Rapid Communication

Failure of free energy relation under non-Markovian heat bath temperature change*

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We investigate the free energy relation for a system contacting with a non-Markovian heat bath and find that the validity of the relation sensitively depends on the non-Markovian memory effect, which is especially related to the initial preparation effect. This memory effect drives the statistical distribution of the system out of the initial preparation, even if the system starts from an equilibrium state. This leads to the violation of the free energy relation. A possible way of eliminating this memory effect is proposed.

Keywords: free energy relation, non-Markovian heat bath, initial preparation effect

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1. Introduction

Equilibrium properties of a system can be well understood by the Boltzmann–Gibbs statistics, but the behavior of systems far from equilibrium is still a challenging topic. A recently developed theorem called the Jarzynski free-energy equality (JE)[1,2] provides a helpful tool for exploring this non-equilibrium region. The JE establishes a relationship between an ensemble average of the work and the free energy change, if the system is initially in equilibrium by contacting a heat bath for a sufficiently long time. The system has a controllable external parameter λ. By changing the parameter from the initial value λ_0 to λ_τ following a protocol $\lambda(t)$ in a time interval $[0,\tau]$, the work done on each individual micro process, which is initially chosen from the equilibrium distribution, will have a specific relationship with the macro free energy change. The JE is written as

$$\langle \mathrm{e}^{-\beta W}\rangle = \mathrm{e}^{-\beta\Delta F}, \tag{1}$$

where $\beta = 1/k_{\mathrm{B}}T$ is the reciprocal of the heat bath temperature T establishing the initial equilibrium with k_{B} being the Boltzmann constant, $\langle\cdot\rangle$ means an ensemble average, W is the work performed in each individual process, and $\Delta F = F_{\mathrm{final}} - F_{\mathrm{initial}}$ is the free-energy difference of the system between the final and initial states at an inverse temperature β. The only restriction of the JE is that the processes should be initially chosen from an equilibrium distribution, but do not need to stay in the equilibrium state during the evolution, so that the general non-equilibrium processes still satisfy the relationship, which makes the JE quite useful in the non-equilibrium field.

The original JE is derived for a system that remains in contact with the initial heat bath during the dynamical process. The connection with a heat bath implies a heat transfer to or from the system. However, the transferred heat does not explicitly appear in the JE expression because it happens to be eliminated in this unique heat bath temperature situation. A generalized relationship called the temperature change free energy equality (TCFE) was recently derived for the purpose of describing the heat influence. The TCFE considers a similar situation to the JE, which also starts from the initial equilibrium distribution and evolves under the external parameter change protocol $\lambda(\tau)$ by connecting with the initial heat bath. The only difference of the above two processes is that in TCFE the initial heat bath (with

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an inverse temperature β_1) is replaced in the period $[t_a, t_b]$ $(0 \le t_a \le t_b \le \tau)$ by another heat bath (inverse temperature β_2). Then the influence of the heat can be clearly written as

$$\langle \mathrm{e}^{-\beta_1 W} \mathrm{e}^{-(\beta_1-\beta_2)Q_2} \rangle = \mathrm{e}^{-\beta_1 \Delta F}, \tag{2}$$

where β and W are the same as those defined in Eq. (1), ΔF is the free-energy difference of the system at inverse temperature β_1, and Q_2 is the heat transferred from heat bath β_2 to the system. The TCFE is fit for both equilibrium and non-equilibrium processes as the original JE does, but it provides a more general relation that builds a connection between the work, the heat, and the free energy difference (When $\beta_2 = \beta_1$, the TCFE is exactly the same with the JE).

The proofs of both JE and TCFE require an assumption of the Markovian process. Prevailingly the Markovian assumption is only an idealization in the real physical world, and it gives a good approximation only when the time scale of the heat bath is much shorter than that of the system (Here, we assume the system itself is simple and has no memory of its own history). For example, in the phenomenon of the Brownian motion, if the mass of a Brownian particle is much larger than that of the surrounding fluid molecules, the time scale of the fluid molecules (so the correlation of successive impacts) is much shorter than that of the Brownian particle, then the Brownian motion can be treated as a Markovian process, which has no memory of history.[3,4] However, the time scale of the heat bath is not necessary to be shorter than that of the system. This naturally brings forth the question of the validity of the JE and TCFE in non-Markovian processes.

A typical non-Markovian process keeps all the memory of the previous history, and one single initial state cannot uniquely determine the subsequent propagation. A natural choice is to prepare the system initially with no past memory and past correlations to the heat bath. The initial preparation influences the evolution of the system for a finite time, then the system can reach a stationary distribution. Note that even if the stationary distribution is chosen as the initial condition, the evolution of the system at the beginning is still different from that in the long-time relaxation stationary region, which is quite different from the Markovian process.[5−7]

The existence of a long-time stationary distribution that needs to be exactly the equilibrium distribution is the crucial point for the previous investigations on the validity of the JE under a non-Markovian heat bath,[8,9] where it was found that the JE is valid. However, the influence of initial preparations has not been considered. For the JE, the initial preparation may not be important because the initial equilibrium distribution is reached by connecting the system with the heat bath for a sufficiently long time, and the effect of the initial preparation vanishes after this long-time relaxation. Nevertheless for the TCFE, as the heat bath is switched at some time in the dynamical process, the initial preparation effect for the system and the second heat bath cannot be ignored, which should bring difference to the TCFE validity (A similar problem is expected for the JE if we skip the long-time initial relaxation and detect the validity from a "put-by-hand" equilibrium distribution immediately).

2. Numerical model

We consider a simple Brownian particle in a harmonic potential as our model to test the validity of the JE and TCFE. The motion of the Brownian particle (mass is rescaled to one) is properly described by a generalized Langevin equation

$$\ddot{x}(t) = -\frac{\mathrm{d}V(x)}{\mathrm{d}x} - \int_0^t \mathrm{d}t' \gamma(t-t')\dot{x}(t') + G(t). \tag{3}$$

Here $V(x) = \lambda x^2/2$ is the harmonic potential with λ being the external parameter, which changes from λ_0 to λ_τ following a protocol $\lambda(t)$ in the time interval $[0, \tau]$. The term $G(t)$ is a colored Gaussian noise with zero mean and exponential correlation function, as already studied in the Ornstein–Uhlenbeck process:

$$\langle G(t) \rangle = 0, \ \langle G(t)G(t') \rangle = \frac{D}{\tau_c} \mathrm{e}^{-|t-t'|/\tau_c}, \tag{4}$$

where τ_c is the noise correlation time. The term $\gamma(t)$ represents the time-dependent friction coefficient. The noise and friction obey Kubo's fluctuation dissipation theorem:[3,4]

$$\langle G(t)G(t') \rangle = k_B T \gamma(t-t'). \tag{5}$$

This Brownian model has a stationary solution that is exactly the equilibrium distribution. The exponentially correlated colored noise makes it a non-Markovian process, which is suitable for our purpose. For numerical simplification, we replace this colored noise model by an additional one-dimensional white

noise model

$$\begin{cases} \dot{x}(t) = p(t), \\ \dot{p}(t) = -\lambda x(t) + y(t), \\ \dot{y}(t) = -\dfrac{1}{\tau_{\rm c}} y(t) - \dfrac{\beta D}{\tau_{\rm c}} p(t) + \dfrac{\sqrt{2D}}{\tau_{\rm c}} \Gamma(t), \end{cases} \tag{6}$$

where y is the auxiliary variable, and Γ is the Gaussian white noise that satisfies

$$\langle \Gamma(t) \rangle = 0, \quad \langle \Gamma(t)\Gamma(t') \rangle = \delta(t - t'). \tag{7}$$

The time scale of the non-Markovian effect is determined by the correlation time $\tau_{\rm c}$, which is crucial for detecting the influence of the initial preparation to the validity of the JE and TCFE. Other time scales in our consideration should be comparable to this one.

In an interval of the total evolution time $[0, \tau]$, we design a modulation scheme by periodically changing the external parameter λ in a zigzag manner as follows (see Fig. 1):

$$\lambda(t) = \begin{cases} \lambda_0 + (\lambda_\tau - \lambda_0)\left(\dfrac{t}{\tau_1} - 2n\right), & 2n \le \dfrac{t}{\tau_1} \le 2n+1, \\ \lambda_\tau - (\lambda_\tau - \lambda_0)\left(\dfrac{t}{\tau_1} - 2n + 1\right), & 2n-1 < \dfrac{t}{\tau_1} < 2n. \end{cases} \tag{8}$$

We can measure the ensemble average at every time when the periodic external parameter $\lambda(t)$ reaches a specific value. These measurements with the same final external parameter but different evolution time can compare with the free-energy difference (here it is a constant because the free energy is a state function that depends only on the initial and final states). This will be convenient for us to detect the strength and duration of the initial preparation influence.

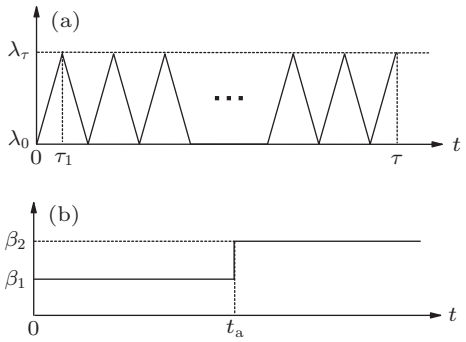


Fig. 1. A scenario for the numerical test. (a) Sketched map for the zigzag $\lambda(t)$ changing protocol; (b) schedule for switching the heat bath.

In Fig. 1, the schedule of switching the heat bath is shown. First, the system contacts with the initial heat bath β_1 for a sufficiently long time, where the initial preparation effect for the system with heat bath β_1 vanishes and the system reaches the equilibrium distribution. Then at time $t = 0$, the periodic $\lambda(t)$ protocol begins, and our test starts. The initial heat bath β_1 remains in connection with the system until $t = t_{\rm a}$, before which the validity of the TCFE and the JE (they are the same in this region) is detected under the non-Markovian heat bath β_1 with a vanished initial preparation effect. When $t > t_{\rm a}$, the initial bath is moved away, and a new heat bath β_2 starts to contact with the system, with a reasonable assumption that it has no memory of the previous system states. The new heat bath β_2 keeps contacting with the system until the final time $t = \tau$, and the TCFE is detected with the initial preparation effect in the region $[t_{\rm a}, \tau]$.

The above detection requires the measurement of the work and heat in every individual process, which is given by

$$W(t) = \int_0^t \frac{\partial H}{\partial \lambda} \frac{{\rm d}\lambda}{{\rm d}t'} {\rm d}t', \tag{9}$$

with $H = \lambda x^2/2 + p^2/2$ being the energy of the system. The heat is given according to the energy conservation as

$$Q(t) = H(t) - H(0) - W(t). \tag{10}$$

3. Effect of initial preparation

We fix the inverse temperature of the two heat baths as $\beta_1 = 1$ and $\beta_2 = 2$, respectively, in all our following numerical tests. The external parameter of the system λ is irrelevant to the heat bath. Without lose of generality, we also confine it between $\lambda_0 = 1$ and $\lambda_\tau = 2$. Consider that λ reflects the frequency of the harmonic oscillation in the harmonic potential, a typical time scale of the system motion is given by $2\pi/\sqrt{\lambda}$ (≈ 6). Comparing with this time scale of the system, we can choose the heat-bath time scale, i.e., the correlation time $\tau_{\rm c}$, as 3, 0.3, and 0.03, respectively. These

three values represent the transition from the strong non-Markovian effect ($\tau_c = 3$) to a nearly Markovian case ($\tau_c = 0.03$). Although the noise strength D from the heat bath influences the interaction between the heat bath and the system, it is not crucial in bringing forth the effect of the non-Markovian memory. For convenience, we fix it to be $D = 0.3$. The half period of the zigzag $\lambda(t)$ is chosen to be $\tau_1 = 0.1$ as a shorter time compared with the above time scales.

The initial state of the system is randomly chosen from an equilibrium distribution at the inverse temperature $\beta_1 = 1$. One million of realizations are used to measure the ensemble average. Different from the Markovian heat bath, the initial equilibrium distribution is not steady under the influence of the memory. We need to keep the evolution under the connection with the initial heat bath β_1 for a sufficiently long time to ensure the system return to the equilibrium distribution. This is similar to the way how a real world experiment gets the equilibrium distribution, but we should insist here that the non-Markovian memory effect is the crucial reason for the unsteady initial distribution in our model.

The total evolution time before measurement is taken to be 100, and a longer time makes no distinct differences for the steady distribution. This make us believe that the influence of the initial preparation with the heat bath β_1 vanishes. After initial preparation, the zigzag $\lambda(t)$ starts at time $t = 0$. The initial heat bath $\beta_1 = 1$ keeps contacting with the system until $t = 10$. We measure the ensemble average at every time when $\lambda(t)$ reaches $\lambda_\tau = 2$. The free energy of the system at $\beta_1 = 1$ is $F = -\beta_1^{-1} \ln Z$, where Z is the partition function. Thus, the exponential free-energy difference in Eq. (2) is $\sqrt{\lambda_0/\lambda_\tau} \approx 0.707$, which is shown by the green lines in Fig. 2(a). Three correlation times $\tau_c = 3$ (blue triangles), 0.3 (red circles), and 0.03 (black squares) are taken and the results are shown in time interval $[0, 10]$, which presents a perfect validity of the TCFE and JE in the vanished non-Markovian initial preparation situation.

When time $t > 10$, the initial heat bath $\beta_1 = 1$ is replaced by the new heat bath $\beta_2 = 2$, without any previous memory. The initial preparation effect appears, and a clear deviation of the ensemble average from the expected free-energy difference (green line) can be observed in the interval $[10, 100]$, as shown in Fig. 2(a). The inset in Fig. 2(a) is an enlarged view in the time interval $[10, 30]$. The correlation time τ_c represents the non-Markovian memory effect, and it determines the strength and the duration of the initial preparation effect. As can be seen from Fig. 2(a), the biggest and longest deviation occurs in case of $\tau_c = 3$ (blue triangles), while the case of $\tau_c = 0.03$ (black squares) is almost Markovian, and the violation of TCFE almost vanishes, which agrees with the validity of the TCFE in Markovian process. The fast oscillation in Fig. 2(a) has a matched time scale with the harmonic oscillation of the system ($2\pi/\sqrt{\lambda}$), which suggests that the fast oscillation depends on the characteristic oscillation of the system under the period $\lambda(t)$ change. The longer-time relaxation comes from the non-Markovian effect, which implies how the initial preparation influences the TCFE validity.

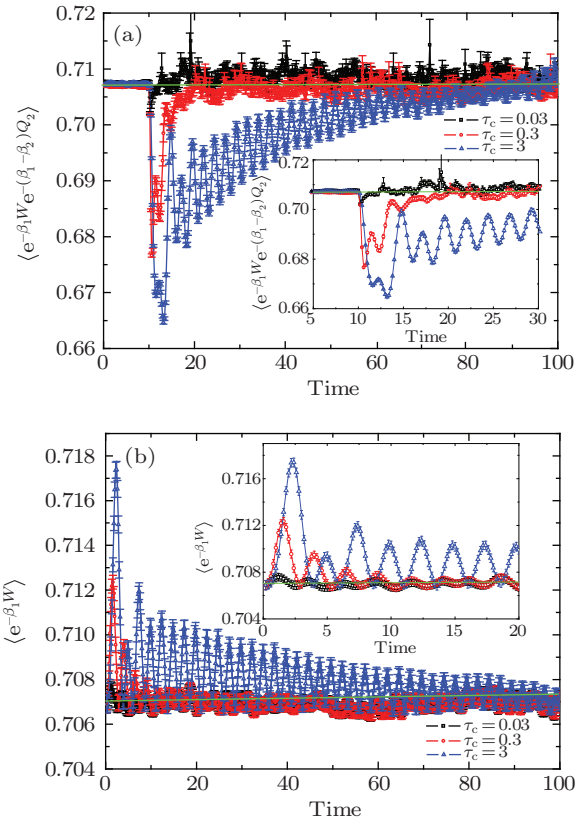


Fig. 2. (colour online) The validity of the TCFE and JE under non-Markovian heat bath. (a) Measurement results after a long-time initial relaxation, the TCFE and JE are valid in the initial heat bath β_1 region $[0, 10]$ but fails in the new bath β_2 region $[10, 100]$, at $\tau_c = 3$ (blue triangles), 0.3 (red circles), and 0.03 (black squares). (b) Measurement results when skipping the initial long-time relaxation. The system is put in an equilibrium distribution "by hand", and then the validity of JE is tested immediately. The green lines denote the expected free-energy difference, and the insets show enlarged time scales.

It should be clear that the crucial reason for the deviation of the TCFE comes from the non-Markovian memory effect, not from the switching of the heat

bath. The presence of the new heat bath β_2 only makes the initial preparation effect have not enough time to vanish. If we test the JE validity under one unique heat bath β_1 by skipping the long-time initial relaxation process from an initial "put-by-hand" equilibrium distribution , a similar violation of the JE can be observed, which is shown in Fig. 2(b), where the initial preparation effect appears again. This violation is not easy to be detected, because previous studies usually keep the system in connection with the initial heat bath for a sufficiently long time to remove the transient and obtain the equilibrium distribution, when the initial preparation already vanishes. However, for the TCFE, as the heat bath is changed to a new one during the dynamical process, the initial preparation effect of the switched heat bath is unavoidable. In this case, one should treat the response of the system to heat reservior switches carefully in the non-Markovian situation, which is different from the Markovian case.

The time scale of the initial preparation is shown in Fig. 3, where we investigate a system with the initial "put-by-hand" equilibrium distribution at temperature $T = 1/\beta$ by contacting with a non-Markovian heat bath at the same temperature $T = 1/\beta$. We detect the evolution of the statistical distribution of the system. The parameters here are chose as: $\lambda = 2$ and $\beta = 2$, which fit for the parameters in the region $[10, 100]$ in Fig. 2(a). It can be found that the system distribution keeps in the Gaussian shape. Therefore, an average of the system energy can be a good parameter to represent the distribution evolution with an expected equilibrium average value $\langle E\rangle = 1/\beta = 0.5$, as shown by the green line in Fig. 2(a). Three different cases of $\tau_c = 3$ (blue triangles), 0.3 (red circles), and 0.03 (black squares) are considered, which represent the different time scales of the initial preparation under the non-Markovian heat bath in Fig. 3(a), and the inset shows an enlarged view in the time scale of $[10, 20]$.

The system distribution keeps in Gaussian form during the evolution and makes the energy distribution $P(E) \propto \mathrm{e}^{-\beta E}$ with only a time changing β value. In Fig. 3(b), the distribution for $\tau_c = 3$ at $t = 2$ is compared with the initial distribution at $t = 0$. The energy distribution at $t = 2$ has the index $\beta = 2.2$, corresponding to an average energy of about 0.455, which accords with the $t = 2$ point (blue triangle) in Fig. 3(a).

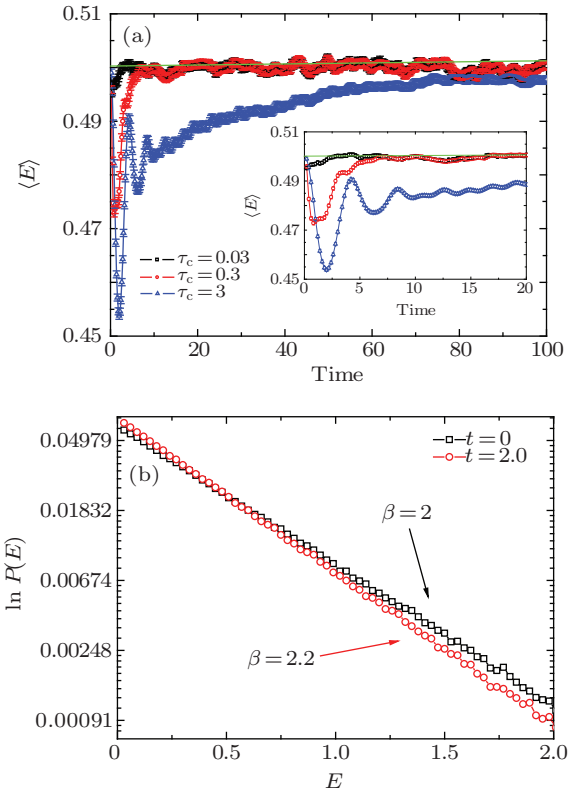


Fig. 3. (colour online) (a) Evolution of the average energy of the system in the case that the system has a "put-by-hand" equilibrium distribution at inverse temperature $\beta = 2$, and evolves by contacting the non-Markovian heat bath at the same inverse temperature $\beta = 2$. The heat bath correlation time τ_c is chosen as 3 (blue triangles), 0.3 (red circles), and 0.03 (black squares), respectively. The inset is the enlarged time scale of $[0, 20]$, and the green line is the expected equilibrium average energy. (b) System energy distributions at time $t = 0$ (black squares) and $t = 2$ (red circles) in the case of $\tau_c = 3$ in (a).

The time scale of the TCFE violation in Fig. 2(a) agrees with that of the distribution violation in Fig. 3(a), with the corresponding correlation time τ_c. This indicates that these two different violations come from the same reason, i.e., the memory effect of the initial preparation under non-Markovian heat bath. This effect drives the system distribution out of equilibrium to make the JE and TCFE invalid. Nevertheless, as soon as this effect vanishes, the JE and TCFE become valid again. This suggests that suitable JE and TCFE measurements require the total evolution time longer than the efficient initial preparation effect time. Whether the recovery of the validity works for a more general case or not is still an open question.

4. Conclusion

To summarize, in this paper a simple Brownian motion model is adopted to investigate the validity

of the JE and TCFE in the presence of the non-Markovian heat bath. We find that the validity sensitively depends on the non-Markovian memory effect, or especially, the initial preparation effect. This memory effect drives the system distribution out of the initial equilibrium state, which leads to the violation of the JE and TCFE. For the JE, this violation can be avoided by adding a sufficiently long-time relaxation to equilibrium distribution before the measurement. For the case of TCFE, we found a different scenario. As the heat bath is changed at some time during the evolution, there is no time for the relaxation to vanish the initial preparation effect with the switched heat bath. A careful consideration should be made during this non-Markovian process.

The memory effect we discuss in this paper is not restricted to the present simple model. Similar behavior can be expected in other complicated systems, which should bring similar violations of the JE and TCFE. Though in our simple model, the steady distribution after the relaxation is exactly the same as the equilibrium distribution. Other systems with broken ergodicity due to the non-Markovian memory effect do not have this steady equilibrium distribution, which should bring new problems to the validity of JE and TCFE aside from the problem from the initial preparation effect. A general discussion of the system behavior under non-Markovian heat bath is valuable to be extended. In our model, when the measurement time is longer than the efficient initial preparation effect time, it is interesting to observe that the JE and TCFE become valid again. Whether this recovery of validity can be found for other systems is still an open question.

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