Letter

Fluctuation theorems and thermodynamic inequalities for nonequilibrium processes stopped at stochastic times

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(Received 4 July 2023; revised 27 September 2023; accepted 10 October 2023; published 7 November 2023)

We investigate the thermodynamics of general nonequilibrium processes stopped at stochastic times. We propose a systematic strategy for constructing fluctuation-theorem-like martingales for each thermodynamic functional, yielding a family of stopping-time fluctuation theorems. We derive second-law-like thermodynamic inequalities for the mean thermodynamic functional at stochastic stopping times, the bounds of which are even stronger than the thermodynamic inequalities resulting from the traditional fluctuation theorems when the stopping time is reduced to a deterministic one. Numerical verification is carried out for three well-known thermodynamic functionals, namely, entropy production, free energy dissipation, and dissipative work. These universal equalities and inequalities are valid for arbitrary stopping strategies, and thus provide a comprehensive framework with insights into the fundamental principles governing nonequilibrium systems.

DOI: 10.1103/PhysRevE.108.L052104

Introduction. Stochastic thermodynamics extends classical thermodynamics to individual trajectories of nonequilibrium processes, encompassing stationary or transient systems with or without external driving forces [1–4]. A first-law-like energy balance equality and various second-law-like thermodynamic inequalities can be derived from fluctuating trajectories. Fluctuation theorems emerging from stochastic thermodynamics, as the equality versions of the second law, impose constraints on probability distributions of thermodynamic functionals along single stochastic trajectories [5–19].

Recently, a gambling demon, which stops the processes at random times, has been proposed for nonstationary stochastic processes without external driving force and feedback of control under an arbitrary deterministic protocol [20–22]. The demon employs martingales, a concept that has been proposed in probability theory for more than 70 years. The authors constructed a martingale for dissipative work, and obtained a stopping-time fluctuation theorem by applying the well-known Doob's optional stopping theorem, which states that the average of a martingale at a stopping time is equal to the average of its initial value [23].

On the other hand, we already know that there are three faces in stochastic thermodynamics [10,24–26], namely, (total) entropy production, housekeeping heat (adiabatic entropy production), and free energy dissipation (nonadiabatic entropy production). In a system with no external driving force, the housekeeping heat vanishes and the entropy production is equal to the free energy dissipation. However, in general nonstationary stochastic processes with an external driving force as well as a time-dependent protocol, we are curious about whether different martingales can be constructed for entropy production and free energy dissipation separately, while the martingale for housekeeping heat is straightforward to construct without any compensated term [27]. Both entropy production and free energy dissipation belong to a class of functionals along a single stochastic trajectory, i.e., general backward thermodynamic functionals, which has been rigorously defined in [28]. Housekeeping heat belongs to another class, called forward thermodynamic functionals [27,28], and entropy production is both a forward and backward martingale at steady state [28,29].

Therefore, in this Letter, we propose a systematic strategy for constructing a class of martingales applicable to each general backward thermodynamic functional, and take entropy production, free energy dissipation, and dissipative work as illustrative examples. Notably, the construction of martingales for forward thermodynamic functionals has been previously established in [28]. By leveraging our constructed martingales, we derive a class of stopping-time fluctuation theorems that hold for each general backward thermodynamic functional, followed by second-law-like thermodynamic inequalities for arbitrary stopping times. When the stochastic stopping time reduces to a deterministic one, we exploit the additional degree of freedom present in our constructed martingales, enabling us to obtain a sharper non-negative bound for the mean thermodynamic functional. In particular, we obtain a stronger inequality for the dissipative work than that obtained through classic Jarzynski equality.

Stopping-time fluctuation theorems and thermodynamic inequalities. First, we will give an even more general definition of the backward thermodynamic functional than [28]. We consider a stochastic thermodynamic system with temperature $\beta = \frac{1}{k_B \mathbf{T}}$. We denote the state (discrete or continuous) of the system at time $s \geqslant 0$ by $X(s)$, whose stochastic

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dynamics is governed by a prescribed deterministic protocol $\Lambda = \{\lambda(s) : s \geqslant 0\}$. For a given duration $[0, t]$, the trajectories are traced by the coordinates in phase space, denoted by $x_{[0,t]} \equiv \{x(s)\}_{0 \leqslant s \leqslant t}$. We further denote the probability of observing a given trajectory $x_{[0,t]}$ by $\mathcal{P}^X(x_{[0,t]})$, and the probability density of $X(s)$ by $\varrho^X(x, s)$ at any given time s. The general backward thermodynamic functional in the duration $[0, t]$ is defined by $\{X(s)\}_{0 \leqslant s \leqslant t}$ and another stochastic process $\{Y(s)\}$ with protocol $\tilde{\Lambda} = \{\tilde{\lambda}(s) : s \geqslant 0\}$ (can be either the same as or different from Λ). The only condition is that the processes $\{X(s)\}_{0 \leqslant s \leqslant t}$ and $\{Y(s)\}_{0 \leqslant s \leqslant t}$ are absolutely continuous with each other, i.e., the probability $\mathcal{P}^X(x_{[0,t]}) > 0$ if and only if $\mathcal{P}^Y(x_{[0,t]}) > 0$ for any given trajectory $x_{[0,t]}$. We define a third process $\{Z^t(s)\}_{0 \leqslant s \leqslant t}$ driven by the time-reversed protocol $\tilde{\Lambda}^{r,t} = \{\tilde{\lambda}(t - s) : 0 \leqslant s \leqslant t\}$ of $\{Y(s)\}$ up to time t. The probability density of $Z^t(s)$ is denoted by $\varrho^{Z^t}(x, s)$ for any given time $s \leqslant t$. Note that there is also an additional degree of freedom, i.e., the arbitrary choice of the initial distribution $\varrho^{Z^t}(x, 0)$ of $\{Z^t(s)\}_{0 \leqslant s \leqslant t}$ for any t, because for different t, only the protocols inherited from $\{Y(s)\}$ are closely related to each other, not the initial distributions.

The probability of observing a given trajectory $x_{[0,t]}$ in $\{Z^t(s)\}_{0 \leqslant s \leqslant t}$ is denoted by $\mathcal{P}^{Z^t}(x_{[0,t]})$. We define a general backward thermodynamic functional by

$$F_t(x_{[0,t]}) \equiv \frac{1}{\beta} \ln \frac{\mathcal{P}^X(x_{[0,t]})}{\mathcal{P}^{Z^t}(\tilde{x}_{[0,t]})},$$

where $\tilde{x}_{[0,t]} \equiv \{x(t - s)\}_{0 \leqslant s \leqslant t}$ denotes the time reversal of $x_{[0,t]}$ in the duration $[0, t]$.

It is straightforward to derive the fluctuation theorem for F_t:

$$\langle e^{-\beta F_t} \rangle = 1.$$

However, F_t is generally not a martingale [28].

A stochastic process $\{M(t)\}$ is called a martingale with respect to $\{X(t)\}$ (hereinafter referred to as martingale) if it is integrable and the average conditioned on the past satisfies

$$\langle M(t) | X_{[0,s]} \rangle = M(s),$$

for any $0 \leqslant s \leqslant t$. Doob's optional stopping theorem in martingale theory [30] states that the average of the martingale at any stochastic stopping time equals the average at the initial time, i.e.,

$$\langle M(\tau) \rangle = \langle M(0) \rangle,$$

where τ is a stopping time, defined by any stopping strategy to decide whether to stop a process based on the current position and past events.

For any given time interval $[0, T]$, we would like to add a compensated term δ_t as a function of $X(t)$ and t, to F_t, so that $e^{-\beta(F_t + \delta_t)}$ becomes a martingale, i.e.,

$$\langle e^{-\beta(F_T + \delta_T)} | X_{[0,t]} \rangle = e^{-\beta(F_t + \delta_t)},$$

for any $t \in [0, T]$.

Then we propose

$$\delta_t[X(t)] \equiv \frac{1}{\beta} \ln \frac{\varrho^{Z^t}(X(t), 0)}{\tilde{\varrho}^{Z^T}(X(t), T - t)}, \tag{1}$$

in which $\tilde{\varrho}^{Z^T}(\cdot, T - t)$ is the distribution of $Z^T(T - t)$ with any arbitrary initial distribution $\tilde{\varrho}^{Z^T}(\cdot, 0)$. $\tilde{\varrho}^{Z^T}(\cdot, 0)$ is not necessarily the same as $\varrho^{Z^T}(\cdot, 0)$ and contributes another extra degree of freedom. It is called "stochastic distinguishability" in [20], measuring the difference between the distribution $\varrho^{Z^t}(\cdot, 0)$ with respect to the distribution $\tilde{\varrho}^{Z^T}(\cdot, T - t)$. During the application to entropy production and free energy dissipation (see below), $\varrho^{Z^t}(\cdot, 0)$ is set to be the distribution of X at time t, and δ_t is the stochastic distinguishability between the distribution of the original process with respect to the distribution in a reference time-reversed process at the same time [20].

We apply the optional stopping theorem to derive the general stopping-time fluctuation theorem

$$\langle e^{-\beta(F_\tau + \delta_\tau)} \rangle = \langle e^{-\beta\{F_t(X_{[0,t]}) + \delta_t[X(t)]\}}|_{t=\tau} \rangle = 1, \tag{2}$$

where the average $\langle \cdot \rangle$ is taken over many trajectories $x_{[0,\tau]}$, stopped at the stopping time τ, i.e., $\langle M(t)|_{t=\tau} \rangle = \sum_{x_{[0,\tau]}} \mathcal{P}^X(x_{[0,\tau]}) M(\tau)$. This type of fluctuation theorem has been proposed for some specific thermodynamic functionals, such as entropy production [29] and dissipative work [20,22].

By Jensen's inequality,

$$\langle F_\tau \rangle \geqslant -\langle \delta_\tau \rangle. \tag{3}$$

The left-hand side is independent of $\tilde{\varrho}^{Z^T}$. Hence we can improve the above inequality into

$$\langle F_\tau \rangle \geqslant \sup_{\tilde{\varrho}^{Z^T}} -\langle \delta_\tau \rangle. \tag{4}$$

A special situation is when the stochastic stopping time τ is fixed at a given deterministic time t with probability 1, followed by

$$\left\langle e^{-\beta(F_t + \delta_t)} \right\rangle = 1,$$

and

$$\langle F_t \rangle \geqslant \sup_{\tilde{\varrho}^{Z^T}} -\langle \delta_t \rangle = \frac{1}{\beta} \left\langle \ln \frac{\varrho^X(X(t), t)}{\varrho^{Z^t}(X(t), 0)} \right\rangle \geqslant 0, \tag{5}$$

in which $\langle \ln \frac{\varrho^X(X(t),t)}{\varrho^{Z^t}(X(t),0)} \rangle$ is the relative entropy of $\varrho^X(\cdot, t)$ with respect to $\varrho^{Z^t}(\cdot, 0)$. The inequality (5) is stronger than the traditional inequality $\langle F_t \rangle \geqslant 0$ derived from the well-known fluctuation theorem $\langle e^{-\beta F_t} \rangle = 1$, as long as $\varrho^X(\cdot, t)$ is not the same as $\varrho^{Z^t}(\cdot, 0)$.

As a corollary, we can derive a certain bound for the infimum of $F_t + \delta_t$ following the strategy in [31], which holds for both equilibrium processes and for general nonequilibrium processes. According to Doob's maximal inequality, we have

$$\Pr\left(\sup_{0 \leqslant t \leqslant T} e^{-\beta(F_t + \delta_t)} \geqslant \lambda \right) \leqslant \frac{1}{\lambda} \langle e^{-\beta(F_t + \delta_t)} \rangle = \frac{1}{\lambda},$$

for any $\lambda \geqslant 0$. It is equivalent to

$$\Pr\left(\inf_{0 \leqslant t \leqslant T} \{\beta(F_t + \delta_t)\} \geqslant -s \right) \geqslant 1 - e^{-s}$$

for $s \geqslant 0$. It implies the random variable $-\inf_{0 \leqslant t \leqslant T}\{\beta(F_t + \delta_t)\}$ dominates stochastically over an exponential random variable with the mean of 1. Thus, we find the following universal bound for the mean infimum of $\beta(F_t+\delta_t)$, i.e.,

$$\left\langle \inf_{0\leqslant t\leqslant T}(F_t+\delta_t)\right\rangle \geqslant -\frac{1}{\beta} = -k_B\mathbf{T}.$$

Applications. The thermodynamic functional F_t becomes the (total) entropy production $S_{\rm tot}(t)$ up to time t if the process $\{Y(t)\}$ is driven by exactly the same protocol as $\{X(t)\}$, and the initial distribution of Z^t is taken to be the distribution of $X(t)$ [7,8,32,33], i.e., $\varrho^{Z^t}(\cdot,0)=\varrho^X(\cdot,t)$. Then

$$\delta_t^{S_{\rm tot}}[X(t)] \equiv \frac{1}{\beta}\ln\frac{\varrho^X(X(t),t)}{\tilde{\varrho}^{Z^T}(X(t),T-t)}, \tag{6}$$

and $e^{-\beta[S_{\rm tot}(t)+\delta_t^{S_{\rm tot}}]}$ is a martingale. It is followed by

$$\langle e^{-\beta[S_{\rm tot}(\tau)+\delta_\tau^{S_{\rm tot}}]}\rangle = 1, \tag{7}$$

for any stopping time τ, and $\langle S_{\rm tot}(\tau)\rangle \geqslant -\langle\delta_\tau^{S_{\rm tot}}\rangle$.

The thermodynamic functional F_t becomes the free energy dissipation (nonadiabatic entropy production) $f_d(t)$ if the process $\{Y(t)\}$ is driven by the adjoint protocol of $\{X(t)\}$, and also the initial distribution of Z^t is set as the distribution of $X(t)$, i.e., $\varrho^{Z^t}(\cdot,0)=\varrho^X(\cdot,t)$ [10,24–26,33]. Then

$$\delta_t^{f_d}[X(t)] \equiv \frac{1}{\beta}\ln\frac{\varrho^X(X(t),t)}{\tilde{\varrho}^{Z^T}(X(t),T-t)}, \tag{8}$$

and $e^{-\beta[f_d(t)+\delta_t^{f_d}]}$ is a martingale. It is followed by

$$\langle e^{-\beta[f_d(\tau)+\delta_\tau^{f_d}]}\rangle = 1, \tag{9}$$

for any stopping time τ, and $\langle f_d(\tau)\rangle \geqslant -\langle\delta_\tau^{f_d}\rangle$.

Let $\pi^X(t)$ be the pseudo-stationary distribution of $X(t)$ corresponding to the protocol $\lambda(t)$, i.e., the stationary distribution of $X(t)$ if the protocol is fixed at $\lambda(t)$. The thermodynamic functional F_t becomes the dissipative work $W_d(t)$ up to time t, if the initial distribution of $\{X(t)\}$ is $\pi^X(0)$, the process $\{Y(t)\}$ is driven by the adjoint protocol of $\{X(t)\}$, and the initial distribution of Z^t is taken as the pseudo-stationary distribution of $X(t)$, i.e., $\varrho^{Z^t}(\cdot,0)=\pi^X(\cdot,t)$ [5–7,20,33,34]. It is a generalized definition of dissipative work, which can be defined in a nonequilibrium system in the presence of external driving force, i.e., nonvanishing housekeeping heat. In the original definition of dissipative work that was used only during the nonequilibrium transitions between two equilibrium states [5–7,20,22], the housekeeping heat vanishes and the adjoint protocol is the same as the original one. Then

$$\delta_t^{W_d}[X(t)] \equiv \frac{1}{\beta}\ln\frac{\pi^X(X(t),t)}{\tilde{\varrho}^{Z^T}(X(t),T-t)}, \tag{10}$$

and $e^{-\beta[W_d(t)+\delta_t^{W_d}]}$ is a martingale. It is followed by

$$\langle e^{-\beta[W_d(\tau)+\delta_\tau^{W_d}]}\rangle = 1, \tag{11}$$

for any stopping time τ, and $\langle W_d(\tau)\rangle \geqslant -\langle\delta_\tau^{W_d}\rangle$.

For the mean W_d up to any fixed time t, we can obtain a stronger inequality than $\langle W_d\rangle\geqslant 0$. Applying (5), we have

$$\langle W_d(t)\rangle \geqslant \frac{1}{\beta}\left\langle \ln\frac{\varrho^X(X(t),t)}{\pi^X(X(t),t)}\right\rangle \geqslant 0. \tag{12}$$

The fluctuation relation of the dissipative work W_d at stopping times is also investigated in [20,22]. The compensated term in [22] is the same as $\delta_t^{W_d}$, if we take $\tilde{\varrho}^{Z^T}(x,0)=\pi^X(x,T)$. However, the compensated term δ_t defined in [20] is the same as $\delta_t^{S_{\rm tot}}$. The mathematical derivation here implies that we should use corresponding δ_t for different thermodynamic functionals.

Numerical verifications. Many mesoscopic biochemical processes such as the kinetics of enzyme or motor molecules, can be modeled in terms of transition rates between discrete states. We apply our theory to a simple stochastic process with only three states. The time-dependent transition rates between different discrete states are set as follows:

$$k_{12}(t)=t,\quad k_{23}(t)=3t^2,\quad k_{31}(t)=1;$$
$$k_{21}(t)=t^2,\quad k_{32}(t)=2,\quad k_{13}(t)=2t,$$

in which the chemical-driven energy

$$\Delta G(t) = k_BT\ \ln\frac{k_{12}(t)k_{23}(t)k_{31}(t)}{k_{21}k_{32}(t)k_{13}(t)} = k_BT\ \ln\frac{3}{4} < 0.$$

For the three thermodynamic functionals $S_{\rm tot}$, f_d, and W_d, the stopping strategy for τ is set as follows: the process is stopped at $\tau<T$ only when the functional reaches a given threshold value before T; while the process is stopped at the final time $\tau=T$ if the threshold value is never reached during the duration $[0,T]$.

Figures 1(a)–1(c) show the numerical results of $\langle S_{\rm tot}(\tau)\rangle$ versus $-\langle\delta_\tau^{S_{\rm tot}}\rangle$, $\langle f_d(\tau)\rangle$ versus $-\langle\delta_\tau^{f_d}\rangle$, and $\langle W_d(\tau)\rangle$ versus $-\langle\delta_\tau^{W_d}\rangle$, as functions of the threshold value. Figures 1(d)–1(f) test the stopping-time fluctuation relations (7), (9), and (11), with and without the compensated term δ_t.

In the special situation that τ is reduced to a deterministic t, Fig. 1(g) shows that the inequality (12) for $\langle W_d(t)\rangle$ is not only stronger than the inequality $\langle W_d(t)\rangle\geqslant-\langle\delta_t^{W_d}\rangle$, but also the traditional Jarzynski inequality $\langle W_d(t)\rangle\geqslant 0$.

Another example is the stochastic dynamics of a colloidal particle with diffusion coefficient D in a time-dependent potential $V(t)$. The dynamics obeys the Langevin equation

$$\frac{dX(t)}{dt} = -\frac{\partial V}{\partial x}(X(t),t)\ +\xi(t),$$

where ξ is a Gaussian white noise with zero mean and autocorrelation $\langle\xi(t)\xi(t')\rangle = 2D\delta(t-t')$.

In such a stochastic system, the housekeeping heat equals to zero and thus the entropy production $S_{\rm tot}(t)$ coincides with the free energy dissipation $f_d(t)$. We follow the same stopping strategy as in the discrete-state model of Fig. 1, and show the numerical results of $\langle S_{\rm tot}(\tau)\rangle$ versus $-\langle\delta_\tau^{S_{\rm tot}}\rangle$ in Fig. 2(a) and $\langle W_d(\tau)\rangle$ versus $-\langle\delta_\tau^{W_d}\rangle$ in Fig. 2(b) with $T=3$. Figures 2(c) and 2(d) test the stopping-time fluctuation relations (7) and (11), with and without the compensated term δ_t.

In the special situation that τ is reduced to a deterministic t, Fig. 2(e) shows that the conclusion (12) for $\langle W_d(t)\rangle$ is stronger than both the inequality $\langle W_d(t)\rangle\geqslant-\langle\delta_t^{W_d}\rangle$ and the Jarzynski inequality $\langle W_d(t)\rangle\geqslant 0$.

In Figs. 1 and 2, the averaged thermodynamic functionals may be negative under certain stopping strategy, but the general stopping-time fluctuation relations and related thermodynamic inequalities always hold. See [33] for more details

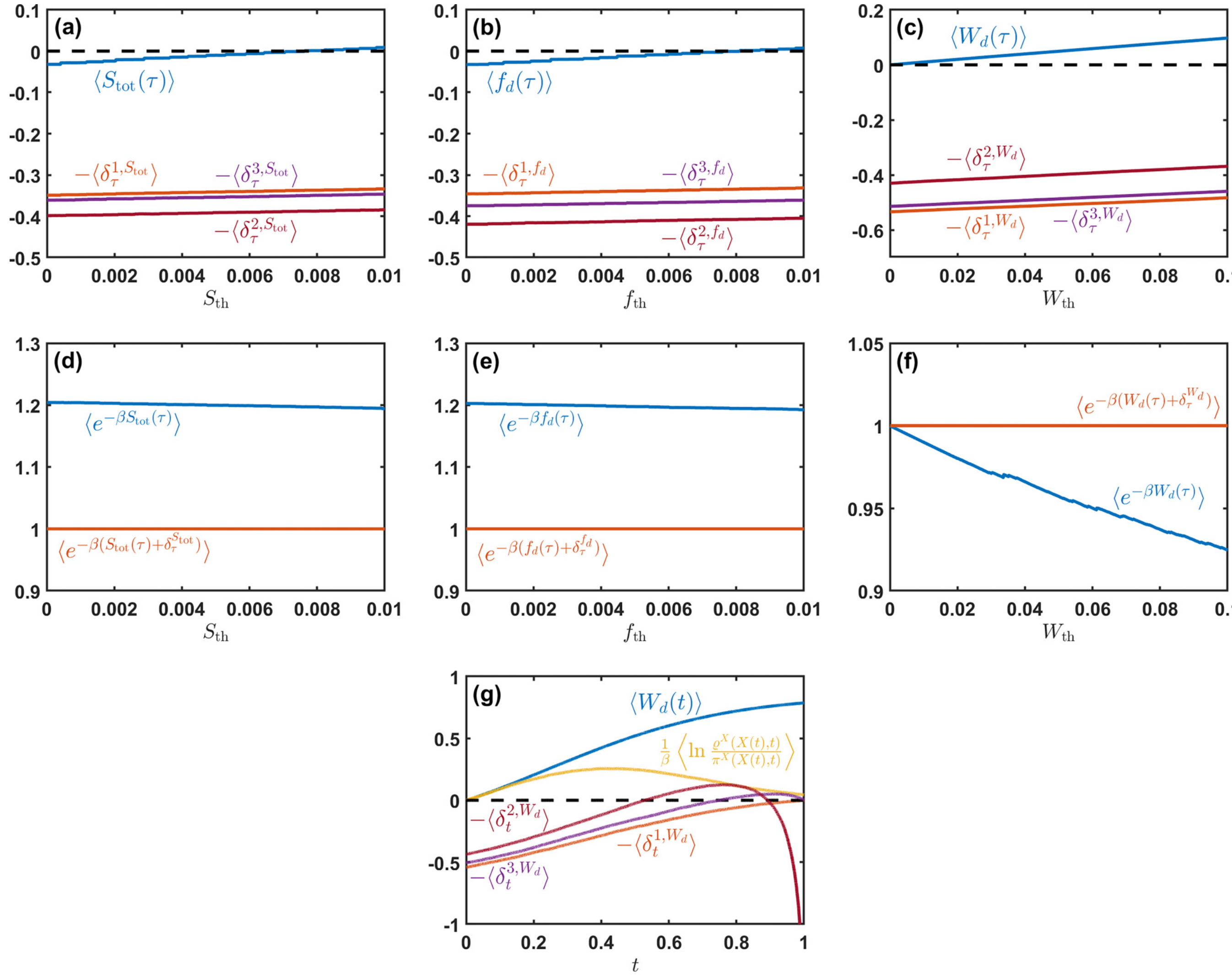

FIG. 1. Numerical verification through a three-state jumping process (see the main text for details). (a) The entropy production $\langle S_{\rm tot}(\tau)\rangle$, (b) the free energy dissipation $\langle f_d(\tau)\rangle$, and (c) the dissipative work $\langle W_d(\tau)\rangle$ (blue) versus the corresponding compensation items (orange, red, and purple) as functions of the threshold value for the duration $T = 1$. (d)–(f) Test of the stopping-time fluctuation theorems (7), (9), and (11) with and without the compensated δ_t. (g) When τ is fixed at a deterministic t, the dissipative work $\langle W_d(t)\rangle$ (blue), the corresponding compensation item $-\langle\delta_t^{W_d}\rangle$ (red, orange, and purple), and the relative entropy $\langle\ln\frac{\varrho^X(X(t),t)}{\pi^X(X(t),t)}\rangle$ (yellow) as functions of t for $0 \leqslant t \leqslant T$. See [33] for the different initial distributions for different δ_τ^i, $i = 1, 2, 3$ of each subfigure. $\langle\delta_\tau^{1,W_d}\rangle$ in (c) and $\langle\delta_t^{1,W_d}\rangle$ in (g) are exactly the bound in [22]. β is set to be 1.

of the numerical verification as well as the expressions of all three thermodynamic functionals.

Derivation. First, we notice that

$$\left\{\frac{\mathcal{P}^{\tilde{Z}^{T,t}}(\widetilde{X}_{[0,t]})}{\mathcal{P}^X(X_{[0,t]})}\right\}_{0\leqslant t\leqslant T} \tag{13}$$

is a martingale for $t \leqslant T$, where $\widetilde{X}_{[0,t]} \equiv \{X(t-s)\}_{0\leqslant s\leqslant t}$ denotes the time reversal of $X_{[0,t]}$ in the duration $[0, t]$, and $\mathcal{P}^{\tilde{Z}^{T,t}}(x_{[0,t]})$ denotes the probability of observing a given trajectory $x_{[0,t]}$ in $\{\tilde{Z}^{T,t}(s) = Z^T(s + T - t)\}_{0\leqslant s\leqslant t}$. The distribution of $Z^T(0)$ is given by $\tilde{\varrho}^{Z^T}(\cdot, 0)$.

The Markovian property of the process $\mathcal{P}^X$ gives

$$\mathcal{P}^X(X_{[0,T]}) = \mathcal{P}^X(X_{[0,T]}|X_{[0,t]})\mathcal{P}^X(X_{[0,t]}), \tag{14}$$

then we have

$$\begin{aligned}\left\langle\frac{\mathcal{P}^{\tilde{Z}^{T,T}}(\widetilde{X}_{[0,T]})}{\mathcal{P}^X(X_{[0,T]})}\middle|X_{[0,t]}\right\rangle &= \sum_{X_{[t,T]}}\frac{\mathcal{P}^{\tilde{Z}^{T,T}}(\widetilde{X}_{[0,T]})}{\mathcal{P}^X(X_{[0,T]})}\mathcal{P}^X(X_{[0,T]}|X_{[0,t]})\\ &= \sum_{X_{[t,T]}}\frac{\mathcal{P}^{\tilde{Z}^{T,T}}(\widetilde{X}_{[0,T]})}{\mathcal{P}^X(X_{[0,t]})},\end{aligned} \tag{15}$$

where the first equality follows from the definition of conditional expectation, and we use (14) in the second equality.

For $0 \leqslant u \leqslant s \leqslant T$, let $\widetilde{X}_{[0,T]}(u, s)$ be the part of the trajectory $\widetilde{X}_{[0,T]}$ in the duration $[u, s]$, then $X_{[t,T]}$ and $\widetilde{X}_{[0,T]}(0, T - t)$ are exactly the time reversal of each other.

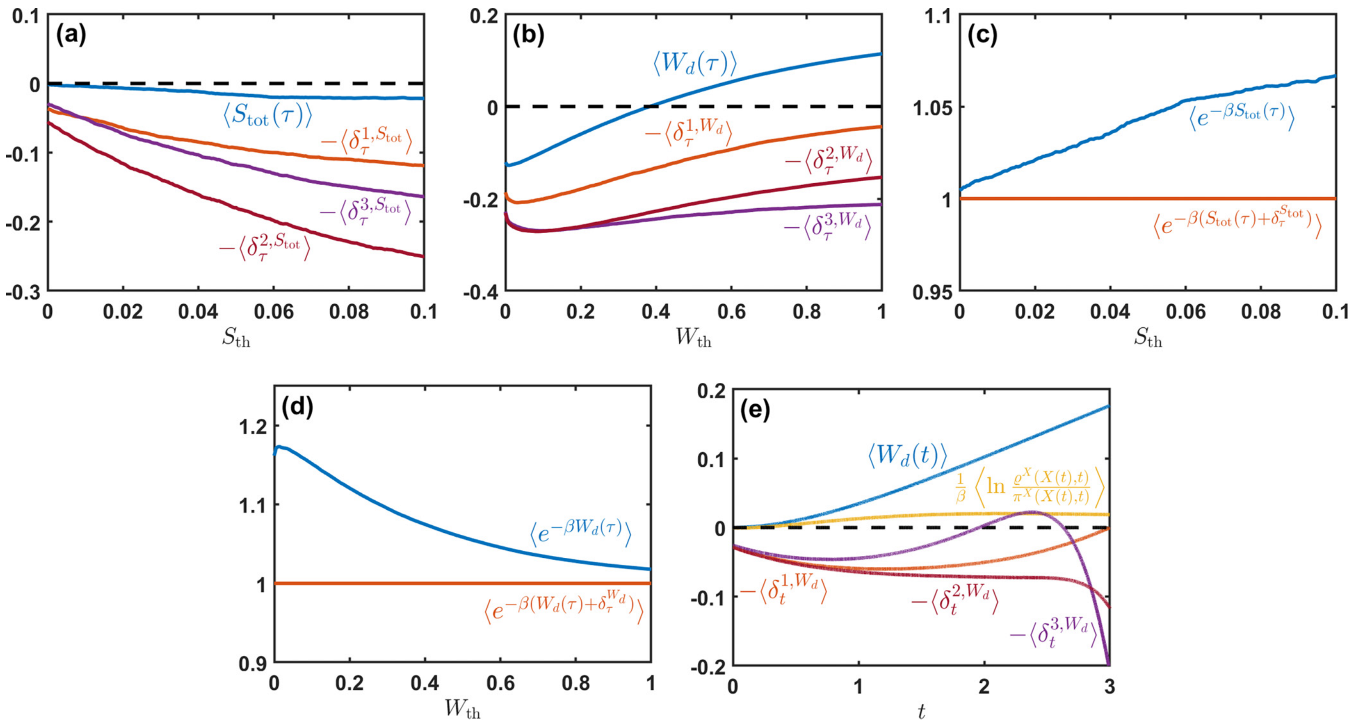

FIG. 2. Numerical verification through a diffusion process (see the main text for details). (a) The entropy production $\langle S_{\rm tot}(\tau)\rangle$ and (b) the dissipative work $\langle W_d(\tau)\rangle$ (blue) versus the corresponding compensation items (red, orange, and purple) as functions of the threshold value for the duration $T=3$. (c),(d) Test of the stopping-time fluctuation theorems (7) and (11) with and without δ_t. (e) When τ is reduced to a deterministic t, the dissipative work $\langle W_d(t)\rangle$ (blue), the corresponding compensation item $-\langle\delta_t^{W_d}\rangle$ (red, orange, and purple), and the relative entropy $\langle\ln\frac{\varrho^X(X(t),t)}{\pi^X(X(t),t)}\rangle$ (yellow) as functions of t for $0\leqslant t\leqslant T$. In this example, $V(x,t)=(t+4)(4x-t)^2/128$, $D=1$. See [33] for the different initial distributions in different δ_τ^i, $i=1,2,3$ of each subfigure. $\langle\delta_\tau^{1,W_d}\rangle$ in (b) and $\langle\delta_t^{1,W_d}\rangle$ in (e) are exactly the bound in [22]. β is set to be 1.

Thus

$$\sum_{X_{[t,T]}}\mathcal{P}^{\tilde{Z}^{T,T}}(\widetilde{X}_{[0,T]})=\sum_{\widetilde{X}_{[0,T]}(0,T-t)}\mathcal{P}^{\tilde{Z}^{T,T}}(\widetilde{X}_{[0,T]})$$
$$=\mathcal{P}^{\tilde{Z}^{T,T}}[\widetilde{X}_{[0,T]}(T-t,T)]$$
$$=\mathcal{P}^{\tilde{Z}^{T,t}}(\widetilde{X}_{[0,t]}),\tag{16}$$

in which the last equality comes from the definition of $\mathcal{P}^{\tilde{Z}^{T,t}}$ and $\widetilde{X}_{[0,T]}(T-t,T)=\widetilde{X}_{[0,t]}$. Combining (15) and (16) results in

$$\left\langle\frac{\mathcal{P}^{\tilde{Z}^{T,T}}(\widetilde{X}_{[0,T]})}{\mathcal{P}^X(X_{[0,T]})}\middle|X_{[0,t]}\right\rangle=\frac{\mathcal{P}^{\tilde{Z}^{T,t}}(\widetilde{X}_{[0,t]})}{\mathcal{P}^X(X_{[0,t]})},$$

which is exactly the definition of the martingale for (13).

Second, we show that $\{e^{-\beta(F_t+\delta_t)}\}_{0\leqslant t\leqslant T}$ is exactly the martingale (13).

By Markovian property, and note that the initial distribution of $\tilde{Z}^{T,t}$ is $\tilde{\varrho}^{Z^T}(\cdot,T-t)$,

$$\mathcal{P}^{\tilde{Z}^{T,t}}(\widetilde{X}_{[0,t]})=\mathcal{P}^{\tilde{Z}^{T,t}}[\widetilde{X}_{[0,t]}|\widetilde{X}(0)]\tilde{\varrho}^{Z^T}(X(t),T-t),$$
$$\mathcal{P}^{Z^t}(\widetilde{X}_{[0,t]})=\mathcal{P}^{Z^t}[\widetilde{X}_{[0,t]}|\widetilde{X}(0)]\varrho^{Z^t}(X(t),0).\tag{17}$$

Notice that $\{\tilde{Z}^{T,t}(s)\}_{0\leqslant s\leqslant t}$ and $\{Z^t(s)\}_{0\leqslant s\leqslant t}$ are driven by the same protocol $\{\tilde{\lambda}(t-s):0\leqslant s\leqslant t\}$; we have

$$\mathcal{P}^{\tilde{Z}^{T,t}}[\widetilde{X}_{[0,t]}|\widetilde{X}(0)]=\mathcal{P}^{Z^t}[\widetilde{X}_{[0,t]}|\widetilde{X}(0)],$$

which combined with (17) implies

$$\frac{\mathcal{P}^{\tilde{Z}^{T,t}}(\widetilde{X}_{[0,t]})}{\mathcal{P}^{Z^t}(\widetilde{X}_{[0,t]})}=\frac{\tilde{\varrho}^{Z^T}(X(t),T-t)}{\varrho^{Z^t}(X(t),0)}=e^{-\beta\delta_t}.\tag{18}$$

And by the definition of F_t, we have

$$e^{-\beta F_t}=\frac{\mathcal{P}^{Z^t}(\widetilde{X}_{[0,t]})}{\mathcal{P}^X(X_{[0,t]})}.\tag{19}$$

Combining (18) and (19) shows that

$$e^{-\beta(F_t+\delta_t)}=\frac{\mathcal{P}^{Z^t}(\widetilde{X}_{[0,t]})}{\mathcal{P}^X(X_{[0,t]})}\frac{\mathcal{P}^{\tilde{Z}^{T,t}}(\widetilde{X}_{[0,t]})}{\mathcal{P}^{Z^t}(\widetilde{X}_{[0,t]})}=\frac{\mathcal{P}^{\tilde{Z}^{T,t}}(\widetilde{X}_{[0,t]})}{\mathcal{P}^X(X_{[0,t]})},$$

so $\{e^{-\beta(F_t+\delta_t)}\}_{0\leqslant t\leqslant T}$ is exactly the martingale (13), and the general stopping-time fluctuation theorem (2) follows from the Doob's optional stopping theorem.

When the stochastic stopping time τ equals a deterministic time t with probability 1, we decompose

$$-\langle\delta_t\rangle=\frac{1}{\beta}\left\langle\ln\frac{\tilde{\varrho}^{Z^T}(X(t),T-t)}{\varrho^{Z^t}(X(t),0)}\right\rangle$$
$$=\frac{1}{\beta}\left\langle\ln\frac{\varrho^X(X(t),t)}{\varrho^{Z^t}(X(t),0)}\right\rangle+\frac{1}{\beta}\left\langle\ln\frac{\tilde{\varrho}^{Z^T}(X(t),T-t)}{\varrho^X(X(t),t)}\right\rangle.$$

By Jensen's inequality, we know

$$\left\langle \ln \frac{\tilde{\varrho}^{Z^T}(X(t), T-t)}{\varrho^X(X(t), t)} \right\rangle \leqslant \ln \left\langle \frac{\tilde{\varrho}^{Z^T}(X(t), T-t)}{\varrho^X(X(t), t)} \right\rangle = 0.$$

Furthermore, for any given t, we can choose $\tilde{\varrho}^{Z^T}(\cdot, 0)$ such that $\tilde{\varrho}^{Z^T}(x, T-t) = \varrho^X(x, t)$, which leads to

$$\sup_{\tilde{\varrho}^{Z^T}} -\langle \delta_t \rangle = \frac{1}{\beta} \left\langle \ln \frac{\varrho^X(X(t), t)}{\varrho^{Z^t}(X(t), 0)} \right\rangle \geqslant 0.$$

See [33] for more details of the derivation.

Conclusion. In summary, our study contributes a general framework for understanding martingales constructed upon thermodynamic functionals. We have successfully derived and proven the stopping-time fluctuation theorems, accompanied by second-law-like inequalities for mean thermodynamic functionals stopped at stochastic times. Our results generalize the recent gambling strategy and stopping-time fluctuation theorems [20–22] to a very general setting. Our framework encompasses the general definition of thermodynamic functionals, accommodates various types of stochastic dynamics, and allows for arbitrary stopping strategies. The validity and applicability of our framework are supported by numerical verifications conducted in stochastic dynamics with both discrete and continuous states.

Furthermore, we highlight the significance of the additional degree of freedom introduced through the compensated term δ_t, which leads to a strengthening of the inequality for dissipative work compared to the well-known Jarzynski inequality when the stopping time is reduced to a deterministic one. Overall, our results provide insights, detailed interpretations, and improved bounds for the fundamental principles underlying the second law of thermodynamics in the context of stochastic processes.

Acknowledgments. H.G. is supported by NSFC Grants No. 11971037 and No. T2225001.

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