the system from the thermal bath. For the system violating this condition, a more general form of JE may exist. This existence is verified by three Gedanken experiments and numerical simulations, and may be confirmed by the real experiment in the nanoscale.

PACS numbers: 05.70.Ln

I. INTRODUCTION

Consider a classic system in contact with a thermal bath at constant temperature, and at some time interval, the system is driven out of the equilibrium by an external field. Two groups of equalities are proved to still hold for this system. One is the fluctuation theorem (FT) \textsuperscript{[1, 2, 3, 4, 5]} which reflects the probability of violating the Second Law of Thermodynamics in the non-equilibrium process. Another is the Jarzynski equality (JE) \textsuperscript{[6, 7, 8]} which ensures us to extract the free energy difference between two equilibrium states from the non-equilibrium work performed on the system in the process between these two states. The quantum versions \textsuperscript{[9, 10, 11]} and experimental verifications \textsuperscript{[12, 13]} of JE are also presented. After it was proposed in 1997, the JE has aroused some controversy \textsuperscript{[14, 15, 16, 17, 18, 19, 20, 21]}, in which two typical gedanken experiments are quite interesting and we summarize them as follows.

Experiment 1: As shown in Fig. 1A, imagine that a closed container, in contact with a thermal bath at constant temperature, is divided into two compartments by a perfectly thin, frictionless but heavy enough piston, and imagine that one compartment initially contains ideal gas of \(N\) (large enough) particles in equilibrium at temperature \(T\), while another compartment is empty. At time \(t_1\), we remove the pins \(P_1\) and \(P_2\), and give the piston a large initial velocity \(v_p\). The gas will fill the whole container with the movement of the piston. After a long time relaxation, the system arrives at an equilibrium state at time \(t_2\).

Experiment 2: As shown in Fig. 1B, imagine that a closed container, in contact with a thermal bath at constant temperature, is divided into two compartments by a perfectly thin and frictionless plate, and imagine that one compartment initially contains ideal gas of \(N\) particles in equilibrium at temperature \(T\), while another compartment is empty. At time \(t_1\), we pull up the plate, and the gas will expand and fill the whole container. After a long time relaxation, the system reaches an equilibrium state at time \(t_2\). Here \(t_1\) and \(t_2\) do not require to have the same values as those in experiment 1.

Assume the initial volume of the gas to be \(V_1\), the whole volume of the container to be \(V_2\). There are two common points in the above two experiments: (i) The macroscopic work in the expansion process is vanishing (i.e. \(W = 0\)); (ii) After the systems arriving at the final equilibrium states, the free energy difference is \(\Delta F = -NT\ln(V_2/V_1)\). The important difference between them is that the microscopic work, \(w\), in the first experiment is non-vanishing although the macroscopic one \(W = \langle w \rangle = 0\) for \(v_p \rightarrow \infty\) \textsuperscript{[18]}, while \(w = 0\) for the second one. Due to this difference, the JE holds in the first experiment (i.e. \(e^{-\beta w} = e^{-\beta \Delta F} = V_2^N/V_1^N\) with \(\beta = 1/T\) \textsuperscript{[18]} but fails in the second one \((e^{-\beta w} = 1, e^{-\beta \Delta F} = V_2^N/V_1^N)\). Jarzynski and Crooks argued that the JE fails because the initial distribution function is not canonical in the second case \textsuperscript{[17, 22]}. We would like to consider this problem from another point of view: the initial distribution function is still canonical but a more underlying reason makes the JE fail. In other words, there is a more general form of JE. The rest of this paper is focus on this topic and organized as follows: In Sec. III we sketch the derivation of JE from the FT and emphasize that the condition of adiabatic incompressibility \textsuperscript{[23]} is crucial to this derivation. In fact, Jarzynski’s original proof \textsuperscript{[6, 17]} also requires this condition. In Sec. III we

*Electronic address: zzhou@mail.tku.edu.tw
check whether this condition holds or not in the above two Gedanken experiments and put forward a generalized JE, Eq. (15). The third Gedanken experiment intermediating between the above two experiments is proposed and the corresponding numerical simulation verifies the existence of generalized JE. In Sec. IV we give further discussions and a brief summary.

II. DERIVATION OF JE FROM FT

An important relation between the FT and JE is that the JE can be derived from the FT for time reversible stochastic or deterministic dynamics. Here we look through the main idea of Evans’ derivation. The phase space of the $N$ particle system is denoted by $\{q,p\}$, where $q = \{q_1, q_2, \ldots, q_N \}$ and $p = \{p_1, p_2, \ldots, p_N\}$ represent the configuration and momentum spaces, respectively. The phase space contraction factor $\Lambda = 2\beta \frac{\partial q}{\partial q} + 2\beta \frac{\partial p}{\partial p}$ depends on the detail dynamics of the system.

Assume that the classic system contacts with a thermal bath at constant temperature $T$, and that it stays at an equilibrium state for $t \leq t_1$. Take a microscopic state $A_1$ corresponding to this equilibrium state. From time $t_1$ to $t_2$, we switch on an external field denoted by a parameter $\lambda$ varying from $\lambda_1$ to $\lambda_2$, and drive the system out of equilibrium. After a sufficient relaxation with fixed $\lambda_2$, the system arrives at the other equilibrium state at time $t_2$. Correspondingly, the microscopic state evolves to $A_2$. From time $t_1$ to $t_2$, the entropy production function along the microscopic path $\gamma(t)$ linking the states $A_1$ and $A_2$ is expressed as

$$s[\gamma(t)] = \ln(f_1/f_2) - \int_{t_1}^{t_2} \Lambda[\gamma(t)]dt, \quad (1)$$

where $f_1$ and $f_2$ are the equilibrium distribution functions at time $t_1$ and $t_2$, respectively. One can prove the FT: $p_F(s)/p_R(-s) = e^s$, where $p_F(s)$ and $p_R(s)$ represent the probability distributions of the entropy production function taking value $s$ along the microscopic path $\gamma(t)$ and its time-reversal path, respectively. If averaging $e^{-s}$ for all paths beginning from all microscopic states corresponding to the macroscopic equilibrium state at time $t_1$, we have

$$\langle e^{-s} \rangle = \int e^{-s} p_F(s)ds = \int p_R(-s)ds = 1. \quad (2)$$

This is nothing but the Kawasaki identity or Hatano-Sasa equality.

If taking canonical distributions for the initial state at time $t_1$ and the final state at time $t_2$, we have $f_1 = e^{\beta(F_1 - H_1)}$ and $f_2 = e^{\beta(F_2 - H_2)}$, where $F_1$ and $F_2$ are the free energies of the system at time $t_1$ and $t_2$ while $H_1$ and $H_2$ are the Hamiltonians of the system at time $t_1$ and $t_2$. Assume that the effective dynamics of the system can be expressed as

$$\dot{q}_n = \frac{\partial H}{\partial p_n}, \quad (3)$$

$$\dot{p}_n = -\frac{\partial H}{\partial q_n} - \alpha[\gamma(t)]p_n, \quad (4)$$

where $\alpha[\gamma(t)]$ is the thermostat multiplier ensuring the kinetic temperature of the system to be fixed at $T$, and it reflects the heat exchange between the system and the thermal bath. $H$ is the $\lambda$-dependent Hamiltonian. Under the above dynamics, the phase space contraction factor is derived as $\Lambda[\gamma(t)] = -3N\alpha[\gamma(t)]$ and its integral from time $t_1$ to $t_2$ is just the entropy production induced by the heat $\{q[\gamma(t)]\}$ absorbed by the system from the thermal bath along the microscopic path $\gamma(t)$ linking the states $A_1$ and $A_2$, i.e.,

$$\int_{t_1}^{t_2} \Lambda[\gamma(t)]dt = \beta q[\gamma(t)]. \quad (5)$$

This equation is crucial to the derivation of JE from the FT. Thus the entropy production function, Eq. (1), is transformed into

$$s[\gamma(t)] = \beta(w[\gamma(t)] - \Delta F), \quad (6)$$

where $w[\gamma(t)] = H_2 - H_1 - q[\gamma(t)]$ (microscopic energy conservation) is the work performed on the system along the microscopic path $\gamma(t)$. $\Delta F = F_2 - F_1$ is the free energy change of the system from time $t_1$ to $t_2$. Assume that $w[\gamma(t)]$ takes value $w$ when $s[\gamma(t)]$ has value $s$, and notice that there is no work from time $t_2$ to $t_2$ because the parameter $\lambda$ is unchanged at this time interval. From Eqs. (2) and (6) we easily arrive at the JE,

$$\langle e^{-\beta w} \rangle = e^{-\beta \Delta F}. \quad (7)$$

We emphasize again that Eq. (15), the time integral of the phase space contraction factor exactly expressed as the entropy production resulting from the heat absorbed by the system from the thermal bath, is the crucial point in the derivation of the JE from the FT. Remember that the phase space contraction factor depends on the microscopic dynamics. If the dynamics satisfies the condition of adiabatic incompressibility, i.e., the phase space contraction factor depends merely on the thermostat multiplier, Eq. (15) holds and the JE is a natural corollary of the FT.

III. GENERALIZED JE

Now, we check whether the condition of adiabatic incompressibility holds for the systems mentioned in the above two experiments.

For the first experiment, because the initial velocity distribution obeys the Maxwell distribution, some particles with velocity larger than $v_p$ will strike the piston and then bounce fully but $v_p$ is unchanged because the mass of the piston is much larger than the total mass of the
particles that collide with it. In each bounces, the piston will do a small work on the gas system. Lua et al. have proved that the mean work is vanishing but the JE still holds for \( v_p \to \infty \) [18]. The effective dynamics can be expressed as:

\[
\begin{align*}
\dot{q}_n &= p_n/m + \dot{R} \cdot q_n, \\
\dot{p}_n &= -\dot{R} \cdot p_n - \alpha [\gamma(t)] p_n, \\
\dot{V} &= V \dot{r},
\end{align*}
\]

(8) where \( m \) is the mass of each particle, the matrix \( \dot{R} = ((\dot{r}, 0, 0)^t, (0, 0, 0)^t, (0, 0, 0)^t) \), and \( \dot{r} \) the time-dependent volume expansion ratio with vanishing value except at the time interval between \( t_1 \) and \( t_2 \). Here the volume \( V \) plays the role of the parameter \( \lambda \) in Evans’ derivation of JE from the FT. The phase space contraction factor is found to be \( \Lambda[\gamma(t)] = -3N\alpha[\gamma(t)] \). Hence Eq. (10) as well as the condition of adiabatic incompressibility still holds and so the JE is valid in this experiment.

The effective term \(-\dot{R} \cdot p_n\) in Eq. (9) reflects the collisions between the piston and particles. For the second experiment, the volume expansion has no direct effect on the momentum of the particles. Thus the term \(-\dot{R} \cdot p_n\) should be removed, and Eq. (9) should be replaced by:

\[
\dot{p}_n = -\alpha[\gamma(t)] p_n,
\]

(11) but Eqs. (8) and (10) are kept intact in the effective dynamics of the second experiment. Consequently, we obtain the phase space contraction factor \( \Lambda[\gamma(t)] = N\dot{r} - 3N\alpha[\gamma(t)] \) and its integral from time \( t_1 \) to \( t_2 \):

\[
\int_{t_1}^{t_2} \Lambda[\gamma(t)] dt = N \ln(V_2/V_1) + \beta q[\gamma(t)],
\]

(12) where we have used \( \int_{t_1}^{t_2} dt = \int_{V_1}^{V_2} d(\ln V) = \ln(V_2/V_1) \) and \(- \int_{t_1}^{t_2} 3N\alpha[\gamma(t)] dt = \beta q[\gamma(t)] \). Obviously, Eq. (10) as well as the condition of adiabatic incompressibility does not hold in this experiment and so the JE fails. However, following the derivation from Eq. (10) to Eq. (11), and replacing Eq. (6) by Eq. (12), we obtain a generalized equality beyond JE:

\[
\langle e^{-\beta w} \rangle = e^{-\beta \Delta F},
\]

(13) where \( w = 0 \) and \( \Delta F = -N\ln(V_2/V_1) \) in the second experiment, the above equation holds although the original form of JE fails.

Through the above discussions, we know that the JE holds in the first experiment but fails in the second one. The underlying reason is that these two experiments have different microscopic dynamics: One satisfies the condition of adiabatic incompressibility but another does not. Especially, the second experiment suggests that a more general form of JE should exist, and we would like to consider this possibility. Enlightened by Eq. (12), we divide the time interval of the phase space contraction factor into two parts: One is \( \beta q[\gamma(t)] \), the entropy production resulting from the heat absorbed by the system from the thermal bath; Another is the entropy induced by the change of the external parameter and expressed as \( \beta \sigma \). That is,

\[
\int_{t_1}^{t_2} \Lambda[\gamma(t)] dt = \beta(q[\gamma(t)] + \sigma).
\]

(14) Following the derivation from Eq. (6) to Eq. (7) and replacing Eq. (6) by Eq. (14), we arrive at a generalized JE:

\[
\langle e^{-\beta (w - \sigma)} \rangle = e^{-\beta \Delta F}.
\]

(15) which is transformed into

\[
\langle e^{-\beta w} \rangle = e^{-\beta (\Delta F + \sigma)}
\]

(16) if \( \sigma \) depends only on the value of the external parameter at time \( t_1 \) and \( t_2 \), but not explicitly on the microscopic pathes. We conjecture that \( \sigma = 0 \) for most macroscopic system and then Eq. (15) is degenerated to the original JE. \( \sigma \neq 0 \) only in some very special systems and correspondingly the original JE fails. For example, \( \sigma = N\ln(V_2/V_1) \neq 0 \) in the second experiment.

Noticing that the mass of the piston in the first experiment is infinitely large. If it has an infinitesimal value, this system is equivalent to that in the second experiment because the collisions between particles and the piston has no effect on the momentum of the particles such that the particles do not feel the existence of the piston. It is interesting to discuss the intermediate case between the above two limits. Let us consider the third gedanken experiment where the experimental setup is the same as the first one except the mass \( M \) of the piston is finite. At time \( t_1 \), we remove the pins \( P_1 \) and \( P_2 \), and the gas will push the piston to the right wall of the container. Once the piston contacts with the wall, it adheres to the wall without bounce. After a long time relaxation, the system arrives at an equilibrium state at time \( t_2 \). When we write the effective dynamics, Eq. (10) should be replaced by

\[
\dot{p}_n = -g \dot{R} \cdot p_n - \alpha[\gamma(t)] p_n,
\]

(17) but Eqs. (8) and (10) are unchanged, where \( g \) is a function of \( m \) and \( M \) taking values between 0 and 1. \( g \) may also depend on \( N \) and \( V_2/V_1 \) because the equations of motion are just the effective ones. With this dynamics, we obtain \( \sigma = (1 - g)N\ln(V_2/V_1) \) from Eq. (14). Thus Eq. (16) gives

\[
\ln \langle e^{-\beta w} \rangle = gN \ln(V_2/V_1).
\]

(18) In order to recover the former two experiments, \( g \) must satisfy \( g \to 1 \) for \( M \to \infty \) and \( g \to 0 \) for \( M \to 0 \). To determine \( g \), we do numerical simulations for ideal gas with different \( N \) (from 1000 to 10000), \( M/m \) (from 0.2 to 1000), and \( V_2/V_1 \) (from 1.1 to 1.9), and calculate \( g \) by Eq. (18). To obtain the ensemble average \( \langle e^{-\beta w} \rangle \), we take 500 systems [28] with different initial microstates corresponding to the same macroscopic equilibrium state.
We find that \( g \) depends only on the combined variable \( x = M/[mN \ln(V_2/V_1)] \). The relation between \( g \) and \( x \) is shown in Fig. 2. For very small \( x \), the numerical data (the inset of Fig. 2) can be fit well by a line \( \ln g = 0.93 + 0.88 \ln x \). That is, \( g \) has the asymptotic form \( g \sim (2.87x)^{0.88} \) for \( x \to 0 \) (corresponding to \( M \to 0 \)). Based on this asymptotic form, noting that \( g \to 1 \) for \( x \to \infty \) (corresponding to \( M \to \infty \)), we conjecture that \( g \) has the form

\[
    g = \left[ \frac{(2.87x)^\nu}{1 + (2.87x)^\nu} \right]^{0.88/\nu}.
\]

(19)

Our numerical data is indeed fitted well by this form. The fitting curve is the dash line in Fig. 2 with the parameter \( \nu = 0.53 \). We use this fitting parameter and Eq. (19) to predict \( g = 0.8795 \) for \( M/m = 4000 \), \( N = 1000 \) and \( V_2/V_1 = 1.1 \), which is quite close to the value 0.8846 obtained from the numerical simulations. This fact implies that our conjecture is reasonable although we cannot intuitively figure out the physical meaning of the numbers 2.87, 0.88 and \( \nu = 0.53 \) in Eq. (19).

![FIG. 2: Numerical results and fitting curve for the relation between \( g \) and \( x \) where \( x \) represents \( M/[mN \ln(V_2/V_1)] \). The squares come from numerical simulations. The result for small \( x < 0.01 \) is magnified in the inset of the figure.](image)

For the macroscopic gas system except for the case in the second experiment, we have in general \( M \gg mN \ln(V_2/V_1) \), so \( g \sim 1 \). Hence \( \sigma = 0 \) and Eq. (15) is degenerated into the JE. Therefore the departure from the JE should occur at the small scale system with finite \( M \) but still large enough \( N \). For example, our result might be verified for the inert gas in a very long single-walled carbon nanotube (SWNT) as shown in Fig. 3. One end of the nanotube is closed while another is opened, and a buckyball \( C_{60} \) is put in it as a piston. Select the proper nanotube, for example (10,10) nanotube, and the gas with large radius, for example Ar, such that \( C_{60} \) can prevent the gas from escaping from the interstice between \( C_{60} \) and the nanotube. A small SWNT can be used to fix the initial position of \( C_{60} \). At some time, pull the small SWNT outward to another position quickly. The gas will push \( C_{60} \) to the new position, and one can measure the velocity of \( C_{60} \) when it arrives at the new position and calculate the corresponding work. Repeat this process for many times and calculate the value of \( -\ln(e^{-\beta w})/\beta \). Comparing this value with the free energy obtained from theoretical calculation, one can obtain the value of \( \sigma \). If \( \sigma \neq 0 \), the JE is violated and a generalized JE should exist.

![FIG. 3: Schematic figure of the experimental setup (in vacuum).](image)

**IV. DISCUSSION AND CONCLUSION**

It is useful to discuss some questions before concluding this paper.

(i) If the volume of the thermal system is fixed but other parameter varies such as in the single molecule mechanical experiments [12, 13], JE always holds because the effective dynamics can be expressed as Eqs. (3) and (4). Generally speaking, one may not construct a parameter-dependent Hamiltonian and express the effective dynamics as Eqs. (3) and (4) if the volume changes. JE may be violated in this case. However, JE still holds if one can control the ratio of volume change because the particles fully bounce when they collide with the piston in this case, i.e., controlling the ratio is equivalent to \( M \to \infty \).

(ii) The derivation of JE from FT does not require the thermostat for the whole process from \( t_1 \) to \( t_2 \). For \( t \leq t_1 \), the system is at an equilibrium state in contact with a thermal bath at temperature \( T \). The external field is switched on from time \( t_1 \) to \( t_2 \). The contact with a thermal bath is unnecessary in this stage (i.e. no heat exchange, \( q = 0 \)). After that, the external field is fixed and let the system contact with the same thermal bath. At time \( t_2 \), the system reaches the equilibrium state through a long time relaxation. The thermostat is merely required in this stage (from \( t_2 \) to \( t_2 \)). In fact, this requirement is the same as the original proof of JE [8], which ensures us to calculate \( \langle e^{-\beta w} \rangle \) easily from numerical simulations.

(iii) Equations (8), (10), (11), and (17) are the effective dynamics of thermal system with the volume changes. Here the “effective” means that the dynamics is not the real microscopic motion (of course, the real motion for each particle still abides by Newtonian laws), while it is the image mapping from the real motion and can give the correct thermodynamic properties of the system through Molecule Dynamics Simulations [23]. The effective term
Argument that the term \( \mathbf{R} \cdot \mathbf{p}_n \) in these equations reflects the collisions between the piston and particles. If the particle fully bounces (i.e. \( M \to \infty \)), the coefficient before this term is 1. If the particle do not bounce (i.e. \( M \to 0 \)), the coefficient is 0. For finite \( M \), the coefficient should intermediate between 0 and 1. We use \( g \) to express this coefficient in Eq. (17). In the second experiment, \( V = V_1 \) for \( t \leq t_1 \), but \( V = V_2 \) for \( t = t_1^+ \). Thus \( \dot{r} \) is a \( \delta \)-function, which implies \( q_n \) changes discontinuously. This is impossible for real dynamics but permitted in the effective dynamics. Our numerical simulation is performed for real dynamics (Newtonian mechanics) and the results reveal that \( g \to 1 \), \( \sigma \to 0 \) thus JE holds for \( M \to \infty \), and that \( g \to 0 \Rightarrow \sigma = N \dot{T} (V_2/V_1) \) thus Eq. (18) holds for \( M \to 0 \). That is, the numerical results obtained from the real dynamics are the same as those derived from the effective dynamics Eqs. (8)–(11), which suggests that the effective dynamics is consistent with the real dynamics and our argument that the term \( -\mathbf{R} \cdot \mathbf{p}_n \) reflects the collisions between the piston and particles is reasonable.

In summary, we have pointed out that the crucial point in the derivation of the JE from the FT is that the time integral of the phase space contraction factor is exactly expressed as the entropy production resulting from the heat absorbed by the system from the thermal bath, i.e. the dynamics of the system satisfies the condition of adiabatic incompressibility. For the system violating this condition, a more general version of JE, Eq. (15), exists. In the future, it is interesting to find some real systems which makes \( \sigma \neq 0 \). Deriving the analytic expression of the quantity \( \sigma \) is another challenge because \( \sigma \) might be system-dependent. These researches will enhance our understanding to non-equilibrium statistics.

Acknowledgements

We are grateful to the useful comments from Prof. C. Jarzynski, U. Seifert, M. Bier and Dr. Gomez-Marin. This work is supported by the National Science Council of Republic of China under grant no. NSC 94-2119-M-032-010 and NSC 94-2816-M-032-003.

References

[1] D. J. Evans, E. G. D. Cohen and G. P. Morriss, Phys. Rev. Lett. 71, 2401 (1993).
[2] G. Gallavotti and E. G. D. Cohen, Phys. Rev. Lett. 74, 2694 (1995).
[3] D. J. Evans and D. J. Searles, Adv. Phys. 51, 1529 (2002).
[4] G. M. Wang, E. Sevick, E. Mittag, D. J. Searles and D. J. Evans Phys. Rev. Lett. 89, 050601 (2002).
[5] U. Seifert, J. Phys. A: Math. Gen. 37, L517 (2004); Phys. Rev. Lett. 95, 040602 (2005).
[6] C. Jarzynski, Phys. Rev. Lett. 78, 2690 (1997); Phys. Rev. E 56, 5018 (1997).
[7] G. E. Crooks, J. Stat. Phys. 90, 1481 (1998).
[8] A. B. Adib, Phys. Rev. E 71, 056128 (2005).
[9] S. Yukawa, J. Phys. Soc. Jap. 69, 2367 (2000).
[10] S. Mukamel, Phys. Rev. Lett. 90, 170604 (2003).
[11] W. D. Roeck and C. Maes, Phys. Rev. E 69, 026115 (2004).
[12] G. Hummer and A. Szabo, Proc. Nat. Acad. Sci. (USA) 98, 3658 (2001).
[13] J. Liphardt, S. Dumont, S. B. Smith, I. Tinoco and C. Bustamante, Science 296, 1832 (2002).
[14] E. G. D. Cohen and D. Maurerall J. Stat. Mech., P07006 (2004).
[15] D. H. E. Gross, cond-mat/0505721.
[16] J. Sung, cond-mat/0506214 cond-mat/0510119.
[17] C. Jarzynski, J. Stat. Mech., P09005 (2004); cond-mat/0509344.
[18] R. C. Lua and A. Y. Grosberg, J. Phys. Chem. B 109, 6805 (2005).
[19] I. Bena, C. van den Broeck and R. Kawai Europhys. Lett. 71, 879 (2005).
[20] M. Bier, cond-mat/0510270.
[21] S. Presse and R. Silbey, J. Chem. Phys. 124, 054117 (2006).
[22] G. E. Crooks, Ph.D. thesis (UC Berkeley, 1999).
[23] D. J. Evans and G. P. Morriss, Statistical Mechanics of Nonequilibrium Liquids (Academic Press, London, 1990).
[24] G. E. Crooks, Phys. Rev. E 60, 2721 (1999).
[25] D. J. Evans, Mol. Phys. 101, 1551 (2003).
[26] T. Yamada and K. Kawasaki, Prog. Theor. Phys. 38, 1031 (1967).
[27] T. Hatano and S. Sasa, Phys. Rev. Lett. 86, 3463 (2001).
[28] We also calculate the ensemble average by using 100 systems and obtain the similar results.