PHYSICAL REVIEW E **109**, 044101 (2024)

Temperature fluctuations in mesoscopic systems

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(Received 25 October 2023; revised 18 January 2024; accepted 26 February 2024; published 1 April 2024)

Temperature is a fundamental concept in thermodynamics. In macroscopic thermodynamics, systems possess their own intrinsic temperature which equals the reservoir temperature when they equilibrate. In stochastic thermodynamics for simple systems at the microscopic level, thermodynamic quantities other than temperature (a deterministic parameter of the reservoir) are stochastic. To bridge the disparity in the perspectives about temperature between the micro- and macroregimes, we assign a generic mesoscopic N-body system an intrinsic fluctuating temperature T in this work. We simplify the complicated dynamics of numerous particles to one stochastic differential equation with respect to T, where the noise term accounts for finite-size effects arising from random energy transfer between the system and the reservoir. Our analysis reveals that these fluctuations make the extensive quantities (in the thermodynamic limit) deviate from being extensive. Moreover, we derive finite-size corrections, characterized by heat capacity of the system, to the Jarzynski equality. A possible violation of the principle of maximum work that scales with N^{-1} is also discussed. Additionally, we examine the impact of temperature fluctuations in a finite-size Carnot engine. We show that irreversible entropy production resulting from the temperature fluctuations of the working substance diminishes the average efficiency of the cycle as $\eta_C - \langle\eta\rangle \sim N^{-1}$, highlighting the unattainability of the Carnot efficiency η_C for mesoscopic heat engines even under the quasistatic limit. Our general framework paves the way for further exploration of nonequilibrium thermodynamics and the corresponding finite-size effects in a mesoscopic regime.

DOI: 10.1103/PhysRevE.109.044101

I. INTRODUCTION

In the field of nonequilibrium thermodynamics, stochastic thermodynamics has attracted much attention recently. Notable among its accomplishments are the fluctuation theorems, which provide a quantitative framework for understanding the statistical behavior of nonequilibrium processes and offer a generalization of the second law. They are widely found and proved in time-dependent driving processes [1–5], nonequilibrium steady states [6–11], and quantum systems [12–20].

In addition to the aforementioned nonequilibrium processes, the departure of a many-body system from thermal equilibrium can be attributed to finite-size effects. In such cases, the system fluctuates around the-maximum-entropy (minimum-free-energy) state, with probabilities governed by the exponential of entropy (free energy) as per Einstein's interpretation of the reverse form of the Boltzmann entropy. Consequently, the system resides not in a full equilibrium state but rather in a quasiequilibrium state, as postulated by the theory of equilibrium fluctuations [21–23].

These studies primarily focused on equilibrium fluctuations, providing limited insights into characterizing the fluctuations and thermodynamic behaviors of mesoscopic systems undergoing nonequilibrium processes. However, the lack of clarity regarding mesoscopic nonequilibrium thermodynamics has created a gap in connecting microscopic dynamics and macroscopic thermodynamics. In particular, system's intrinsic temperature is a fundamental concept in macroscopic thermodynamics, while its counterpart in microscopic regime becomes ambiguous. In stochastic thermodynamics applied to simple systems with only a few degrees of freedom, temperature is a deterministic parameter of the reservoir, whereas other thermodynamic quantities (such as energy, entropy, work, and heat) are subject to stochastic behavior [1–5].

To eliminate the disparity in the viewpoints on temperature between the micro- and macroregimes, while also accounting for the fact that temperature fluctuates in equilibrium states [21–23], we propose a stochastic thermodynamics for mesoscopic systems that incorporates an intrinsic fluctuating temperature. Our framework pushes the traditional stochastic thermodynamics applied to small and simple systems into exploring the complex nonequilibrium thermodynamic behaviors at the mesoscopic level.

In this study, we delve into the finite-size effects of a generic N-body system undergoing an isothermal process through the fluctuating temperature. A stochastic differential equation (SDE) is formulated to simplify the complicated dynamics of numerous particles, where the noise term accounts for finite-size effects arising from random energy exchanges between the system and its reservoir. The temperature fluctuation, characterized by the temperature distribution, leads

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to modifications of the Jarzynski equality and the average efficiency of a quasistatic Carnot cycle at the mesoscopic scale. These modifications result in deviations from the well-established results typically applicable to systems in the thermodynamic limit.

As a general framework for describing temperature fluctuations in mesoscopic systems during nonequilibrium processes, our theory unifies various results from pioneering studies and different models. We extend the SDE that describes the fluctuations of a levitated nanoparticle in a specific trap [24–27] to encompass the temperature fluctuations of a mesoscopic many-particle system confined in an arbitrary potential well. In addition, it has been reported that the irreversible entropy production in a finite-size Carnot cycle diminishes the maximum efficiency [28], while our theory comes up with a general formula for quantitatively calculating the maximum efficiency and yields consistent results with those presented in Ref. [28] for specific models. Furthermore, the authors in Ref. [29] analyzed the performance and the stability of the Carnot cycle by considering the variance of the output work for systems with scale-invariant spectra. Notably, our results clearly demonstrate that the expression of the variance remains unchanged for systems without scale-invariant spectra.

The power of our theory lies not only in providing universal phenomenological interpretations of previous results but also in exploring the statistical laws governing finite-size systems in nonequilibrium processes. For instance, we derive finite-size corrections to the Jarzynski equality and predict a possible violation of the principle of maximum work by an amount proportional to N^{-1}. These findings facilitate the analysis and future experimental realization of nanotechnology or mesoscopic heat engines.

This paper is organized as follows: In Sec. II the stochastic differential equation for the system's temperature is derived. We further obtain the Fokker-Planck equation for the system's temperature in Sec. III. In Sec. IV the stochastic thermodynamics in terms of the fluctuating temperature is developed, and the finite-size correction to the Jarzynski equality is obtained. As a demonstration of our theory, we study the efficiency of a finite-size heat engine in a quasistatic Carnot cycle in Sec. V. Conclusions and outlooks of this study are given in Sec. VI.

II. TEMPERATURE FLUCTUATIONS IN ISOTHERMAL PROCESSES AT MESOSCOPIC SCALE

In this section we begin by providing a brief introduction to the stochastic Fokker-Planck equation [30], where the noise term characterizes the fluctuation of the flux density arising from the random collisions between the system and the reservoir at the mesoscopic level. We regard the equation as the generalization of the theory of equilibrium fluctuations in nonequilibrium processes.

Subsequently, we present the corresponding stochastic differential equation governing the system's temperature under the ergodic approximation. As a result, the stationary solution represents a quasiequilibrium state in a canonical system, in alignment with the theory of equilibrium fluctuation (see Sec. III). It is noteworthy that although the derivation of the stochastic differential equation for the system's temperature relies on the stochastic Fokker-Planck equation, we contend that our findings remain independent of the specific details concerning the system's evolution in nonequilibrium processes. These results can be applied to study discrete-state systems or other systems not described by the stochastic Fokker-Planck equation.

A. Stochastic Fokker-Planck equation

Let $\rho(z), z=(\boldsymbol{x},\boldsymbol{p}),\ \boldsymbol{x}=(x_1,\dots,x_d),\ \boldsymbol{p}=(p_1,\dots,p_d)$ denote the one-particle phase-space distribution of the system (d denotes the dimension of the system). The stochastic Fokker-Planck equation is given by [30]

$$\frac{\partial\rho}{\partial t}=L_{\mathrm{st}}\rho+\frac{\partial}{\partial\boldsymbol{p}}\cdot\boldsymbol{j}, \tag{1}$$

where

$$\boldsymbol{j}=\gamma\boldsymbol{p}\rho(1+\epsilon\rho)+\gamma mk_{\mathrm{B}}T_{\mathrm{r}}\frac{\partial\rho}{\partial\boldsymbol{p}}+\boldsymbol{\zeta} \tag{2}$$

is the flux density in phase space which originates from collisions between the system and the reservoir, and

$$L_{\mathrm{st}}=-\frac{\boldsymbol{p}}{m}\cdot\frac{\partial}{\partial\boldsymbol{x}}+\frac{\partial U}{\partial\boldsymbol{x}}\cdot\frac{\partial}{\partial\boldsymbol{p}} \tag{3}$$

denotes the streaming operator. Here m is the mass of the particle, γ the damping coefficient, U the potential energy, k_{B} the Boltzmann constant, and T_{r} the temperature of the reservoir, and $\epsilon=1,-1,0$ for (noncondensed) bosons, fermions and distinguishable particles, respectively. Hereafter, we do not show the time dependence of the functions explicitly without ambiguity. We emphasize that similar results to Eq. (1) can be obtained with various approaches [31–39].

Due to the discreteness of particle number and the randomness of collisions between the system and the reservoir, the noise term characterizes the finite-size effects of the dynamics. Here $\boldsymbol{\zeta}$ is a d-dimensional Gaussian white noise satisfying $\langle\zeta_i(z,t)\rangle=0$, $\langle\zeta_i(z,t)\zeta_j(z',t')\rangle=2h^d m\gamma k_{\mathrm{B}}T_{\mathrm{r}}\rho(z,t)[1+\epsilon\rho(z,t)]\delta_{ij}\delta(z-z')\delta(t-t')$ (h denotes the Planck constant). In the thermodynamic limit, the suppression of the noise ζ is shown in Refs. [30,36].

Equation (1) is conservative in particle number

$$N=\int\rho\,dz, \tag{4}$$

where $dz=\prod_{i=1}^{d}dx_i\,dp_i/h^d$. The internal energy E and the Boltzmann entropy S of the system are, respectively, given by

$$E=\int\left(\frac{p^2}{2m}+U\right)\rho\,dz \tag{5}$$

and

$$S=k_{\mathrm{B}}\int[-\rho\ln\rho+\epsilon^{-1}(1+\epsilon\rho)\ln(1+\epsilon\rho)]\,dz. \tag{6}$$

Also, we define $F=E-T_{\mathrm{r}}S$ as the nonequilibrium free energy of the system.

In the absence of the noise term $\boldsymbol{\zeta}$, Eq. (1) determines a steady state (a semiclassical equilibrium state in phase space)

$$\rho_{\mathrm{eq}}(z)=\frac{1}{e^{\beta_{\mathrm{r}}[p^2/(2m)+U(\boldsymbol{x})-\mu_{\mathrm{r}}]}-\epsilon}, \tag{7}$$

where $\beta_{\mathrm{r}} = 1/(k_{\mathrm{B}}T_{\mathrm{r}})$ is the inverse temperature, and μ_{r} the chemical potential, $p^2 = \sum_{i=1}^{d} p_i^2$. In fact, the equilibrium state ρ_{eq} is the minimum point of the nonequilibrium free energy F with constant N.

B. Ergodic approximation

Let τ_{p} denote the characteristic time of the motion due to the potential (e.g., the oscillating period of the harmonic trap). When τ_{p} is much smaller than the relaxation time γ^{-1}, the variation of ρ along the equienergy surface in the phase space is relatively small. The distribution function therefore depends only on the phase-space variables through the energy variable $\varepsilon(z) = p^2/(2m) + U(\boldsymbol{x})$. Such an approximation is called an ergodic approximation, which has been widely used in the literature on kinetic theory [40–45] (in Refs. [25–27], it is called highly underdamped regime).

Moreover, we assume that the potential energy U explicitly depends on a time-dependent parameter $\lambda(t)$, called the work parameter. The ergodic approximation requires that $\tau_{\mathrm{p}} \ll \tau_{\mathrm{d}}$, where τ_{d} is the driving time of λ. Then, following the similar procedure in Ref. [45] and using Eq. (1), we obtain the evolution equation of the mean occupation number $\tilde{\rho}(\varepsilon)$ at the single-particle energy ε:

$$\frac{\partial}{\partial t}(g\tilde{\rho}) + \frac{d\lambda}{dt}\frac{\partial}{\partial \varepsilon}\left(\overline{\frac{\partial U}{\partial \lambda}} g\tilde{\rho}\right) = \frac{\partial}{\partial \varepsilon}\left[\frac{\gamma g\overline{p^2}}{m}\left(\tilde{\rho} + \epsilon\tilde{\rho}^2 + k_{\mathrm{B}}T_{\mathrm{r}}\frac{\partial \tilde{\rho}}{\partial \varepsilon}\right) + \tilde{\zeta}\right], \tag{8}$$

where

$$g(\varepsilon, t) = \int \delta\left[\varepsilon - \frac{p^2}{2m} - U(\boldsymbol{x}, \lambda_t)\right] dz \tag{9}$$

denotes the density of states [$\lambda_t \equiv \lambda(t)$], and

$$\tilde{\rho}(\varepsilon, t) = g(\varepsilon, t)^{-1} \int \delta\left[\varepsilon - \frac{p^2}{2m} - U(\boldsymbol{x}, \lambda_t)\right] \rho(z, t)\, dz, \tag{10}$$

with $\tilde{\rho}(\varepsilon(z), t) = \rho(z, t)$ under the ergodic approximation. Here we have used the abbreviation

$$\overline{O(z)} \equiv \frac{1}{g(\varepsilon, t)} \int \delta\left[\varepsilon - \frac{p^2}{2m} - U(\boldsymbol{x}, \lambda_t)\right] O(z)\, dz, \tag{11}$$

and

$$\tilde{\zeta}(\varepsilon, t) \equiv \int \delta\left[\varepsilon - \frac{p^2}{2m} - U(\boldsymbol{x}, \lambda_t)\right] \frac{\boldsymbol{p}}{m} \cdot \boldsymbol{\zeta}(z, t)\, dz \tag{12}$$

is a Gaussian white noise satisfying $\langle \tilde{\zeta}(\varepsilon, t) \rangle = 0$, $\langle \tilde{\zeta}(\varepsilon, t)\tilde{\zeta}(\varepsilon', t') \rangle = 2m^{-1}\gamma k_{\mathrm{B}}T_{\mathrm{r}}\tilde{\rho}(\varepsilon, t)[1 + \epsilon\,\tilde{\rho}\,(\varepsilon, t)]\, g\,(\varepsilon, t) \overline{p^2}(\varepsilon, t)\delta(\varepsilon - \varepsilon')\delta(t - t')$. Such a noise characterizes the fluctuation of the density distribution of the system in the single-particle energy space.

C. SDE for the system temperature

The right-hand side (r.h.s.) of Eq. (8) describes random collisions between the particles and the reservoir. Also, there are also collisions among the particles. Let τ_{a} denote the relaxation time due to the internal collisions. We assume $\tau_{\mathrm{a}} \ll \gamma^{-1}$, τ_{d} so that the system is approximately a equilibrium state during the timescales γ^{-1}, τ_d. Thus, it is characterized by a time-dependent effective temperature T and a time-dependent effective chemical potential μ, which is called endoreversibility [27,46–49]. Specifically, we have [the mean occupation number at ε, Eq. (7)]

$$\tilde{\rho} = \frac{1}{e^{\beta(\varepsilon - \mu)} - \epsilon}. \tag{13}$$

Substituting Eq. (13) into Eqs. (4), (5), and (6), one finds

$$N = k_{\mathrm{B}}T\left(\frac{\partial \ln \mathcal{Z}}{\partial \mu}\right)_{\beta}, \tag{14}$$

$$E = -\left(\frac{\partial \ln \mathcal{Z}}{\partial \beta}\right)_{\beta\mu}, \tag{15}$$

and

$$S = k_{\mathrm{B}}(\ln \mathcal{Z} - \beta\mu N + \beta E), \tag{16}$$

with the partition function

$$\mathcal{Z} = -\epsilon \int \ln[1 - \epsilon e^{\beta(\mu - \varepsilon)}] g\, d\varepsilon. \tag{17}$$

Here Eqs. (14) and (15) determine the value of $\beta = 1/(k_{\mathrm{B}}T)$ and μ, and $\mathcal{Z}$ is the grand canonical partition function of the system.

Equations (13)–(17) connect the dynamical variables $\tilde{\rho}$ and the thermodynamic variables T, μ, E, S. Accordingly, the dynamic equation Eq. (1) can be represented by a thermodynamic equation. Taking the time derivative of E on both sides of Eq. (5) and using Eqs. (8), (13), and (17), we obtain a stochastic differential equation for internal energy

$$\frac{dE}{dt} = \Lambda\frac{d\lambda}{dt} + \Gamma(T_{\mathrm{r}} - T) + \xi, \tag{18}$$

where

$$\Lambda = -k_{\mathrm{B}}T\frac{\partial \ln \mathcal{Z}}{\partial \lambda} \tag{19}$$

denotes thermodynamic force conjugate to λ, $\Gamma \equiv \gamma dNk_{\mathrm{B}}$, and

$$\xi(t) \equiv -\int \tilde{\zeta}(\varepsilon, t)\, d\varepsilon \tag{20}$$

is a Gaussian white noise satisfying $\langle \xi(t) \rangle = 0$, $\langle \xi(t)\xi(t') \rangle = 2\Gamma k_{\mathrm{B}}T_{\mathrm{r}}T(t)\delta(t - t')$. In the derivation, we have used the identity

$$\int \frac{e^{\beta(\varepsilon - \mu)}\overline{p^2} g}{[e^{\beta(\varepsilon - \mu)} - \epsilon]^2}\, d\varepsilon = dNmk_{\mathrm{B}}T. \tag{21}$$

The first two terms on the r.h.s. of Eq. (18) correspond to the power and the rate of heat flow respectively. The rate of heat flow satisfies Newton's law of cooling with Γ as the cooling rate. The noise term accounts for the random energy transfer between the system and the reservoir. For a single particle in a single-well potential, similar results have been reported in Refs. [25–27]. Equation (18) is thus considered as a generalization to an N-body system in a general potential.

As a thermodynamic equation, Eq. (18) describes the evolution of the system in a nonequilibrium isothermal process, which should satisfy thermodynamic relations. To proceed, we consider λ, T, N as independent thermodynamic variables and do not show their dependence of functions for simplicity. We introduce $C \equiv \partial E/\partial T$ as the heat capacity with constant λ and obtain the following thermodynamic relations from Eqs. (15), (16), and (19):

$$\frac{\partial S}{\partial T} = \frac{C}{T}, \frac{\partial S}{\partial \lambda} = -\frac{\partial \Lambda}{\partial T}, \frac{\partial C}{\partial \lambda} = -T\frac{\partial^2 \Lambda}{\partial T^2}. \tag{22}$$

Moreover, taking the time derivative on both sides of Eq. (15), we obtain the first law by using Eqs. (16) and (22)

$$\begin{aligned}\frac{dE}{dt} &= \Lambda\frac{d\lambda}{dt} + T \circ \frac{dS}{dt}\\ &= \left(\Lambda - T\frac{\partial \Lambda}{\partial T}\right)\frac{d\lambda}{dt} + C \circ \frac{dT}{dt},\end{aligned} \tag{23}$$

where $\circ$ indicates the Stratonovich integral, which enables us to use ordinary calculus. Due to the noise ξ, the Stratonovich integral and the Itô integral are related by

$$C \circ \frac{dT}{dt} = C\frac{dT}{dt} + \frac{\Gamma k_B T_r T}{C^2}\frac{\partial C}{\partial T}. \tag{24}$$

Comparing Eq. (23) with Eq. (18) and transforming the Stratonovich integral into the Itô integral [Eq. (24)], we finally obtain the stochastic differential equation for the system temperature

$$C\frac{dT}{dt} = T\frac{\partial \Lambda}{\partial T}\frac{d\lambda}{dt} + \Gamma(T_r - T) - \frac{\Gamma k_B T_r T}{C^2}\frac{\partial C}{\partial T} + \xi. \tag{25}$$

III. FOKKER-PLANCK EQUATION FOR THE SYSTEM TEMPERATURE

The system's temperature fluctuate due to the noise term in Eq. (25). The Fokker-Planck equation for its probability distribution $P(T, t) = \langle \delta(T - T(t)) \rangle$ ($\langle \cdots \rangle$ denotes the average over the noise ξ) is

$$\begin{aligned}\frac{\partial P}{\partial t} &= \frac{\partial}{\partial T}\left[-\frac{T}{C}\frac{\partial \Lambda}{\partial T}\frac{d\lambda}{dt}P + \frac{\Gamma}{C}(T - T_r)P + \frac{\Gamma k_B T_r}{C}\frac{\partial}{\partial T}\left(\frac{TP}{C}\right)\right]\\ &= \frac{\partial}{\partial T}\left[-\frac{T}{C}\frac{\partial \Lambda}{\partial T}\frac{d\lambda}{dt}P + \frac{\Gamma T}{C^2}P\frac{\partial}{\partial T}\left(F + k_B T_r \ln\frac{k_B T P}{C}\right)\right].\end{aligned} \tag{26}$$

Here $T \in [0, \infty)$, and we assume that P quickly goes to zero when $T \to \infty$ or $T \to 0$. The second equality in Eq. (26) shows the thermodynamic nature implied in it. When $t \to \infty$, let λ be a constant, and then Eq. (26) determines a stationary solution

$$P_s(T, \lambda) = \frac{C}{\tilde{\mathcal{Z}} k_B T}e^{-\beta_r F}, \tag{27}$$

where $\tilde{\mathcal{Z}} \equiv \int C(k_B T)^{-1} e^{S/k_B - \beta_r E}\, dT$ denotes the generalized partition function of the system [30]. In the absence of the factor $C/(\tilde{\mathcal{Z}} k_B T)$, P_s is actually the quasiequilibrium state in a canonical system according to the theory of equilibrium fluctuation [21–23] and satisfies the large deviation principle.

Similar to the equilibrium free energy in statistical mechanics, we define

$$\mathcal{F} \equiv -k_B T_r \ln \tilde{\mathcal{Z}} \tag{28}$$

as the generalized free energy of the system. Then we have the relation $\mathcal{F} = \mathcal{E} - T_r \mathcal{S}$, where

$$\mathcal{E} \equiv \int E P_s\, dT = -\frac{\partial \ln \tilde{\mathcal{Z}}}{\partial \beta_r} \tag{29}$$

is the mean internal energy of the system at the quasiequilibrium state, and

$$\mathcal{S} \equiv \int \left(S - k_B \ln\frac{k_B T P_s}{C}\right)P_s\, dT = k_B \beta_r (\mathcal{E} - \mathcal{F}) \tag{30}$$

is the mean entropy of the system at the quasiequilibrium state. Here the mean entropy is a sum of the mean Boltzmann entropy (the first term in the integral) and the contribution from the distribution of the system's temperature (the second term in the integral), the latter of which is consistent with the perspective of information theory [50,51]. Also, we confirm the fundamental relation in thermodynamics

$$d\mathcal{E} = T_r\, d\mathcal{S} + \tilde{\Lambda}\, d\lambda \tag{31}$$

and

$$d\mathcal{F} = -\mathcal{S}\, dT_r + \tilde{\Lambda}\, d\lambda, \tag{32}$$

where $\tilde{\Lambda} \equiv -k_B T_r \partial \ln \tilde{\mathcal{Z}}/\partial \lambda$ denotes the generalized thermodynamic force conjugate to λ at the quasiequilibrium state. We want to emphasize here that these generalized quantities $\mathcal{F}, \mathcal{E}, \mathcal{S}$, which are extensive in the thermodynamic limit, are no longer extensive due to the finite-size effect of the system.

In the thermodynamic limit, we apply the Gaussian approximation of Eq. (27) as (central limit theorem)

$$P_s(T, \lambda) \simeq \sqrt{\frac{C_r}{2\pi k_B T_r^2}}\exp\left[-\frac{C_r (T - T_r)^2}{2k_B T_r^2}\right], \tag{33}$$

where $C_r \equiv C|_{T=T_r}$. Equation (33) approximates the system's temperature fluctuation at the equilibrium state. Its mean value T_r and variance $k_B T_r^2/C_r$ are consistent with the theory of equilibrium fluctuation [21–23]. Then, substituting Eq. (33) into Eq. (28), we obtain

$$\mathcal{F} = F_r - \frac{k_B T_r}{2}\ln\frac{2\pi C_r}{k_B} + O\left(\frac{1}{N}\right), \tag{34}$$

where $F_r \equiv F|_{T=T_r}$. The first term on the r.h.s. is the equilibrium free energy of the system at temperature T_r and the second term on the r.h.s. is the finite-size correction to it.

IV. STOCHASTIC THERMODYNAMICS

In the spirit of stochastic thermodynamics [1–3], in this section we are going to define stochastic thermodynamic quantities corresponding to Eqs. (18), (23), and (26). First, a trajectory of the system's temperature is defined as $T_{[0,\tau]} := \{T(t) | t \in [0, \tau]\}$. According to Eqs. (18) and (23), the stochastic work $w[T_{[0,t]}]$ and the stochastic heat $q[T_{[0,t]}]$ are, respectively, given by

$$w[T_{[0,\tau]}] = \int_0^\tau \Lambda\, d\lambda \tag{35}$$

and

$$\begin{aligned} q[T_{[0,\tau]}] &= \int_0^\tau T \circ dS \\ &= \int_0^\tau \left(-T \frac{\partial \Lambda}{\partial T} d\lambda + C \circ dT \right) \\ &= \int_0^\tau [\Gamma(T_\mathrm{r} - T) + \xi] dt. \end{aligned} \tag{36}$$

Thus, we have the conservation law of energy

$$E(\tau) - E(0) = w[T_{[0,\tau]}] + q[T_{[0,\tau]}] \tag{37}$$

at the mesoscopic level.

Corresponding to Eq. (26), the stochastic entropy $s(t)$ and stochastic free energy $f(t)$ are respectively given by (also see Ref. [30])

$$\begin{aligned} s(t) &= S(t) - k_\mathrm{B} \ln \frac{k_\mathrm{B} T(t) P(T(t), t)}{C(t)} \\ &= k_\mathrm{B} \left[\beta_\mathrm{r} E(t) - \beta_\mathrm{r} \mathcal{F}(t) - \ln \frac{P(T(t), t)}{P_\mathrm{s}(T(t), \lambda(t))} \right], \end{aligned} \tag{38}$$

and

$$\begin{aligned} f(t) &= E(t) - T_\mathrm{r} s(t) \\ &= F(t) + k_\mathrm{B} T_\mathrm{r} \ln \frac{k_\mathrm{B} T(t) P(T(t), t)}{C(t)} \\ &= \mathcal{F}(t) + k_\mathrm{B} T_\mathrm{r} \ln \frac{P(T(t), t)}{P_s(T(t), \lambda(t))}. \end{aligned} \tag{39}$$

Here $P(T, t)$ is the solution of Eq. (26), S (F) denotes the Boltzmann entropy (nonequilibrium free energy) of the system, and the term $-k_\mathrm{B} \ln[k_\mathrm{B} T P C^{-1}]$ ($k_\mathrm{B} T_\mathrm{r} \ln[k_\mathrm{B} T P C^{-1}]$) denotes the finite-size correction to S (F) from the distribution of the system's temperature. The term $k_\mathrm{B} \beta_\mathrm{r}(E - \mathcal{F})$ corresponds to the mean entropy at the quasiequilibrium state $\mathcal{S}$ in Eq. (30). The term $-k_\mathrm{B} \ln(P/P_\mathrm{s})$ (after taking the average over P) corresponds to the relative entropy, which measures how far the temperature distribution is from the quasiequilibrium state. Consequently, we have $\mathcal{E} = \langle E \rangle|_{P=P_\mathrm{s}}$, $\mathcal{S} = \langle s \rangle|_{P=P_\mathrm{s}}$, and $\mathcal{F} = \langle f \rangle|_{P=P_\mathrm{s}}$. It is worth mentioning that the stochastic free energy f, the difference between which and the generalized free energy $\mathcal{F}$ measures how far the system departures from the quasiequilibrium state, has not been reported in previous papers (but for Ref. [30]).

Moreover, the stochastic total entropy production $s_\mathrm{p}[T_{[0,\tau]}]$ reads

$$s_\mathrm{p}[T_{[0,\tau]}] = s(\tau) - s(0) + s_\mathrm{r}[T_{[0,\tau]}], \tag{40}$$

where $s_\mathrm{r}[T_{[0,\tau]}] = -q[T_{[0,\tau]}]/T_\mathrm{r}$ is the stochastic entropy change of the reservoir.

Then we prove the fluctuation theorems based these stochastic quantities. According to Eq. (25), the probability distribution of the trajectory $T_{[0,\tau]}$ conditioned with a fixed initial temperature $T_0 \equiv T(0)$ reads [52–54]

$$P[T_{[0,\tau]}|T_0] = e^{-\tilde{\mathcal{S}}[T_{[0,\tau]}]}, \tag{41}$$

where the integral measure is $\mathcal{D}T \equiv \prod_{i=1}^N dT_i \sqrt{C_i^2/(2\pi T_i^* \Delta t)}$, with the Stratonovich discretization $0 = t_0 < t_1 < \cdots < t_{N-1} < t_N = \tau$, $\Delta t \equiv t_i - t_{i-1}$, $T_i \equiv T(t_i)$, $T_i^* \equiv (T_i + T_{i-1})/2$, $\lambda_i \equiv \lambda(t_i)$, $\lambda_i^* \equiv (\lambda_i + \lambda_{i-1})/2$, $C_i \equiv C|_{T=T_i^*, \lambda=\lambda_i^*}$. Here the action $\tilde{\mathcal{S}}$ as a generalized Onsager-Machlup functional is given by

$$\begin{aligned} \tilde{\mathcal{S}}[T_{[0,\tau]}] = \frac{1}{4\Gamma k_\mathrm{B} T_\mathrm{r}} \int_0^\tau \bigg[& C \frac{dT}{dt} - T \frac{\partial \Lambda}{\partial T} \frac{d\lambda}{dt} \\ & - \Gamma(T_\mathrm{r} - T) - \frac{\Gamma k_\mathrm{B} T_\mathrm{r} T}{C} \frac{\partial}{\partial T} \ln \frac{C}{T} \bigg]^2 \frac{dt}{T} \\ & + \frac{1}{2} \int_0^\tau \frac{\partial}{\partial T} \left[\frac{T}{C} \frac{\partial \Lambda}{\partial T} \frac{d\lambda}{dt} + \frac{\Gamma}{C}(T_\mathrm{r} - T) - \frac{\Gamma k_\mathrm{B} T_\mathrm{r}}{2C^2} \right] dt. \end{aligned} \tag{42}$$

In Eq. (42) we also have chosen the Stratonovich discretization. Such a choice ensures that the time reversal of $P[T_{[0,\tau]}|T_0]$ is also under the Stratonovich discretization [52,53].

To proceed, let $P^\dagger[T^\dagger_{[0,\tau]}|T^\dagger_0]$ denote the conditional probability distribution of the reverse trajectory $T^\dagger_{[0,\tau]} := \{T(\tau - t) | t \in [0, \tau]\}$ with another fixed initial temperature $T^\dagger_0 \equiv T^\dagger(0)$ and a reverse protocol $\lambda^\dagger(t) := \lambda(\tau - t)$ (the superscript † indicates the reverse trajectory). It follows from Eqs. (41) and (42) that

$$\begin{aligned} P^\dagger[T^\dagger_{[0,\tau]}|T^\dagger_0] &= e^{-\tilde{\mathcal{S}}[T^\dagger_{[0,\tau]}]} \\ &= e^{-\tilde{\mathcal{S}}[T_{[0,\tau]}]} \Big|_{\{\frac{dT}{dt}, \frac{d\lambda}{dt}\} \to \{-\frac{dT}{dt}, -\frac{d\lambda}{dt}\}}, \end{aligned} \tag{43}$$

and thus the detailed fluctuation theorem is obtained as

$$\ln \frac{P[T_{[0,\tau]}|T_0]}{P^\dagger[T^\dagger_{[0,\tau]}|T^\dagger_0]} = \ln \frac{P(T_\tau, \tau)}{P(T_0, 0)} + \frac{s_\mathrm{p}[T_{[0,\tau]}]}{k_\mathrm{B}}, \tag{44}$$

where $T_\tau \equiv T(\tau)$. By adding an arbitrary normalized distribution at the initial time of the reverse process $P'(T^\dagger_0, 0)$ and noticing $\mathcal{D}T = \mathcal{D}T^\dagger$, we obtain the integral fluctuation theorem as

$$\left\langle \frac{P'(T^\dagger_0, 0)}{P(T_\tau, \tau)} e^{-\frac{s_\mathrm{p}}{k_\mathrm{B}}} \right\rangle = 1. \tag{45}$$

Such an equality is formally consistent with the integral fluctuation theorems in previous studies [1,2]. For a choice of $P'(T^\dagger_0, 0) = P(T_\tau, \tau)$, we obtain the integral fluctuation theorem for total entropy production [1,2,30]

$$\langle e^{-s_\mathrm{p}/k_\mathrm{B}} \rangle = 1. \tag{46}$$

As a corollary, the second law $\langle s_\mathrm{p} \rangle \geqslant 0$ follows from the fluctuation theorem by using Jensen's inequality.

When both $P(T_0, 0), P'(T^\dagger_0, 0)$ are stationary solutions of the Fokker-Planck equation [quasiequilibrium state in Eq. (27)], i.e., $P(T_0, 0) = P_\mathrm{s}(T_0, \lambda_0), P'(T^\dagger_0, 0) = P_\mathrm{s}(T_\tau, \lambda_\tau)$, we obtain the generalized Jarzynski equality [30]

$$\langle e^{-\beta_\mathrm{r} w} \rangle = e^{-\beta_\mathrm{r} \Delta \mathcal{F}}, \tag{47}$$

and the generalized principle of maximum work $\langle w \rangle \geqslant \Delta \mathcal{F}$ by using Jensen's inequality [30], where $\Delta A \equiv A(\tau) - A(0)$ for some time-dependent function A. In the thermodynamic

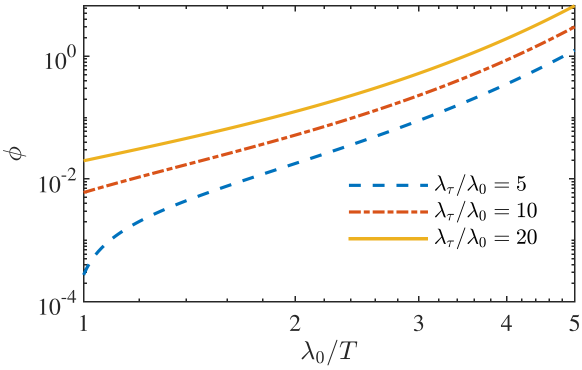

FIG. 1. ϕ as a function of T for different λ_τ/λ_0.

limit, it follows from Eq. (34) that

$$\langle e^{-\beta_r w}\rangle = e^{-\beta_r \Delta F_r}\sqrt{\frac{C_r(\lambda_\tau)}{C_r(\lambda_0)}} + O\left(\frac{1}{N}\right) \tag{48}$$

and

$$\langle w\rangle \geqslant \Delta F_r - \frac{k_B T_r}{2}\ln\left[\frac{C_r(\lambda_\tau)}{C_r(\lambda_0)}\right] + O\left(\frac{1}{N}\right). \tag{49}$$

Here the ratio of the heat capacity is a finite-size correction to the Jarzynski equality and the principle of maximum work. Equation (49) indicates that when $C_r(\lambda_\tau) > C_r(\lambda_0)$, a possible violation of the principle of maximum work by an amount on the order of N^{-1} is possible. We further define the following quantity to characterize such a correction:

$$\phi \equiv \left|\frac{\ln\left[C_r(\lambda_\tau)/C_r(\lambda_0)\right]}{2\beta_r \Delta F_r}\right|. \tag{50}$$

For example, if the system is specified as $N = 1000$ two-level particles with energy spacing λ (see Appendix A for details), we plot ϕ as a function of temperature T_r in Fig. 1 for different λ_τ/λ_0. In this figure we see that ϕ significantly increases as the temperature decreases. It is hence possible in principle to observe the finite-size correction to Jarzynski equality in some experimental platforms. In addition, for systems with quantum phase transitions [55,56], the dependence of heat capacity on parameters near the critical point is remarkable. In such cases, the finite-size correction will be particularly important for the Jarzynski equality.

V. FLUCTUATING CARNOT CYCLE

As an application of our theory, we study a fluctuating Carnot cycle with finite-size working substance using Eq. (25). As illustrated in Fig. 2, the Carnot cycle consists of four processes: $1 \to 2$, adiabatic compression ($\gamma = 0$); $2 \to 3$, isothermal expansion (hot reservoir's temperature T_h); $3 \to 4$, adiabatic expansion ($\gamma = 0$); and $4 \to 1$, isothermal compression (cold reservoir temperature T_c). Let $T_n, n = 1, \ldots, 4$ denote the corresponding temperature of the working substance at state n. Then we have $\langle T_1\rangle = \langle T_4\rangle = T_c$ and $\langle T_2\rangle = \langle T_3\rangle = T_h$. Let $\lambda_n, E_n, C_n, S_n, s_n, n = 1, \ldots, 4$ denote the corresponding work parameter, internal energy, heat capacity, Boltzmann entropy, and stochastic entropy of the working substance, respectively. By using Eq. (26) with $\gamma = 0$, it is straightforward to prove that in the adiabatic processes, both the average Boltzmann entropy and stochastic entropy are constants,

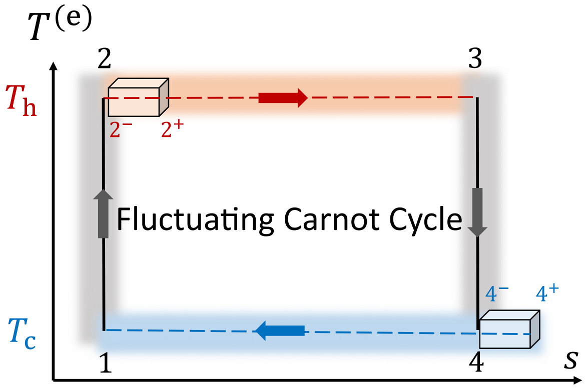

FIG. 2. Carnot cycle in the temperature-entropy diagram. The shaded regions represent the temperature fluctuation due to the finite-size effect of the working substance.

$$\langle S_1\rangle = \langle S_2\rangle, \quad \langle S_3\rangle = \langle S_4\rangle \tag{51}$$

and

$$\langle s_1\rangle = \langle s_2\rangle, \quad \langle s_3\rangle = \langle s_4\rangle. \tag{52}$$

Then let $P_n, P_{sn}, \mathcal{F}_n, n = 1, \ldots, 4$ denote the corresponding temperature distribution, quasiequilibrium state, and generalized free energy of the working substance, respectively. In the quasistatic limit, $d\lambda/dt \to 0$ and the working substance is a quasiequilibrium state with $T_r = T_h$ ($T_r = T_c$) all the time in the isothermal expansion (compression) process according to Eq. (26). Meanwhile according to Appendix B, the working substance at the end of the adiabatic processes is generally not a quasiequilibrium anymore. That is to say, $P_1 = P_{s1}, P_3 = P_{s3}$, and $P_2 \neq P_{s2}, P_4 \neq P_{s4}$. Such a result reflects the fact that from state $2^- \to 2^+$ ($4^- \to 4^+$), the working substance has quickly thermalized during a vanishing small timescale γ^{-1}, where the average temperature of the working substance remains the same but the variance of the temperature of the working substance changes. Consequently, no work is done during the vanishing small time, and the finite irreversible entropy production occurs due to the contribution from the relative entropy [see Eqs. (38)–(40)], which is a finite-size effect and first reported in Ref. [28] to our best knowledge.

In Fig. 2 we illustrate the finite-size effects of the fluctuating Carnot cycle in terms of the temperature and entropy of the working substance. The end-to-end solid and dashed lines represent their mean values, while the shaded regions signify the fluctuations attributable to finite-size effects. We accentuate the irreversible entropy production depicted within the two cuboids, which diminishes the average efficiency of the Carnot cycle.

In the two isothermal processes, the variances of the input work both vanish (see the example in Ref. [57]). Therefore, the input work in the two isothermal processes is a constant, $\mathcal{F}_3 - \mathcal{F}_2 + \mathcal{F}_1 - \mathcal{F}_4$, corresponding to the generalized principle of maximum work. In the two adiabatic processes, there is no heat transfer and the input work is equal to the internal energy change according to the conservation law of energy, $E_2 - E_1 + E_4 - E_3$. Thus, using Eq. (38), the total input work reads

$$\begin{aligned} w_{\text{in}} &= E_2 - E_1 + E_4 - E_3 + \mathcal{F}_3 - \mathcal{F}_2 + \mathcal{F}_1 - \mathcal{F}_4 \\ &= T_{\text{h}}\left(s_2 - s_3 + k_{\text{B}} \ln \frac{P_2}{P_{\text{s}2}}\right) + T_{\text{c}}\left(s_4 - s_1 + k_{\text{B}} \ln \frac{P_4}{P_{\text{s}4}}\right). \end{aligned} \tag{53}$$

Accordingly, the absorbed heat from the hot reservoir reads

$$q_{\text{h}} = T_{\text{h}}\left(s_3 - s_2 - k_{\text{B}} \ln \frac{P_2}{P_{\text{s}2}}\right), \tag{54}$$

where s_1, s_2 are independent of s_3, s_4 due to the thermalization in the two isothermal processes. Note that the connections between s_1, s_2 or s_3, s_4 satisfy the energy-conservation equation in the adiabatic process [Eq. (25) with $\gamma = 0$]. It follows from Eq. (40) that the entropy production of the cycle is (also see Refs. [58,59])

$$\begin{aligned} s_{\text{p}} &= \frac{q_{\text{h}} + w_{\text{in}}}{T_{\text{c}}} - \frac{q_{\text{h}}}{T_{\text{h}}} \\ &= s_4 - s_1 - s_3 + s_2 + k_{\text{B}} \ln \frac{P_4}{P_{\text{s}4}} + k_{\text{B}} \ln \frac{P_2}{P_{\text{s}2}}. \end{aligned} \tag{55}$$

To study the efficiency of the cycle, we adopt the definition of the stochastic efficiency in Ref. [60],

$$\eta = -\frac{w_{\text{in}}}{\langle q_{\text{h}} \rangle}, \tag{56}$$

which is called the scaled fluctuating efficiency. The moments of the efficiency always exist, and its mean value is equal to the conventional efficiency of a cycle. Using Eqs. (52)–(54), the average efficiency of the cycle is

$$\begin{aligned} \langle \eta \rangle &= 1 - \frac{T_{\text{c}}[\Delta\bar{s} + D(P_4||P_{\text{s}4})]}{T_{\text{h}}[\Delta\bar{s} - D(P_2||P_{\text{s}2})]} \\ &= \eta_{\text{C}} - (1 - \eta_{\text{C}})\frac{\langle s_{\text{p}} \rangle}{\Delta\bar{s}} + O\left(\frac{1}{N^2}\right). \end{aligned} \tag{57}$$

Here $\eta_{\text{C}} \equiv 1 - T_{\text{c}}/T_{\text{h}}$ is the Carnot efficiency, $\Delta\bar{s} \equiv \langle s_3 \rangle - \langle s_2 \rangle = \langle s_4 \rangle - \langle s_1 \rangle$ is the average entropy change of the working substance in the isothermal expansion process,

$$D(P||P_{\text{s}}) \equiv \int P \ln \frac{P}{P_{\text{s}}}\, dT, \tag{58}$$

is the relative entropy, and $\langle s_{\text{p}} \rangle = D(P_2||P_{\text{s}2}) + D(P_4||P_{\text{s}4})$ following from Eqs. (52) and (55) is the total average entropy production of the cycle according to Eq. (55). Since $\Delta\bar{s} > 0$ and $\langle s_{\text{p}} \rangle \geqslant 0$, we conclude that the irreversible entropy production due to the temperature fluctuation of the working substance diminishes the average efficiency of the cycle. Consequently, even in the quasistatic limit, the Carnot efficiency remains unattainable. Such an equation is also shown in Ref. [28].

In the thermodynamic limit, we are only concerned about the mean value $\langle A \rangle$ and the variance $\sigma_A^2 = \langle (A - \langle A \rangle)^2 \rangle$ for some T-dependent function A. As a result, the temperature distribution of the working substance is approximately a Gaussian distribution, $T_n \sim \mathcal{N}(\langle T_n \rangle, \sigma_{T_n}^2)$, for $n = 1, \ldots, 4$. Therefore, we find

$$\Delta\bar{s} = S_{3\text{h}} - S_{2\text{h}} + O\left(\frac{k_{\text{B}}}{N}\right) = S_{4\text{c}} - S_{1\text{c}} + O\left(\frac{k_{\text{B}}}{N}\right) \tag{59}$$

and

$$\langle s_{\text{p}} \rangle = \frac{1}{2}\left[\ln(\kappa\kappa') + \frac{1}{\kappa} + \frac{1}{\kappa'} - 2\right], \tag{60}$$

where $S_{n\text{c(h)}} \equiv S_n|_{T=T_{\text{c(h)}}}$ for $n = 1, \ldots, 4$, $\kappa \equiv C(T_{\text{c}}, \lambda_2)/C(T_{\text{h}}, \lambda_1)$, and $\kappa' \equiv C(T_{\text{h}}, \lambda_4)/C(T_{\text{c}}, \lambda_3)$ (see Appendix B).

As an example, we specific the working substance as the N-particle system studied in Ref. [28], with the Hamiltonian

$$H = \sum_{i=1}^{dN}\left(\frac{p_i^2}{2m} + a\left|\frac{x_i}{L}\right|^{\lambda}\right) + V, \tag{61}$$

where m denotes the mass of the N particles, a the characteristic energy of the system, L the characteristic length of the system, λ the work parameter, and V the interactions among these particles (which can be ignored in comparison with the kinetic and potential energy but is strong enough to make the particles ergodic). Taking use of the internal energy of the system at the equilibrium state [Eq. (B15) in Ref. [28]], we obtain the total average entropy production of the cycle from Eq. (60) as

$$\begin{aligned} \langle s_{\text{p}} \rangle = \frac{1}{2}\ln\left[\frac{\lambda_1(\lambda_2+2)\lambda_3(\lambda_4+2)}{(\lambda_1+2)\lambda_2(\lambda_3+2)\lambda_4}\right] \\ + \frac{(\lambda_2-\lambda_1)}{\lambda_1(\lambda_2+2)} + \frac{(\lambda_4-\lambda_3)}{\lambda_3(\lambda_4+2)}, \end{aligned} \tag{62}$$

with $\kappa = \lambda_1(\lambda_2+2)/[(\lambda_1+2)\lambda_2]$, and $\kappa' = \lambda_3(\lambda_4+2)/[(\lambda_3+2)\lambda_4]$. Such a result is consistent with the leading order of the expression of the relative entropy shown in Eq. (7) of Ref. [28] in the large-N limit, while the latter was previously obtained through complicated calculation. Such a consistence indicates that our formalism is universal and is able to exactly capture the entropy production of the cycles due to the finite-N effects of the working substance.

Substituting Eqs. (59) and (60) into Eq. (57), the average efficiency is obtained as

$$\langle \eta \rangle = \eta_{\text{C}} - (1-\eta_{\text{C}})\frac{\kappa\kappa' \ln(\kappa\kappa') + \kappa + \kappa' - 2\kappa\kappa'}{2\kappa\kappa'(S_{3\text{h}} - S_{2\text{h}})} + O\left(\frac{1}{N^2}\right). \tag{63}$$

In particular, for a constant heat capacity of the working substance (such as ideal gas), $\kappa = \kappa' = 1$ and the Carnot efficiency is recovered $\langle \eta \rangle = \eta_{\text{C}}$ to the order of N^{-1}.

Furthermore, we consider the variance of the efficiency σ_η^2. It follows from Eq. (56) that $\sigma_\eta^2 = \sigma_{w_{\text{in}}}^2/\langle q_{\text{h}} \rangle^2$. Using the linear relation between the initial and final internal energy in the adiabatic process (Appendix B), we obtain the correlation functions

$$\langle E_1E_2 \rangle - \langle E_1 \rangle\langle E_2 \rangle = k_{\text{B}}T_{\text{c}}T_{\text{h}}C_{1\text{c}} + O\left(k_{\text{B}}^2T^2\right), \tag{64}$$

$$\langle E_3E_4 \rangle - \langle E_3 \rangle\langle E_4 \rangle = k_{\text{B}}T_{\text{c}}T_{\text{h}}C_{3\text{h}} + O\left(k_{\text{B}}^2T^2\right). \tag{65}$$

Combining Eqs. (53), (54), and (59), one finds

$$\sigma_\eta^2 = \frac{\sigma_{E_2-E_1}^2 + \sigma_{E_4-E_3}^2}{\langle q_\mathrm{h}\rangle^2} = \frac{k_\mathrm{B}(T_\mathrm{h}-T_\mathrm{c})^2(C_{1\mathrm{c}}+C_{3\mathrm{h}})}{T_\mathrm{h}^2(S_{3\mathrm{h}}-S_{2\mathrm{h}})^2} + O\left(\frac{1}{N^2}\right). \tag{66}$$

It is worth mentioning here that such a result also appeared in Ref. [29] for the spectra of the working substance with scale property, while our result is not limited to this case. That is to say that our theory is independent of the details of the working substance and is thus universal.

VI. CONCLUSION AND OUTLOOK

In this paper we have studied the temperature fluctuations of a finite-size system. Initially, we drive a stochastic differential equation to describe the evolution of the system's temperature during a isothermal process. The noise term in the equation accounts for finite-size effects resulting from random energy exchanges between the system and its reservoir. Consequently, the system's stationary state represents a quasiequilibrium state according to the theory of equilibrium fluctuation, in which the generalized thermodynamic quantities (which are extensive in the thermodynamic limit) deviate from being extensive due to finite-size effects.

Furthermore, we develop stochastic thermodynamics based on the temperature fluctuations of the system and substantiate the fluctuation theorems. The obtained results provide finite-size corrections to the Jarzynski equality, which is quantified by the square root of the ratio of the system's heat capacities at the final and initial stages of the driving. Additionally, we observe a breach of the principle of maximum work by an amount on the order of N^{-1}.

To demonstrate the impact of temperature fluctuations at the mesoscopic level in typical thermodynamic processes, we analyze the efficiency of a finite-size heat engine operating in a quasistatic Carnot cycle. Our findings reveal that even under the quasistatic limit, the Carnot efficiency η_C remains unattainable due to the irreversible entropy production arising from temperature fluctuations of the working substance. For some specific models, our general results of the mean value and variance of the efficiency align with previous findings in Refs. [28] and [29], respectively.

In closing, our framework paves the way for further exploration of mesoscopic nonequilibrium thermodynamics and the corresponding finite-size effects [39]. Several theoretical predictions made in this work can potentially be verified on a mature experimental platform [61]. As possible extensions of our current results, the finite-time performance [27,60,62] and optimization [46,63,64] of the proposed fluctuating Carnot cycle are worth further investigation. Moreover, considering both the temperature fluctuations of the working substance and the finiteness of the heat reservoirs [48,49,65–67], finding the power-efficiency trade-off relation [62,68,69] and relevant optimizations of the heat engine present another challenging task with implications for mesoscopic heat engines.

ACKNOWLEDGMENTS

Y.H.M. thanks the National Natural Science Foundation of China for support under Grant No. 12305037 and the Fundamental Research Funds for the Central Universities under Grant No. 2023NTST017.

APPENDIX A: THERMODYNAMIC QUANTITIES OF TWO-LEVEL SYSTEMS

We consider an ensemble of noninteracting two-level systems, such as N free spin-1/2 particles. The excited state and ground state of the ith subsystem are denoted as $|e\rangle_i$ and $|g\rangle_i$, respectively, and the Hamiltonian of the system reads

$$H = \sum_{i=1}^{N} \lambda |e\rangle_{ii}\langle e|, \tag{A1}$$

where λ is the energy spacing of the two states and the ground state energy is set to zero. When this system is at the thermal equilibrium state with inverse temperature β, the populations in the excited and ground state are

$$p_e = \frac{e^{-\beta\lambda}}{1+e^{-\beta\lambda}}, \tag{A2}$$

$$p_g = \frac{1}{1+e^{-\beta\lambda}}, \tag{A3}$$

with the partition function $Z(\lambda) = 1 + e^{-\beta\lambda}$, and the internal energy

$$U = Np_e\lambda = \frac{N\lambda}{1+e^{-\beta\lambda}}. \tag{A4}$$

Then the heat capacity of the system is

$$C = \frac{\partial U}{\partial T} = \frac{N\beta^2\lambda^2 e^{\beta\lambda}}{(1+e^{-\beta\lambda})^2}, \tag{A5}$$

where the λ-dependent heat capacity contributes to the finite-size correction of the Jarzynski equality.

By using Eq. (A5) and noting that

$$\Delta F = -N\beta^{-1}\ln\left[\frac{Z(\lambda_\tau)}{Z(\lambda_0)}\right] = N\beta^{-1}\ln\left(\frac{1+e^{-\beta\lambda_0}}{1+e^{-\beta\lambda_\tau}}\right), \tag{A6}$$

the quality ϕ defined in Eq. (50) is specifically obtained as

$$\phi = \frac{1}{2N}\left|\frac{2\ln\left[\frac{\lambda_\tau(1+e^{-\beta\lambda_0})}{\lambda_0(1+e^{-\beta\lambda_\tau})}\right] + \beta(\lambda_\tau-\lambda_0)}{\ln\left(\frac{1+e^{-\beta\lambda_0}}{1+e^{-\beta\lambda_\tau}}\right)}\right|. \tag{A7}$$

APPENDIX B: SOLUTION OF THE SYSTEM'S TEMPERATURE IN THE ADIABATIC PROCESS

Taking the average on the both sides of Eq. (25) with $\gamma = 0$ (adiabatic process), we have

$$\frac{dT_e}{dt} = \left\langle\frac{T}{C}\frac{\partial\Lambda}{\partial T}\right\rangle\frac{d\lambda}{dt} = \left[\frac{T_e}{C_e}\frac{\partial\Lambda_e}{\partial T_e} + \frac{\sigma_T^2}{2}\frac{\partial^2}{\partial T_e^2}\left(\frac{T_e}{C_e}\frac{\partial\Lambda_e}{\partial T}\right)\right]\frac{d\lambda}{dt} + O\left(\frac{T}{N^2\tau}\right), \tag{B1}$$

where $T_e \equiv \langle T\rangle$, $\Lambda_e \equiv \Lambda|_{T=T_e}$, and $C_e \equiv C|_{T=T_e}$. Since the adiabatic process connects two isothermal processes, let T_a (T_b) denote the temperature of the reservoir at the initial (final) time $t = 0$ ($t = \tau$), and we have the following boundary conditions:

$$T_e(0) = T_a, \quad T_e(\tau) = T_b. \tag{B2}$$

Let $\delta T(t) \equiv T(t) - T_e(t)$. In the thermodynamic limit, we have $\delta T(t) \sim T_e N^{-1/2} \to 0$. Therefore, the linearization of Eq. (25) with $\gamma = 0$ around $T_e(t)$ reads

$$\begin{aligned}\frac{d\delta T}{dt} &= \delta T \frac{\partial}{\partial T_e}\left(\frac{T_e}{C_e}\frac{\partial \Lambda_e}{\partial T_e}\right)\frac{d\lambda}{dt} + O\left(\frac{T}{N\tau}\right)\\ &= \delta T \frac{d}{dt}\ln\frac{T_e}{C_e} + O\left(\frac{T}{N\tau}\right),\end{aligned} \tag{B3}$$

where we have used Eq. (B1) in the second equality. The solution of Eq. (B3) is

$$\delta T(\tau) = \delta T(0)\frac{T_b C_a(\lambda_0)}{T_a C_b(\lambda_\tau)}. \tag{B4}$$

That is to say, $T(\tau)$ linearly depends on $T(0)$. Moreover, the standard deviation reads

$$\sigma_T(\tau) = \sigma_T(0)\frac{T_b C_a(\lambda_0)}{T_a C_b(\lambda_\tau)}. \tag{B5}$$

Equations (B4) and (B5) serve as the equation for the temperature fluctuation of the system in the adiabatic process.

For an adiabatic process with an initial quasiequilibrium state

$$P(T,0) = \sqrt{\frac{C_a(\lambda_0)}{2\pi k_B T_a^2}}\exp\left[-\frac{C_a(\lambda_0)(T-T_a)^2}{2k_B T_a^2}\right], \tag{B6}$$

$\sigma_e^2(0) = k_B T_e^2(0)/C_e(0)$. According to Eq. (B5), the corresponding temperature distribution at the end of the adiabatic process during time τ is obtained as

$$P(T,\tau) = \sqrt{\frac{\kappa C_b(\lambda_\tau)}{2\pi k_B T_b^2}}\exp\left[-\frac{\kappa C_b(\lambda_\tau)(T-T_b)^2}{2k_B T_b^2}\right], \tag{B7}$$

where $\kappa \equiv C_b(\lambda_\tau)/C_a(\lambda_0)$ is the ratio of the heat capacity at the final and initial times. Hence for $\kappa \neq 1$, the work substance at time t is not at an quasiequilibrium state anymore.

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