TOPICAL REVIEW — Statistical physics and complex systems

# Nonequilibrium thermodynamics and fluctuation relations for small systems*

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In this review, we give a retrospect of the recent progress in nonequilibrium statistical mechanics and thermodynamics in small dynamical systems. For systems with only a few number of particles, fluctuations and nonlinearity become significant and contribute to the nonequilibrium behaviors of the systems, hence the statistical properties and thermodynamics should be carefully studied. We review recent developments of this topic by starting from the Gallavotti–Cohen fluctuation theorem, and then to the Evans–Searles transient fluctuation theorem, Jarzynski free-energy equality, and the Crooks fluctuation relation. We also investigate the nonequilibrium free energy theorem for trajectories involving changes of the heat bath temperature and propose a generalized free-energy relation. It should be noticed that the non-Markovian property of the heat bath may lead to the violation of the free-energy relation.

**Keywords:** free-energy equality, fluctuation theorem, Markov process, detailed balance

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## 1. Introduction

Statistical mechanics is one of the most charming fields in physics, in which one faces an extremely large number of individual particles in real systems and tries to reveal the macroscopic law that governs the behaviors and the properties of the system. Because the macroscopic property of a system is not directly reflected by the laws of microscopic mechanics, one can simplify the situation by using statistical mechanics as the bridge between the microscopic and macroscopic worlds. Statistical mechanics was first built by Ludwig Boltzmann in the late 19th century and developed by Gibbs in the early 20th century.[1,2] Since then, statistical mechanics has made great success in other related regions, such as phase transitions, critical phenomena, and the renormalization group theory.[3,4]

The statistical theory for nonequilibrium cases, however, is quite difficult, where complicated processes such as energy and matter transport, entropy productions, and even a dissipative structure become dominant.[5] Boltzmann first realized the importance of dynamics and made an attempt to develop his kinetic theory called the Boltzmann equation for the time evolution of the single-particle distribution function and proposed the H theorem to describe the irreversible process from nonequilibrium to equilibrium states for the long-standing issue about the second law (the time arrow).[6] Other attempts to understand non-equilibrium situations grew out after Boltzmann's, however, there still lacks a universal and elegant framework for understanding the non-equilibrium situation. The linear response theory and the Green–Kubo fluctuation dissipation theorem[7,8] were the first attempts to understand the non-equilibrium properties and describe the relation of the energy dissipation and the correlation or the fluctuation of the system variables under a small perturbation from the thermal equilibrium situation.

In the last two decades, thanks to the computer simulation and nano-scale technology, the properties of non-equilibrium systems can now be studied in detail, and some new understandings of the general properties in the non-equilibrium situation under the name of fluctuation theorem have been obtained. Evans, Cohen, and Morriss[9] in 1993 numerically found a relation about the entropy production in the steady state of a viscous flow, then Gallavotti and Cohen made a dynamical description about the statistic probability in the chaotic hypothesis from the viewpoint of the Sinai–Ruelle–Bowen distribution,[10,11] and developed a fluctuation theorem (FT) to describe the probability of positive and negative entropy productions in one single process of the non-equilibrium stationary state in 1995.[12,13] Evans and Searles in 1994 established a transient fluctuation theorem (TFT), which has the same form of the FT but describes an ensemble measurement of the entropy production over many trajectories initially from a given distribution.[14] Jarzynski in 1997 found a free energy equality (JE) which describes the relationship between an ensemble average of the non-equilibrium work and the equilibrium free energy change.[15,16] Crooks in 1998 tried to prove the JE in the stochastic process and derived a fluctuation re-

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lation (CFR) which describes the non-equilibrium work distribution in the forward and time reversed processes.[17,18] All the above four relations can be applied to the systems far from equilibrium.

In the present review, it is our task to give a mini-summary of the recent progresses in statistical mechanics and thermodynamics of small dynamical systems. For systems with only a few particles and in the nano scale, fluctuations and nonlinearity become significant and contribute to the nonequilibrium behaviors. Some fascinating new progresses in recent years, such as the Gallavotti–Cohen fluctuation theorem, the Evans–Searles transient fluctuation theorem, the Jarzynski free-energy equality, and the Crooks fluctuation relation, are extensively discussed. We further investigate the nonequilibrium free energy theorem for trajectories involving changes of the heat bath temperature and propose a generalized free-energy relation. This generalization not only extends the previous relations to non-steady nonequilibrium processes, but also gives a hint in reducing measurement errors in experiments of free energy detections. The non-Markov property of the heat bath may lead to the violation of the free-energy relation, and this violation is important in the case of temperature modulations.

## 2. The Sinai–Ruelle–Bowen invariant measure

The dynamical foundation of equilibrium statistical mechanics is based on the ergodic theory starting from Boltzmann and developed by Poincare *et al.*[19] However, similar foundations for nonequilibrium cases still remain an unsolved topic. Referred to as the equilibrium case, for the steady nonequilibrium state, Gallavotti and Cohen proposed the so-called chaotic hypothesis,[12,13] which states that a reversible dissipative macroscopic system in a nonequilibrium stationary state can be regraded as a transitive Anosov system for the calculation of its macroscopic properties.

This chaoticity is based on the Anosov system,[20] which exhibits strong dynamical stochasticity. A system with the Anosov stochasticity indicates that a given point in the phase space has two sub-manifolds with both shrinking and stretching directions. Moreover, all the points in the phase space are hyperbolic, i.e., the shrinking and stretching directions are dense everywhere in the phase space. A good example of the Anosov system is the Arnold-cat map, see Fig. 1[21] for a presentation of one step of transformation

$$\begin{pmatrix} x_{n+1} \\ y_{n+1} \end{pmatrix} = \begin{pmatrix} 1 & 1 \\ 1 & 2 \end{pmatrix} \begin{pmatrix} x_n \\ y_n \end{pmatrix} \mod \quad 2\pi. \tag{1}$$

It has not been proved that all dissipative systems are transitive Anosov systems, however, they argued that the chaotic hypothesis can be considered to play the similar role of the harmonic oscillator in classical mechanics, which is not true for most real systems but can give a good approximation.

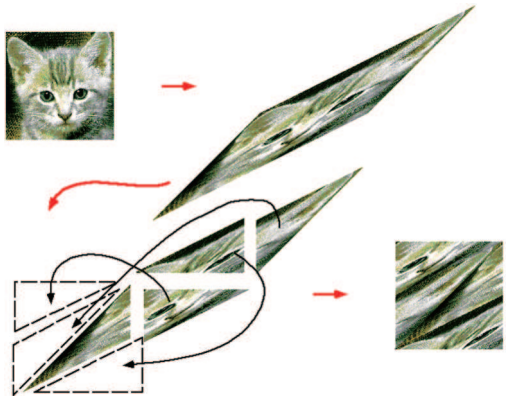


**Fig. 1.** A sketch of one step of the Arnold-cat map. Each step can be decomposed into the stretching and the folding substeps. It can be vividly found that the cat's face becomes strongly deformed with only one-step operation, implying a strong randomness of dynamics of this map.[22]

By assuming that all the dissipative systems are transitive Anosov systems using the chaotic hypothesis, Sinai[10,11] has proved that for such a system, there exists a unique distribution $\mu$, which is called the Sinai–Ruelle–Bowen (SRB) distribution, and it can be used to compute the macroscopic properties of the system in a non-equilibrium stationary state. This implies that the time average of the macroscopic observable can be obtained for sufficiently chaotic systems (Anosov like) from the phase space averages, computed with the SRB distribution $\mu_{\rm SRB}$

$$\lim_{T\to\infty} \frac{1}{T} \int_0^T F(x(t))\,\mathrm{d}t = \int_C \mu_{\rm SRB}\,\mathrm{d}x F(x). \tag{2}$$

Here $\mu_{\rm SRB}$ is the phase space density in the SRB distribution for a non-equilibrium stationary state. This provides a way to obtain the non-smooth distribution due to the typical chaotic dynamics.

To obtain the phase space distribution, one needs to consider a coarse-graining size in phase space cell $E_j$, see Fig. 2. In each cell $E_j$, the probability of the system to visit the cell can be considered as follows. The probability weight is based on the characteristic phase space volume change in the time interval from $-\tau/2$ to $\tau/2$ along a trajectory going through center $x_j$ of the corresponding cell $E_j$. The larger the phase space volume changes, the less the system tends to stay in this cell, so the instability of the system near $x_j$ is characterized. Based on the above understanding, the average value of a macroscopic quantity will be given as

$$\begin{aligned} F_{\rm mac} &\equiv \lim_{T\to\infty} \frac{1}{T} \int_0^T F(x(t))\,\mathrm{d}t \\ &= \int_C \mu_{\rm SRB}\,\mathrm{d}x F(x) \\ &= \lim_{\tau\to\infty} \lim_{E_j\to 0} \frac{\sum_j F(x_j) \Lambda_{\tau,\mu}^{-1}(x_j)}{\sum_j \Lambda_{\tau,\mu}^{-1}(x_j)}, \end{aligned} \tag{3}$$

here the size of cell $E_j \longrightarrow 0$ first before the long-time limit $\tau \longrightarrow \infty$, and $\Lambda_{\tau,\mu}$ is the characteristic phase space volume

change of cell $E_j$ from time $-\tau/2$ to $\tau$. Notice the subscript $\mu$ is for the unstable direction, the key idea of the SRB distribution is to describe the typical chaotic dynamics in the phase space (the attractor) by the manifold of the unstable direction.

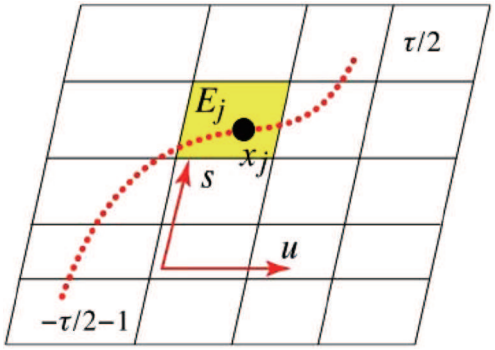



**Fig. 2.** The SRB distribution: trajectory segment of duration $\tau$ through the center $x_j$ of cell $E_j$ of a Markov partition of the system in the phase space.[26]

The SRB distribution describes the probability on the system dynamics rather than on the equal *a priori* probabilities or the ergodic hypothesis. In thermal equilibrium, the SRB distribution reduces to the Gibbs micro-canonical ensemble; and in non-equilibrium chaotic cases, it gives the dynamical description to get the stationary state probability.

## 3. The Gallavotti–Cohen fluctuation theorem

The Gallavotti–Cohen fluctuation theorem (GCFT) was first found in a numerical simulation of the steady state of a viscous flow,[9] then Gallavotti and Cohen proved the theorem in 1995.[12,13] They used the SRB distribution[10,11] as the statistical distribution in a transitive Anosov system, gave the dynamical description of the statistical probability in the nonequilibrium stationary state, and finally derived the fluctuation theorem. The GCFT describes the probability of positive and negative entropy productions in one single process of the non-equilibrium stationary state and can be written as

$$\frac{\pi_\tau(a)}{\pi_\tau(-a)} = \exp(dN\tau a), \tag{4}$$

where $d$ is the dimension of space, $N$ is the number of particles, and $\pi_\tau(a)$ is the probability to find the phase space volume contraction rate $a$ (or, equivalently an entropy production rate $a$) over a trajectory time segment $\tau$. It is clear that when $N \longrightarrow \infty$ or $\tau \longrightarrow \infty$, the ratio in Eq. (4) will be zero, this implies that for a long time $\tau$, the probability to find the unphysical fluctuation of $a$ goes exponentially fast to zero. This fluctuation theorem is valid not only for small perturbations near equilibrium, but also for large deviations far from equilibrium.

## 4. The Evans–Searles transient fluctuation theorem

The Evans–Searles transient fluctuation theorem (ESTFT) was also first found numerically in 1993,[9] but after that, a different fluctuation theorem from the Gallavotti–Cohen FT, called the transient fluctuation theorem, was proposed in 1994.[14,23–25] The ESTFT describes the relation between the entropy productions in the forward process of the system and in the time reversed process. As the physics law is time reversible for every trajectory, there is a conjugate, the time reversed trajectory is also a solution to the dynamics equation. The ESTFT describes the transition probability of a forward trajectory of a corresponding dissipation function which has value $A$ to its time reversed anti-trajectory with the dissipation $-A$.

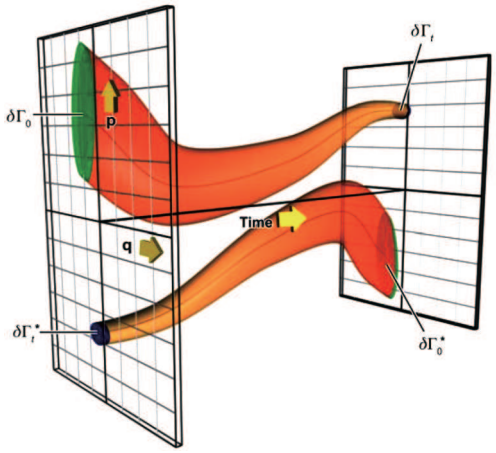



**Fig. 3.** A sketch map of deterministic trajectories and their corresponding time reverse trajectories.[26]

A sketch map of the two corresponding processes is shown in Fig. 3. Defining the probability density of trajectories at duration time $t$ in the phase space by selecting all the initial coordinates $\Gamma_0$ for which the dissipation function $\Omega_t$ takes on some value $A$, $P(\Omega_t = A) = \int \mathrm{d}\Gamma_0 \delta[\Omega_t(\Gamma_0) - A] f(\Gamma_0, 0)$, and the conjugate probability density $P(\Omega_t = -A) = \int \mathrm{d}\Gamma_0^* \delta[\Omega_t(\Gamma_t^*) - A] f(\Gamma_t^*, 0)$, we can obtain the ESTFT

$$\frac{P(\Omega_t = A)}{P(\Omega_t = -A)} = \exp(At). \tag{5}$$

The ESTFT can be considered as follows. If the system is reversible and dissipative, then for a set of initial conditions with the Liouville measure, the phase space trajectories over any time $t$ satisfy Eq. (5). It gives the precise mathematical expression for the probability with which the entropy will flow in a direction opposite to that dictated by the second law of thermodynamics. Notice that this refers to an ensemble of many trajectories starting from a special (Liouville) initial state, it differs from the GCFT that describes a single trajectory in a

non-equilibrium stationary state. A brief review of the ESTFT can be found in Ref. [26], and some new achievements such as the relation of heat flow under this theorem can be seen in Ref. [27].

## 5. Jarzynski free energy equality

In thermodynamics, the free energy describes the useful work obtainable from a system when a macroscopic parameter of the system is changed: to obtain this maximum work, one needs to follow a quasi-static process, and then the work done in this process equals the free energy difference. The process needs to be infinitesimally close to equilibrium and takes an infinitely long time. Jarzynski claimed a more general relation than that for the equilibrium case, where the processes do not need to stay quasi-static during the evolution except initially chosen from an equilibrium distribution, i.e., general nonequilibrium processes still satisfy an equality rather than an inequality. This free energy equality (JE) was first derived by Jarzynski in 1997.[15,16]

Consider an external parameter $\lambda$ and change $\lambda$ from $\lambda_0$ to $\lambda_1$ by a protocol $\lambda(t)$ in the time interval $[0,\tau]$. The JE shows that the free energy difference between states of macroscopic systems can be measured by averaging a function of the work done in change with arbitrary time dependencies including rapid ones, which is written as

$$\langle \exp(-\beta W)\rangle = \exp(-\beta \Delta F). \tag{6}$$

Here $\beta = 1/k_{\rm B}T$ is the temperature of the system in equilibrium, $\Delta F = F_{\rm final} - F_{\rm initial}$ is the free energy difference between the final and the initial states, $W$ is the work performed on every single process, and $\langle\cdot\rangle$ denotes an ensemble average $\int {\rm d}\Gamma \rho(\Gamma)$ over the phase space.

A simple proof of the JE on an adiabatic Hamiltonian system was first made by Jarzynski. Consider a system with a controllable external parameter $\lambda$. By changing the parameter from $\lambda_0$ to $\lambda_\tau$ following the protocol $\lambda(t)$ in $[0,\tau]$, the work done on each individual process is defined by

$$W(\tau) = \int_0^\tau \frac{\partial H}{\partial \lambda}\frac{{\rm d}\lambda}{{\rm d}t'}{\rm d}t'. \tag{7}$$

The system is initially set in an equilibrium distribution, which in a given phase space region $\Gamma$ is given by

$$P_\lambda(\Gamma) = Z_\lambda^{-1}\exp[-\beta E(\Gamma,\lambda_0)]. \tag{8}$$

Note that the partition function $Z$ is given by

$$Z_\lambda = \int {\rm d}\Gamma \exp[-\beta E(\Gamma,\lambda)], \tag{9}$$

and that the free energy associated with an equilibrium state is given by the relation

$$F_\lambda = \beta^{-1}\ln Z_\lambda. \tag{10}$$

Then the JE can be derived as

$$\begin{aligned}\langle \exp(-\beta W)\rangle &\equiv \int {\rm d}\Gamma_0 P_{\lambda_0}(\Gamma_0)\exp(-\beta W)\\ &= \frac{1}{Z_0}\int {\rm d}\Gamma_0 \exp(-\beta E_0)\exp(-\beta W)\\ &= \frac{1}{Z_0}\int {\rm d}\Gamma_0 \exp(-\beta E_\tau)\\ &= \frac{1}{Z_\tau}\int {\rm d}\Gamma_0 \exp(-\beta E_\tau)\\ &= \frac{Z_\tau}{Z_0} = \exp(-\beta\Delta F),\end{aligned} \tag{11}$$

where ${\rm d}\Gamma$ denotes a small region in the phase space near $\Gamma$. The Liouvilles theorem is used for ${\rm d}\Gamma_0 = {\rm d}\Gamma_\tau$ in the Hamiltonian system, and the energy conservation law is $E_\tau = E_0 + W$.

The JE provides a method to calculate the system's free energy difference between two configurations by an ensemble average of the work performed on the system from one configuration to another, even these processes are non-equilibrium. This is very useful in the measurements of non-equilibrium processes, especially in small systems such as nano-scale experiments, to get the free energy.[28] A recent brief summary about this topic can be found in Ref. [29].

## 6. Crooks fluctuation relation

The Crooks fluctuation relation (CFR) was first derived to give another proof of the JE[17,18,30] in the stochastic dynamics, then Crooks developed a general relation. The CFR considers the probability of observing trajectories from two different equilibrium states, one is the forward process and the other is the reverse process, both processes are initially chosen from the equilibrium distribution, then one can calculate the probability distribution of work performed in the two processes. The CFR is written as

$$\frac{P_{\rm F}(+W)}{P_{\rm R}(-W)} = \exp[\beta(W-\Delta F)], \tag{12}$$

where $P_{\rm F}(+W)$ is the probability of getting work $+W$ in the forward process starting from an equilibrium distribution and following a protocol $\lambda(t)$, and $P_{\rm R}(W)$ is the probability of getting $W$ in the corresponding time reversed process under $\lambda(\tau - t)$. Microscopical time reversible dynamics is needed in this proof.

The JE can be derived from the CFR.[17] Consider the forward process in which the external parameter follows the sequence $\lambda_0,\lambda_1,\ldots,\lambda_\tau$. We can describe one single path from the initial state $i_0$ to the final state $i_\tau$ as $i_0 \xrightarrow{\lambda_1} i_1 \xrightarrow{\lambda_2} i_2 \xrightarrow{\lambda_3} \cdots \xrightarrow{\lambda_\tau} i_\tau$, and the corresponding reversed path is $i_0 \xleftarrow{\lambda_1} i_1 \xleftarrow{\lambda_2} i_2 \xleftarrow{\lambda_3} \cdots \xleftarrow{\lambda_\tau} i_\tau$. For a Markovian heat bath, we may write the transition probability from $i_0$ to $i_\tau$ along the particular path as

$$P(i_0 \xrightarrow{\lambda_1} i_1 \xrightarrow{\lambda_2} i_2 \xrightarrow{\lambda_3} \cdots \xrightarrow{\lambda_\tau} i_\tau)$$

$$= P(i_0 \xrightarrow{\lambda_1} i_1)P(i_1 \xrightarrow{\lambda_2} i_2)\cdots P(i_{\tau-1} \xrightarrow{\lambda_\tau} i_\tau). \quad (13)$$

Assume that the system satisfies the detailed balance, i.e., the transition rate between two states for fixed $\lambda$ is

$$\frac{P(i \xrightarrow{\lambda} j)}{P(i \xleftarrow{\lambda} j)} = \frac{\exp(-\beta E(j,\lambda)}{\exp(-\beta E(i,\lambda)} = \exp(-\beta q_\lambda), \quad (14)$$

where $q_\lambda = E(j,\lambda) - E(i,\lambda)$ is the heat transferred from the heat bath $\beta$ at the fixed external parameter $\lambda$.

The assumption of detailed balance was introduced and discussed in Crooks' papers.[17,18] Since the principle of the detailed balance describes the transition relation in an equilibrium state, the application to the general non-equilibrium processes should be considered carefully.[31] The applicability of Eq. (14) in non-equilibrium processes can be heuristically understood as follows. First, we divide every single evolution sequence into two substeps, and we only need the transition relation at the second substep, where $\lambda$ is fixed and so the transition rate in Eq. (14) is only the transitions caused by the heat bath. Second, since we assume that the heat bath is Markovian, the particular transition rate, which is physically caused by the interaction between the system and the heat bath, should only depend on the current system state, no matter whether the system is in equilibrium or not. This means that the transition rate ratio in the non-equilibrium situation should be the same as that in the equilibrium one.

Using the above assumptions, we find the ratio between probabilities of a forward process from a particular initial state and the corresponding reverse process

$$\frac{P(i_0 \xrightarrow{\lambda_1} i_1 \xrightarrow{\lambda_2} i_2 \xrightarrow{\lambda_3} \cdots \xrightarrow{\lambda_\tau} i_\tau)}{P(i_0 \xleftarrow{\lambda_1} i_1 \xleftarrow{\lambda_2} i_2 \xleftarrow{\lambda_3} \cdots \xleftarrow{\lambda_\tau} i_\tau)} = \prod_{i=1}^{\tau} \exp(-\beta q_i) = \exp(-\beta Q), \quad (15)$$

where $Q = q_1 + q_2 + \cdots$ is the total heat transferred from the heat bath.

Now let us consider the forward and the reverse processes both starting from their equilibrium distributions. We define $P(A \to B)$ as the probability of starting from an equilibrium state $A(i_0,\lambda_0)$ and ending in a final state $B(i_\tau,\lambda_\tau)$; similarly, $P(A \leftarrow B)$ is the probability starting from the equilibrium state $B(i_\tau,\lambda_\tau)$ and ending in the state $A(i_0,\lambda_0)$. Thus the ratio between these two probabilities is

$$\frac{P(A \to B)}{P(A \leftarrow B)} = \frac{\rho_{\rm eq}(i_0,\lambda_0)P(i_0 \xrightarrow{\lambda_1} i_1 \xrightarrow{\lambda_2} i_2 \xrightarrow{\lambda_3} \cdots \xrightarrow{\lambda_\tau} i_\tau)}{\rho_{\rm eq}(i_\tau,\lambda_\tau)P(i_0 \xleftarrow{\lambda_1} i_1 \xleftarrow{\lambda_2} i_2 \xleftarrow{\lambda_3} \cdots \xleftarrow{\lambda_\tau} i_\tau)} = \frac{Z(\lambda_\tau,\beta)}{Z(\lambda_0,\beta)} \exp[\beta(E_B - E_A)]\exp(-\beta Q) = \exp(-\beta\Delta F)\exp(\beta W), \quad (16)$$

where the free energy $F = -\beta^{-1}\ln Z$ and the energy conservation $E_B = E_A + W + Q$ are used in the last step. If we rewrite $P(A \to B)$ and $P(A \leftarrow B)$ as $P(W)$ and $P(-W)$, respectively, and integral all over the phase space, we will obtain the CFR: $P_{\rm F}(+W)/P_{\rm R}(-W) = \exp[\beta(W - \Delta F)]$.

The JE (6) can be derived from Eq. (16) using

$$\begin{aligned}\langle \exp(-\beta W)\rangle &\equiv \int {\rm d}A \int {\rm d}B P(A \to B)\exp(-\beta W) \\ &= \int {\rm d}A \int {\rm d}B P(A \leftarrow B)\exp(-\beta\Delta F) \\ &= \exp(-\beta\Delta F), \end{aligned} \quad (17)$$

where a normalization of the probability is used in the last step.

Some recent progresses about the CFR such as the non-Gaussian work fluctuations[32] and the length of time arrow[33] can be found in the related papers.

## 7. The temperature-changing free-energy equality

The initial derivation of the JE[15,16] was for a system isolated from the heat bath (heat interaction negligible) during the dynamical process, the result was later[34] generalized to a system that remains in contact with the initial heat bath. In the latter case, heat can be transferred to or from the system, but it does not appear in relationship (6). Most subsequent studies on non-equilibrium free energy theorems, e.g., the Crooks' fluctuation relation,[17,18] are based on similar adiabatic or constant heat bath situations. A natural question is: what happens if we change the heat bath temperature, and how does the heat influence the free energy relation?

A few previous works have considered the change of the environment's temperature,[35–37] however, they needed to define a generalized "work", which plays a similar role to the work in the JE. This generalized work is abstract, depending on the specific description of the system, and it is not easy to understand the individual contributions from the true work and the heat. Another shortage of this generalized work is that more information is needed to form the ensemble average, for example, every initial state energy is needed, which is usually hard to access in experiments.

Here we show that there exists a simple relationship among work, heat, and the free energy difference if we change the inverse temperature of the heat bath from $\beta_1$ to $\beta_2$ during the process. We call it the temperature-changing free-energy equality (TCFE). The relationship is

$$\langle \exp(-\beta_1 W)\exp[-(\beta_1 - \beta_2)Q_2]\rangle = \exp(-\beta_1\Delta F). \quad (18)$$

Here $\beta$ and $W$ are the same as those defined in Eq. (6), $\Delta F$ is the free energy difference of the system at inverse temperature $\beta_1$, and $Q_2$ is the heat transferred from heat bath $\beta_2$ to the system. The contribution of the heat to the identity is apparent. This also provides a scenario of more accurate measurement of free energy changes in practice by reducing the estimation error using the extra heat contribution.

Let us consider an equilibrium system in contact with a heat bath of temperature $1/\beta_1$. The external control parameter $\lambda$ evolves from the initial value $\lambda_0$ to $\lambda_\tau$ following a protocol $\lambda(t)$ in a time interval $[0,\tau]$. Usually for the JE, the system remains in contact with the same heat bath $\beta_1$ during the interval, but now we consider a different situation. We start by keeping the system in contact with the initial heat bath $\beta_1$ for a time period $[0,t_a]$ and then replace $\beta_1$ by a different heat bath $\beta_2$ for a time period $[t_a,t_b]$. After this period, the heat bath is set back to $\beta_1$, see Fig. 4. Under this scenario, we can show that both the work performed on each process and the heat transfer from heat bath $\beta_2$ contribute to measuring the free energy difference, which is given by the relation (18). If $\beta_2=\beta_1$, the relation (18) goes back to the original JE.

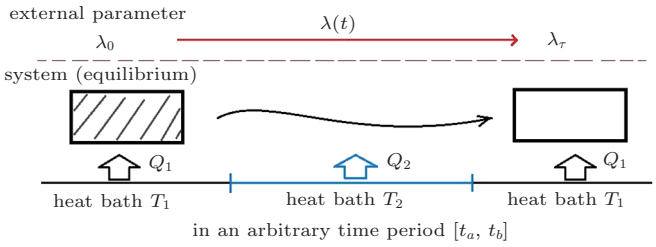



**Fig. 4.** Scenario of changing heat bath temperature. The initial heat bath $\beta_1$ is replaced by a different bath $\beta_2$ over an arbitrary time period $[t_a,t_b]$.

### 7.1. Theoretical derivation

We can follow Crooks' method to prove the relation (18).[17] Consider the forward process $\{\lambda_0,\lambda_1,\ldots,\lambda_a,\ldots,\lambda_b,\ldots,\lambda_\tau\}$. For $t\in[t_a,t_b]$, as shown in Fig. 4, the heat bath temperature is $\beta=\beta_2$. Because one has both the bath temperature $\beta$ and the external parameter $\lambda$ changing, the evolution over each step in the sequence can be divided into two substeps: (i) $\lambda$ changes to a new value by performing work on the system; (ii) $\lambda$ is kept constant, and heat is transferred to or from the bath. If the time interval of each step in the sequence is small enough, this division describes the same dynamical evolution as that in the real process where work and heat contribute together. We can describe one single path from the initial state $i_0$ to the final state $i_\tau$ as $i_0\xrightarrow{\lambda_1,\beta_1}i_1\xrightarrow{\lambda_2,\beta_1}i_2\cdots i_{a-1}\xrightarrow{\lambda_a,\beta_2}i_a\cdots i_{b-1}\xrightarrow{\lambda_b,\beta_2}i_b\cdots i_{\tau-1}\xrightarrow{\lambda_\tau,\beta_1}i_\tau$, and the corresponding reverse path as $i_0\xleftarrow{\lambda_1,\beta_1}i_1\xleftarrow{\lambda_2,\beta_1}i_2\cdots i_{a-1}\xleftarrow{\lambda_a,\beta_2}i_a\cdots i_{b-1}\xleftarrow{\lambda_b,\beta_2}i_b\cdots i_{\tau-1}\xleftarrow{\lambda_\tau,\beta_1}i_\tau$. The forward and the reverse paths are shortened as $i_0\dashrightarrow i_\tau$ and $i_0\dashleftarrow i_\tau$, respectively. We will consider them both starting from their equilibrium distributions.

For a Markovian heat bath, the transition probability from $i_0$ to $i_\tau$ along a given path satisfies

$$\begin{aligned}&P(i_0\dashrightarrow i_\tau)\\ &=P(i_0\xrightarrow{\lambda_1,\beta_1}i_1)P(i_1\xrightarrow{\lambda_2,\beta_1}i_2)\cdots P(i_{a-1}\xrightarrow{\lambda_a,\beta_2}i_a)\cdots\\ &\quad\times\cdots P(i_{b-1}\xrightarrow{\lambda_b,\beta_2}i_b)\cdots P(i_{\tau-1}\xrightarrow{\lambda_\tau,\beta_1}i_\tau).\end{aligned}\tag{19}$$

Following the detailed balance condition, the transition rate between two states at fixed $\lambda$ is

$$\frac{P(i\xrightarrow{\lambda,\beta}j)}{P(i\xleftarrow{\lambda,\beta}j)}=\frac{\exp[-\beta E(j,\lambda)]}{\exp[-\beta E(i,\lambda)]}=\exp(-\beta q_\lambda),\tag{20}$$

where $q_\lambda=E(j,\lambda)-E(i,\lambda)$ is the heat transferred from the heat bath $\beta$ at the fixed external parameter $\lambda$ (work does not appear here because $\lambda$ is fixed in this substep).

By combining Eqs. (19) and (20), the ratio between probabilities of a forward process and the corresponding reverse process is

$$\begin{aligned}\frac{P(i_0\dashrightarrow i_\tau)}{P(i_0\dashleftarrow i_\tau)}&=\prod_{i=1}^{\tau}\exp(-\beta_1 q_i)\prod_{j=a}^{b}\exp(-\beta_2 q_j)\\ &=\exp(-\beta_1 Q_1)\exp(-\beta_2 Q_2),\end{aligned}\tag{21}$$

where $Q_1=q_1+q_2+\cdots+q_\tau$ and $Q_2=q_a+\cdots+q_b$ is the total heat transferred from heat baths $\beta_1$ and $\beta_2$, respectively.

Now let us consider the forward and the reverse processes both starting from their equilibrium distributions. We define $P(A\to B)$ as the probability starting from an equilibrium state $A(i_0,\lambda_0)$ and ending in a final state $B(i_\tau,\lambda_\tau)$; similarly, $P(A\leftarrow B)$ denotes the probability starting from the equilibrium state $B(i_\tau,\lambda_\tau)$ and ending in the state $A(i_0,\lambda_0)$. Thus the ratio between these two probabilities is

$$\begin{aligned}\frac{P(A\to B)}{P(A\leftarrow B)}&=\frac{\rho_{\rm eq}(i_0,\lambda_0)P(i_0\dashrightarrow i_\tau)}{\rho_{\rm eq}(i_\tau,\lambda_\tau)P(i_0\dashleftarrow i_\tau)}\\ &=\frac{Z(\lambda_\tau,\beta_1)}{Z(\lambda_0,\beta_1)}\exp[\beta_1(E_B-E_A)]\\ &\quad\times\exp(-\beta_1 Q_1)\exp(-\beta_2 Q_2)\\ &=\exp(-\beta_1\Delta F)\exp(\beta_1 W)\exp[(\beta_1-\beta_2)Q_2],\end{aligned}\tag{22}$$

where the free energy $F=-\beta^{-1}\ln Z$ and the energy conservation $E_B=E_A+W+Q_1+Q_2$ are used.

If we have positive work and positive heat $(+W,+Q_2)$ during $A\to B$, the corresponding reverse process $A\leftarrow B$ will have negative work and negative heat $(-W,-Q_2)$, and then the relation (22) is a generalized CFR relation (GCFR) by integrating over the phase space

$$\begin{aligned}\frac{P(+W,+Q_2)}{P(-W,-Q_2)}&=\exp(-\beta_1\Delta F)\exp(\beta_1 W)\\ &\quad\times\exp[(\beta_1-\beta_2)Q_2].\end{aligned}\tag{23}$$

The TCFE (18) can be derived from Eq. (22) by using

$$\begin{aligned}&\langle\exp(-\beta_1 W)\exp[-(\beta_1-\beta_2)Q_2]\rangle\\ &\equiv\int{\rm d}A\int{\rm d}B P(A\to B)\exp(-\beta_1 W)\exp[-(\beta_1-\beta_2)Q_2]\\ &=\int{\rm d}A\int{\rm d}B P(A\leftarrow B)\exp(-\beta_1\Delta F)\\ &=\exp(-\beta_1\Delta F).\end{aligned}\tag{24}$$

This gives us the TCFE (18) containing the influences of both work and heat. Equation (18) is the microscopic approach to

the macroscopic free energy difference. By using Jensen's inequality

$$\langle \exp(x) \rangle \geq \exp(\langle x \rangle),$$

one has

$$\langle W + (1 - T_1/T_2) Q_2 \rangle \geq \Delta F.$$

Remember that $\Delta F = \Delta \bar{U} - T_1 \Delta S$ at constant temperature $T_1$ and $\Delta \bar{U} = \langle W + Q_1 + Q_2 \rangle$, one obtains

$$\left\langle \frac{Q_1}{T_1} \right\rangle + \left\langle \frac{Q_2}{T_2} \right\rangle \leq \Delta S. \tag{25}$$

This gives the thermodynamic second law with ensemble averages. The equality in relation (25) only applies when the processes are quasi-static, leading to the familiar expression for the change in entropy in quasistatic processes. As in the JE, relation (18) is more general, and does not require processes remaining in equilibrium.

### 7.2. A numerical test

We use the one-dimensional harmonic oscillator $H = \lambda x^2/2 + p^2/2$ as our model to test the validity of TCFE (18), and the external parameter $\lambda$ changes from $\lambda_0$ to $\lambda_1$. The oscillator contacts with a Gaussian heat bath

$$\dot{x} = p, \quad \dot{p} = -\lambda x - \gamma p + g_{\rm w}(t), \tag{26}$$

where $\gamma$ is the friction coefficient, $g_{\rm w}(t)$ is the Gaussian white noise, $\langle g_{\rm w}(t) g_{\rm w}(t') \rangle = 2D\delta(t - t')$, with $D$ the noise strength,[7] and the heat bath inverse temperature is $\beta = \gamma/D$. We set $\gamma = 0.03$ for all our heat baths, and different $\beta$ is realized by choosing different $D$. The work done on the system is measured by $W(\tau) = \int_0^\tau {\rm d}t \dot{\lambda} \partial H/\partial \lambda$, and the heat is measured by energy conservation $Q(\tau) = H(\tau) - H(0) - W(\tau)$. We choose a zigzag $\lambda$ change, as in Fig. 5(a): the half period of one zigzag $\lambda$ cycle is too short ($\tau_1 = 0.1$) to draw the system out of equilibrium; many cycles of the interaction make the total evolution time $\tau$ long enough to experience a significant heat influence.

We set $\lambda_0 = 1$, $\lambda_1 = 4$, and $t_a = 1$. The initial heat bath temperature is chosen as $\beta_1 = 1$ and the second heat bath temperature is $\beta_2 = 2$ in Fig. 5(b) and $\beta_2 = 0.5$ in Fig. 5(c). We measure the ensemble averages at different times (always at the end of an increasing $\lambda$ half cycle) from 1 to 200, and find that the free energy relation is satisfied for both colder and hotter second heat baths, and for a short time when the influence of the heat is weak and a long time when the influence is strong. The total number of test systems used is $10^6$, which makes the 0.1% deviation from the known free energy difference reasonable. Thus the simulations verify the free energy relation (18).

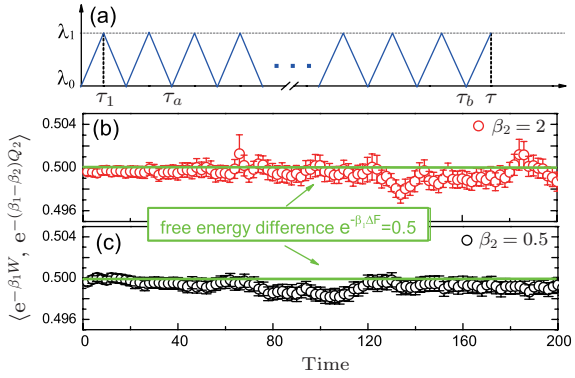



**Fig. 5.** Numerical test for the free energy relation with different heat bath temperatures. (a) Zigzag $\lambda$ change as $\lambda(t) = \lambda_0 + ct$ in one half cycle of length $\tau_1$, and then back in the next half cycle. (b) and (c) Free energy measurements with $\beta_2 = 0.5$ in panel (b) and $\beta_2 = 2$ in panel (c). They both fit for the known free energy differences, which are shown as the green lines.

### 7.3. Generalizations

The above TCFE can be well extended to more complicated cases. Consider an arbitrary temperature protocol $\beta(t)$. For simplicity, we restrict to the temperature protocol always returning to its initial value $\beta_1$. We follow the argument of the previous derivation by only modifying Eq. (22) to

$$\frac{P(A \to B)}{P(A \leftarrow B)} = \frac{Z(\lambda_\tau, \beta_n)}{Z(\lambda_0, \beta_1)} \exp(\beta_n E_B - \beta_1 E_A) \times \prod_{i=1}^{n} \exp(-\beta_i q_i), \tag{27}$$

where $q_i$ is the individual heat transfers from bath $\beta_i$ to the system. Now consider

$$-\sum_{i=1}^{n} \beta_i q_i = \sum_{i=1}^{n-1} \left[ (\beta_{i+1} - \beta_i) \sum_{j=1}^{i} q_j \right] - \beta_n \sum_{j=1}^{n} q_j. \tag{28}$$

We define a time-dependent heat $Q(t) = q_1 + q_2 + \cdots + q_t$ representing the total heat transferred from the heat bath to the system up to time $t$. By rewriting $\beta_{i+1} - \beta_i$ as ${\rm d}\beta_i$ and using the energy conservation $E_B = E_A + W + q_1 + q_2 + \cdots + q_n$, we obtain from Eq. (27)

$$\frac{P(A \to B)}{P(A \leftarrow B)} = \exp[-(\beta_n F_n - \beta_1 F_1)] \exp[(\beta_n - \beta_1) E_A] \times \exp(\beta_n W) \exp\left[ \int_0^\tau {\rm d}\beta(t) Q(t) \right]. \tag{29}$$

Following the same procedure in Eq. (24) leads to

$$\left\langle \exp[-(\beta_n - \beta_1) E_0] \exp(-\beta_n W) \exp[-\int_0^\tau {\rm d}t \dot{\beta}(t) Q(t)] \right\rangle = \exp[-(\beta_n F_n - \beta_1 F_1)]. \tag{30}$$

Here $E_0$ is the initial state energy of each process, $F_n$ and $F_1$ are the free energies of the system at $(\beta_n, \lambda_\tau)$ and $(\beta_1, \lambda_0)$, respectively. Equation (30) gives the free energy relation with an arbitrary heat bath temperature variation. If we keep the external parameter constant, there is no work performed to the system, relation (30) can be reduced to that of the Nose–Hoover model studied in Ref. [35] (Eq. (18) therein).

Usually the initial state energy is hard to detect experimentally. By restricting the final heat bath temperature $\beta_n = \beta_1$, equation (30) can be simplified to

$$\left\langle \exp(-\beta_1 W)\exp[-\int_0^\tau \mathrm{d}t\dot{\beta}(t)Q(t)]\right\rangle = \exp(-\beta_1\Delta F), \quad (31)$$

where $\Delta F = F(\beta_1,\lambda_\tau) - F(\beta_1,\lambda_0)$ is the free-energy difference at temperature $\beta_1$. This is again a microscopic description of the free energy difference, and the processes in the ensemble do not need to be in equilibrium. The dependence on the detailed information of every initial state, for example, the energy, is eliminated; only the work done on each system and the heat transferred to the system are needed. One limitation to bear in mind is that the heat bath needs to be always kept in equilibrium throughout the temperature changes.

## 8. Failure of the free energy relation: non-Markovian effect

The proofs of both the JE and the TCFE require the Markovian assumption, which is an idealization of the real physical world. It gives a good approximation only when the time scale of the heat bath is much shorter than that of the system.[7,8] However, the time scale of the heat bath is not necessarily shorter than that of the system. This naturally brings forth the question of the validity of the JE and the TCFE in non-Markovian processes.[38]

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 JE validity under a non-Markovian heat bath,[39–43] where it is found that the JE is valid. However, the influence of the initial preparations has not been considered. For the JE, this consideration is necessary because the initial equilibrium distribution is reached by connecting the system and the heat bath for a sufficiently long time, and the effect of the initial preparation vanishes after this long-time relaxation.

We consider the motion of a Brownian particle described by a generalized Langevin equation

$$\ddot{x}(t) = -\frac{\mathrm{d}V(x)}{\mathrm{d}x} - \int_0^t \mathrm{d}t'\gamma(t-t')\dot{x}(t') + G(t). \quad (32)$$

Here $V(x) = -\lambda x^2/2$ is the harmonic potential, with $\lambda$ taken as the external parameter by changing from $\lambda_0$ to $\lambda_\tau$ following a protocol $\lambda(t)$ in the time interval $[0,\tau]$. The term $G(t)$ is a colored Gaussian noise with a zero mean and an exponential correlation function, as already studied in the Ornstein–Uhlenbeck process

$$\langle G(t)\rangle = 0, \quad \langle G(t)G(t')\rangle = \frac{D}{\tau_\mathrm{c}}\mathrm{e}^{-|t-t'|/\tau_\mathrm{c}}, \quad (33)$$

with $\tau_\mathrm{c}$ being the noise correlation time. The term $\gamma(t)$ represents the friction coefficient. The noise and the friction obey Kubo's fluctuation dissipation theorem[7,8]

$$\langle G(t)G(t')\rangle = k_\mathrm{B}T\gamma(t-t'). \quad (34)$$

For numerical simplification, we replace this colored noise model by an additional one-dimensional white noise model

$$\begin{cases} \dot{x}(t) = p(t), \\ \dot{p}(t) = -\lambda x(t) + y(t), \\ \dot{y}(t) = -\dfrac{1}{\tau_\mathrm{c}}y(t) - \dfrac{\beta D}{\tau_\mathrm{c}}p(t) + \dfrac{\sqrt{2D}}{\tau_\mathrm{c}}\Gamma(t), \end{cases} \quad (35)$$

with $y$ the auxiliary variable and $\Gamma$ the Gaussian white noise that satisfies

$$\langle\Gamma(t)\rangle = 0, \quad \langle\Gamma(t)\Gamma(t')\rangle = \delta(t-t'). \quad (36)$$

In an interval of the total evolution time $[0,\tau]$, we design a modulation scheme by periodically changing the external parameter $\lambda(t)$ in a zigzag manner shown above. We measure the ensemble average at every time when the periodic external parameter $\lambda(t)$ reaches a specific value. The detection requires the measurements of the work and the heat in every individual process, which is given by

$$W(t) = \int_0^t \frac{\partial H}{\partial\lambda}\frac{\mathrm{d}\lambda}{\mathrm{d}t'}\mathrm{d}t', \quad (37)$$

with $H = \frac{\lambda}{2}x^2 + \frac{1}{2}p^2$ being the energy of the system. The heat is given by the energy conservation as

$$Q(t) = H(t) - H(0) - W(t). \quad (38)$$

We fix $\beta_1 = 1$, $\beta_2 = 2$, $\lambda_0 = 1$, and $\lambda_\tau = 2$ in numerical tests. We choose the correlation time $\tau_\mathrm{c} = 3$, 0.3, and 0.03, which respectively represent the non-Markovian effect from a strong one ($\tau_\mathrm{c} = 3$) to a nearly Markovian case ($\tau_\mathrm{c} = 0.03$). Noise strength $D$ is not crucial for the non-Markovian memory and is fixed to $D = 0.3$. The half period of the zigzag $\lambda(t)$ is chosen to be $\tau_1 = 0.1$ as a shorter time compared to the above time scales. The initial state of the system is randomly chosen from an equilibrium distribution at $\beta_1 = 1$ for $N = 10^6$ realizations to measure the ensemble average. For the non-Markovian heat bath, we need to keep the evolution with the initial heat bath $\beta_1$ for a sufficiently long time. The total evolution time before the measurement is taken to be 100, and a longer time makes no distinct differences for the steady distribution. After this preparation, the zigzag $\lambda(t)$ starts at $t = 0$. We measure the ensemble average at each time when $\lambda_\tau = 2$. The exponential free energy difference is $\sqrt{\lambda_0/\lambda_\tau} \approx 0.707$, as shown by the green line in Fig. 6(a). The correlations for $\tau_\mathrm{c} = 3$ (blue triangles), 0.3 (red circles), and 0.03 (black squares) are tested in time interval $[0,10]$, which show a perfect validity of the TCFE (and the JE) in the vanished non-Markovian initial preparation situation.

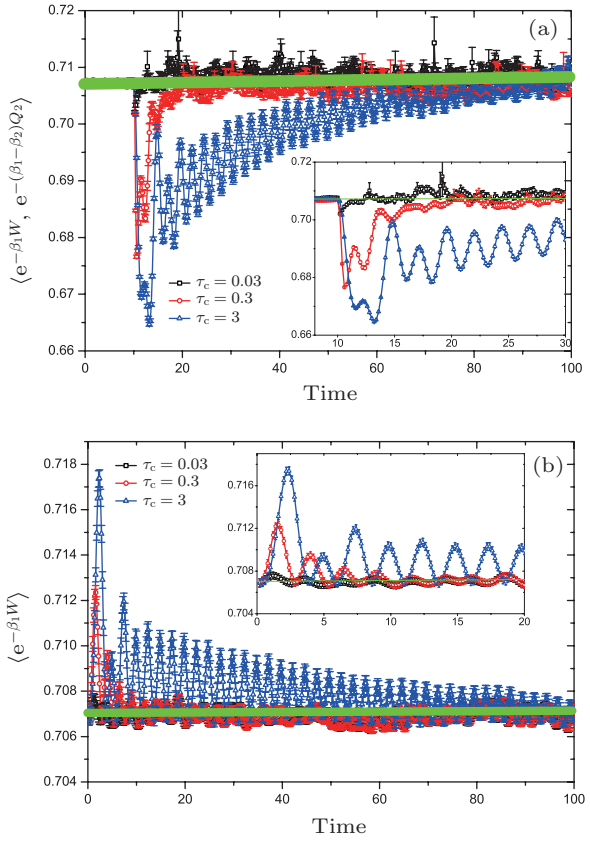



**Fig. 6.** The validity of the TCFE and the JE under non-Markovian heat bath. (a) The measurement after a long-time initial relaxation, the TCFE and the JE fit under the initial heat bath $\beta_1$ region $[0,10]$ but fail at the new bath $\beta_2$ region $[10,100]$, at $\tau_c = 3$ (blue triangles), 0.3 (red circles), and 0.03 (black squares). (b) The measurement that skips the initial long-time relaxation but puts the system in an equilibrium distribution by hand and tests the JE validity immediately. The green lines are the expected free energy difference, and the insets show the results in the enlarged time scales.

After $t = 10$, the initial heat bath $\beta_1 = 1$ is removed and the new heat bath $\beta_2 = 2$ starts to contact the system 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. 6(a). The inset picture in Fig. 6(a) is an enlarged view in the interval $[10,30]$. The correlation time $\tau_c$ represents the non-Markovian memory effect, and determines the strength and the length of the initial preparation effect. As can be seen from Fig. 6(a), the $\tau_c = 3$ case (blue triangles) has the largest and longest deviation, while the $\tau_c = 0.03$ case (black squares) is almost Markovian and the violation is almost vanished, which agrees with the validity of the TCFE in the Markovian process.[44] The fast oscillation in Fig. 6(a) comes from an oscillating work distribution, which depends on the characteristic oscillation of the system under the period $\lambda(t)$ change with a matched time scale. The longer-time relaxation originates from the non-Markovian effect, which implies how the initial preparation influences the TCFE validity.

It is 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. If we test the JE validity under one unique heat bath $\beta_1$ by skipping the long-time initial relaxation process from an initial equilibrium distribution, a similar violation of the JE can be observed, which is shown in Fig. 6(b) with an enlarged view of the time interval $[10,20]$ in the inset, where the initial preparation effect appears again. 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.

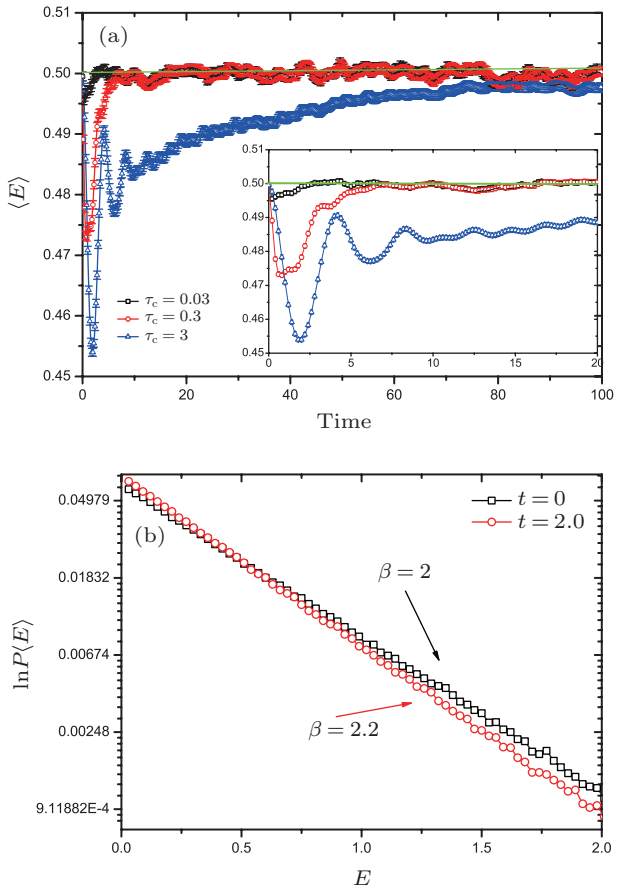



**Fig. 7.** The time scale of the initial preparation effect. (a) The evolution of the average energy when the system has an equilibrium distribution at $\beta = 2$ and evolves by contacting with a non-Markovian heat bath at the same temperature. The heat bath correlation time $\tau_c$ is chosen as 3 (blue triangles), 0.3 (red circles), and 0.03 (black squares) respectively. The inset is the results in the enlarged time scale of $[0,20]$, and the green line is the expected equilibrium average energy. (b) The energy distributions at $t = 0$ (black squares) and $t = 2$ (red circles) for $\tau_c = 3$ in panel (a).

The time scale of the initial preparation is shown in Fig. 7. We detect the evolution of the statistical distribution of the system for $\lambda = 2$ and $\beta = 2$. It can be found that the system distribution keeps the Gaussian shape. Therefore, the average of the system energy can be a good parameter to represent the distribution evolution with an expected equilibrium average value $1/\beta = 0.5$, as shown by the green line in Fig. 6(a). We take correlation time $\tau_c = 3$ (blue triangles), 0.3 (red circles), and 0.03 (black squares) to represent different time scales of

the initial preparation under the non-Markovian heat bath in Fig. 7(a), and the inset is the results in an enlarged time scale of $[10,20]$. The distribution keeps in Gaussian shape during the evolution and makes the energy distribution be $P(E) \propto \mathrm{e}^{-\beta E}$ with only a time changing $\beta$ value. This is shown in Fig. 7(b): a distribution under the $\tau_c = 3$ case at time $t = 2$ compared to 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 fits the $t = 2$ point (blue triangle) in Fig. 7(a).

The time scale of the TCFE violation in Fig. 6(a) agrees with that of the distribution violation in Fig. 7(a), with the corresponding correlation time $\tau_c$. This indicates that these two different violations come from the same origin, i.e., the memory effect of the initial preparation under the non-Markovian heat bath. This effect drives the system distribution out of equilibrium to make the JE and the TCFE invalid. Nevertheless, as soon as this effect vanishes, the JE and the TCFE become valid again. This suggests that a suitable JE or TCFE measurement should be put on the total evolution time longer than the efficient initial preparation effect time. Whether the recovery of the validity works for the specific simple model we are discussing or for a more general case is still an open question.

## 9. Concluding remarks

Heat transfer is as important as other thermodynamic processes such as internal energy change and work, and it may play a significant role in the free-energy relation and the fluctuation theorem. Nanotechnology has been rapidly developed in recent years, and some devices are now of the size of only a few hundred Å. Studies of the thermal properties have been extended to such systems. For the small systems, nonlinearity and fluctuations become significant in influencing the nonequilibrium properties. The stochasticity of nanoscopic devices is caused by the thermal motion at the atomic level. Nanosystems and their environment form a high-dimensional chaotic system due to the strong nonlinearity of the interatomic forces. Due to their nature as averages, the thermodynamic laws cannot be directly applied to the small systems in which the motion of single atoms is relevant. On the other hand, the classical thermodynamics is limited in application to large systems where intensive thermodynamic functions do not change their values if the system size is increased.

In the last few decades, several new theorems have been proven that revolutionize our understanding of thermodynamics. Firstly, these new theorems loose the need for taking the thermodynamic limit. Therefore, the application of the thermodynamic concepts can be extended to finite, and even nano systems. Secondly, these new theorems can be applied to systems far from equilibrium. It is very important that one has equilities rather than inequilities. Thirdly, and for the first time, these theorems explain how the macroscopic irreversibility appears naturally in systems that obey time reversible microscopic dynamics. In this case, the second law should be rechecked and small systems can violate this law in a single process.

In this paper, we give a retrospect of recent progresses in statistical mechanics and thermodynamics in small dynamical systems. For few-body systems, fluctuations and nonlinearity become significant and contribute to the nonequilibrium behaviors of the systems. We review by starting from the Gallavotti–Cohen fluctuation theorem, to the Evans–Searles transient fluctuation theorem, Jarzynski free-energy equality, and the Crooks fluctuation relation.

we also investigate the role of heat transfer in the case with heat bath temperature changes. A new thermodynamic relation (18) among the work, the heat, and the free-energy difference is analytically derived. The influence of the heat in each individual process can be considered to be a microscopic contribution to the entropy, giving rise to a contribution to the macroscopic free-energy difference. The index of heat appearing in the exponential average is different from that of work in relation (18). In practical situations, this suggests possible ways in finding an optimized heat-bath temperature $\beta_2$ to help reduce the statistical errors in the ensemble average, yielding a more accurate estimate for the free-energy difference. The free-energy relation can be naturally generalized to cases of arbitrarily modulations of the heat bath temperature (relation (31)). In this case, no energy information of the initial state is needed in the ensemble average: the work and the heat transfer are sufficient to form the needed averages, which should be simpler for experiments.

Finally, we find that the validity of fluctuation relations sensitively depends on the non-Markovian memory effect or 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 the TCFE. For the JE, this violation can be avoided by adding a sufficiently long-time relaxation to the equilibrium distribution before the measurement. For the TCFE, we find a different scenario. As the heat bath is changed at some time during the evolution, there is no time for the relaxation to eliminate the initial preparation effect with the switched heat bath. A careful consideration should be made during this non-Markovian process. It is valuable to extend the discussion to other dynamical systems. When the measurement time is longer than the initial-preparation time, it is interesting to observe that the JE and the TCFE again become valid. Whether this recovery of validity can be found for other systems is still an open question.

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