Stochastic thermodynamics of periodically driven systems: Fluctuation theorem for currents and unification of two classes

Somrita Ray and Andre C. Barato*

Max Planck Institute for the Physics of Complex Systems, Nöthnizer Strasse 38, 01187 Dresden, Germany

(Received 23 July 2017; revised manuscript received 29 September 2017; published 14 November 2017)

Periodic driving is used to operate machines that go from standard macroscopic engines to small nonequilibrium microsized systems. Two classes of such systems are small heat engines driven by periodic temperature variations, and molecular pumps driven by external stimuli. Well-known results that are valid for nonequilibrium steady states of systems driven by fixed thermodynamic forces, instead of an external periodic driving, have been generalized to periodically driven heat engines only recently. These results include a general expression for entropy production in terms of currents and affinities, and symmetry relations for the Onsager coefficients from linear-response theory. For nonequilibrium steady states, the Onsager reciprocity relations can be obtained from the more general fluctuation theorem for the currents. We prove a fluctuation theorem for the currents for periodically driven systems. We show that this fluctuation theorem implies a fluctuation dissipation relation, symmetry relations for Onsager coefficients, and further relations for nonlinear response coefficients. The setup in this paper is more general than previous studies, i.e., our results are valid for both heat engines and molecular pumps. The external protocol is assumed to be stochastic in our framework, which leads to a particularly convenient way to treat periodically driven systems.

DOI: 10.1103/PhysRevE.96.052120

I. INTRODUCTION

Thermodynamic cycles of macroscopic systems directed by periodic variation of parameters such as pressure, temperature, and volume were a primary motivation for the development of the classical theory of thermodynamics [1]. The generalization of thermodynamics to systems that can have large fluctuations and can be arbitrarily far from equilibrium is a current active area of research known as stochastic thermodynamics [2]. This theoretical framework is equipped with the tools to deal with periodically driven systems that are small, far from equilibrium, and operate under finite-time conditions. Two main classes of such systems that have been realized experimentally are heat engines that are driven by a periodic temperature variation [3–7] and artificial molecular pumps that generate internal net motion due to periodic modulation of energies and energy barriers [8–11].

The expression of the entropy production in terms of currents (or fluxes) and affinities [12], and the reciprocity relation of Onsager coefficients [13,14], are two known fundamental results valid for nonequilibrium steady states, which, in contrast to periodically driven systems, are driven by fixed thermodynamic forces. This second result is a cornerstone of linear irreversible thermodynamics [15], an older framework that applies to nonequilibrium systems in the linear-response regime.

As an important theoretical advancement for periodically driven heat engines, a general expression of the entropy production in terms of currents (or fluxes) and affinities and symmetry relations for the Onsager coefficients have been recently obtained in [16]. Further general results concerning the linear-response regime of periodically driven systems have been derived in [17,18]. Periodically driven heat engines have also been analyzed in several models in the linear-response regime [19–21] and arbitrarily far from equilibrium [22–24].

For periodically driven molecular pumps, if the system has an internal fixed load, the periodic driving can lead to output work against this load. A key difference between this situation and the theoretical approaches considered in [16–18] is that in this case there is a fixed thermodynamic force, i.e., the system would be out of equilibrium even with no periodic variation of parameters. Such molecular pumps (also known as "stochastic pumps" [25]) have received much attention in recent theoretical studies [26–36].

The fluctuation theorem for the currents is a central result in stochastic thermodynamics valid for nonequilibrium steady states [37,38] (see [39] for a finite-time generalization). This result can be expressed as a symmetry on the scaled cumulant-generating function of the currents. It implies the Onsager reciprocity relations and further relations for nonlinear response coefficients [40]. In this paper, we prove a fluctuation theorem for the currents for periodically driven systems. We show that this fluctuation theorem implies a fluctuation dissipation relation for periodically driven systems, a symmetry of the Onsager coefficients and further relations for nonlinear-response coefficients. Our result on the symmetry of Onsager coefficients is a generalization of the symmetry from [16] for heat engines to a case that also includes molecular pumps.

In our approach, we consider discrete-state Markov processes with a stochastic protocol [31,35], instead of the more usual deterministic protocol. Systems driven by such stochastic protocols have been realized experimentally [41,42]. The use of a stochastic protocol is a mathematical convenience, since in this case the protocol and system together form a bipartite Markov process [43–45]. The periodically driven system is then analyzed within the steady state of this bipartite Markov process. We provide evidence that our results are

*Corresponding author: barato@pks.mpg.de

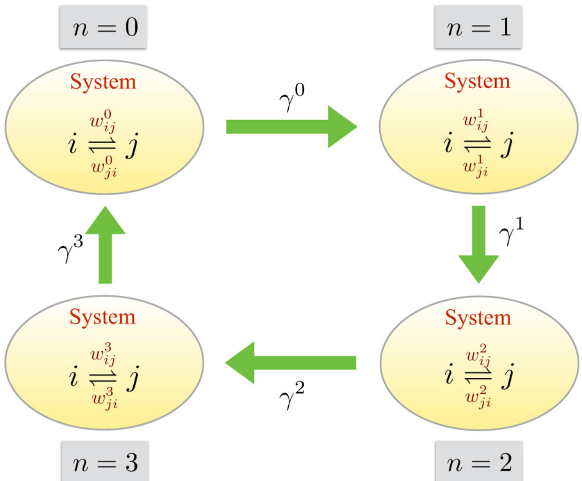

FIG. 1. Periodically driven system with a stochastic protocol modeled as a bipartite Markov process. For this case, the number of different states of the external protocol is $N = 4$. Transition rates that change the state of the system w_{ij}^n depend of the state of the external protocol, whereas a transition rate that changes the state of the protocol γ^n is independent of the state of the system.

also valid for deterministic protocols, which are modeled as a stochastic protocol with a large number of jumps. We note that a fluctuation theorem for currents for periodically driven systems with a deterministic protocol has been proven in [46]. Their result is more restrictive than ours as it requires the transition rates to fulfill some constraints that, for example, do not allow for the realization of a molecular pump that generates an internal current.

The structure of the paper is as follows. In Sec. II we define the basic setup and write down an expression for the entropy production in terms of currents and affinities. The fluctuation theorem for the currents is proved in Sec. III. The response relations, including the symmetry of the Onsager coefficients, are derived in Sec. IV. We conclude in Sec. V. The limit of a deterministic protocol is discussed in Appendix A. Technical aspects of the proof of the fluctuation theorem for the currents are discussed in Appendix B.

II. GENERAL FRAMEWORK

A. Transition rates and generalized detailed balance

The system and protocol together form a bipartite Markov process, which can be used to analyze thermodynamic systems driven by a stochastic protocol [31,35]. The variables i,j represent a state of the system, which has a finite number of states Ω. The variable $n = 0,1,\ldots,N-1$ represents a state of the periodic protocol, as shown in Fig. 1. This variable n is analogous to the time in a periodically driven system with a deterministic protocol leading to time-dependent transition rates.

The transition rate from state (i,n) to state (j,n) is denoted w_{ij}^n. If $w_{ij}^n \neq 0$, then $w_{ji}^n \neq 0$. The transition rate for the protocol in state n to the protocol in state $n+1$ with the system in state i is $w_i^{nn+1} = \gamma^n$, while the reversed transition rate is zero. This transition rate is independent of the state of the system i, and from $n = N-1$ the protocol transitions back to state $n = 0$. All other rates for transitions that involve a change in the protocol are zero. The stationary master equation for the whole bipartite process of system and protocol together reads

$$\frac{d}{dt} P_i^n = \sum_j \left(P_j^n w_{ji}^n - P_i^n w_{ij}^n\right) + \gamma^{n-1} P_i^{n-1} - \gamma^n P_i^n = 0, \tag{1}$$

where P_i^n is the stationary probability of state (i,n).

Thermodynamic quantities such as temperature and energy are defined in the following way. The energy of state i with the protocol in state n is

$$E_i^n = E_i + \Delta E f_i^n. \tag{2}$$

The dimensionless function f_i^n characterizes the influence of the external protocol on the energy. The energy ΔE quantifies the amplitude of the part of the energy that depends on the external protocol. The periodicity of the external protocol, as depicted in Fig. 1, implies $f_i^{n+N} = f_i^n$. The inverse temperature β^n can take values between a hot inverse temperature β_h and a cold inverse temperature $\beta_c \geqslant \beta_h$. It is written as

$$\beta^n = \beta_c(1 - \mathcal{F}_q h^n), \tag{3}$$

where $h^n \leqslant 1$ and $\mathcal{F}_q \equiv (\beta_c - \beta_h)/\beta_c$. The periodic function $h^{n+N} = h^n$ characterizes the dependence of the temperature on the external protocol. Similar forms for the dependence of energy and temperature on the external protocol for the case of a deterministic protocol have been used in [16,18]. The comparison between a stochastic protocol and a deterministic protocol is discussed in Appendix A.

The transition rates for changes in the state of the system fulfill the generalized detailed balance relation [2]

$$\ln \frac{w_{ij}^n}{w_{ji}^n} = \beta^n \left[E_i^n - E_j^n + (\beta_c)^{-1} \sum_\alpha \mathcal{F}_\alpha d_{ij}^{(\alpha)} \right], \tag{4}$$

where $\mathcal{F}_\alpha$ are internal affinities and $d_{ij}^{(\alpha)} = -d_{ji}^{(\alpha)}$ are generalized dimensionless distances. For example, if $\mathcal{F}_\alpha$ is a torque applied to a rotatory motor, then $d_{ij}^{(\alpha)}$ is the amount that the angle changes in a transition from i to j. For a heat engine, all $\mathcal{F}_\alpha$ are zero. A molecular pump corresponds to the case of a fixed temperature $\beta^n = \beta_c$ and nonzero internal force $\mathcal{F}_\alpha$. The comparison between Eq. (4) and the standard form of the generalized detailed balance relation for a deterministic protocol is presented in Appendix A.

B. Currents and affinities

The mathematical form of the rate of entropy production, i.e., the rate of entropy increase of the external medium, reads [35]

$$\sigma \equiv \sum_n \sum_{ij} P_i^n w_{ij}^n \ln \frac{w_{ij}^n}{w_{ji}^n} \geqslant 0. \tag{5}$$

The class of Markov processes considered here is different from the class of Markov processes considered in standard stochastic thermodynamics [2]. In particular, transitions that change the state of the external protocol are irreversible, and their transition rates do not appear in Eq. (5). We note that, as usual in thermodynamics, the thermodynamic cost of the external protocol is not taken into account in this paper. Hence, the second law in Eq. (5) applies to a nonautonomous physical system, like a heat engine driven by an external control of the temperature. The cost of the external protocol becomes relevant if the external control is exerted by, for example, a chemical reaction. In this case, one must consider a thermodynamically consistent external protocol without irreversible jumps, which leads to a different statement of the second law [47].

The average elementary probability current from state (i,n) to state (j,n) is defined as

$$J_{ij}^n \equiv P_i^n w_{ij}^n - P_j^n w_{ji}^n. \tag{6}$$

The rate of entropy production in Eq. (5) in terms of this elementary probability current becomes

$$\sigma = \sum_n \sum_{i<j} J_{ij}^n \ln \frac{w_{ij}^n}{w_{ji}^n}, \tag{7}$$

where the sum $\sum_{i<j}$ is over all links between states of the system. Using the generalized detailed balance relation in Eq. (4), we obtain

$$\sigma = \sum_\alpha \mathcal{F}_\alpha J_\alpha + \sum_n \sum_{i<j} J_{ij}^n \beta^n \left(E_i^n - E_j^n\right), \tag{8}$$

where

$$J_\alpha \equiv \sum_n \sum_{i<j} (\beta_c)^{-1} \beta^n J_{ij}^n d_{ij}^{(\alpha)}. \tag{9}$$

Using Eq. (3), the second term on the right-hand side of Eq. (8) becomes

$$\sum_n \sum_{i<j} J_{ij}^n \beta^n \left(E_i^n - E_j^n\right) = \beta_c \sum_n \sum_{i<j} J_{ij}^n \left(E_i^n - E_j^n\right) + \mathcal{F}_q J_q, \tag{10}$$

where

$$J_q \equiv \sum_n \sum_{i<j} J_{ij}^n h^n \beta_c \left(E_j^n - E_i^n\right). \tag{11}$$

This current is the generalized heat flux from [16]. For the case of $\mathcal{F}_\alpha = 0$ and a temperature that takes only the values β_c (for $h^n = 0$) and β_h (for $h^n = 1$), J_q is the rate at which heat is taken from the hot reservoir multiplied by β_c.

The work current J_e is defined as

$$J_e \equiv \sum_n \sum_{i<j} J_{ij}^n \left(f_i^n - f_j^n\right) = \sum_n \sum_i P_i^n \gamma^n \left(f_i^{n+1} - f_i^n\right), \tag{12}$$

where the second equality follows from the master equation in Eq. (1), which leads to $\frac{d}{dt}\sum_i \sum_n f_i^n P_i^n = 0$. The term $\Delta E J_e$ is the rate of work exerted on the system due to the variation of the external protocol: from the second line of Eq. (12), γ^n is the speed of the change of the protocol from n to $n+1$, and $\Delta E(f_i^{n+1} - f_i^n)$ is the energy change associated with the protocol jump. Finally, using Eqs. (8), (10), (12), and the dimensionless affinity $\mathcal{F}_e = \beta_c \Delta E$, we obtain

$$\sigma = \mathcal{F}_q J_q + \mathcal{F}_e J_e + \sum_\alpha \mathcal{F}_\alpha J_\alpha, \tag{13}$$

which is the expression of the entropy production in terms of currents and affinities. Note that we have defined the currents in Eqs. (9), (11), and (12) in such a way that the affinities $\mathcal{F}_\alpha$, $\mathcal{F}_q$, and $\mathcal{F}_e$ are dimensionless. The comparison between this expression for σ and the more usual expression for the entropy production for a deterministic protocol is discussed in Appendix B. To illustrate the general theory, we introduce two specific models: one for a heat engine and one for molecular pump.

C. Illustrative examples

1. Heat engine

The model for a heat engine is illustrated in Fig. 2. The system has two states, a down state with energy 0 and an up state with energy $E^n = E + \Delta E f^n$. The protocol has four states. The first jump of the protocol corresponds to an isothermal step at temperature β_c^{-1}, with the energy of the up state lifted from E to $E + \Delta E$. In the second jump of the protocol, the temperature is changed from β_c^{-1} to β_h^{-1}. In the third jump, the energy is lowered back from $E + \Delta E$ to E in an isothermal process at temperature β_h^{-1}. In the fourth jump, the engine returns to the initial state, with a temperature change from β_h^{-1} to β_c^{-1}. In the isothermal steps, work is exerted on the system when the higher energy level is elevated by ΔE at temperature β_c^{-1} and work is extracted from the system when the higher energy level is lowered at temperature β_h^{-1}. If the temperature difference is high enough, the system is more likely to be in the state of higher energy during the work extraction step, leading to net work extraction. For this model, $f^n = \delta_{n,1} + \delta_{n,2}$, and h^n from Eq. (3) is $h^n = \delta_{n,2} + \delta_{n,3}$.

The entropy production for the heat engine reads

$$\sigma = \mathcal{F}_q J_q + \mathcal{F}_e J_e, \tag{14}$$

where J_q is the rate of heat taken from the hot reservoir and $-\mathcal{F}_e J_e$ is the rate of extracted work, both in units of β_c^{-1} per time. Taking the transition rates given in the caption of Fig. 2, we consider the following limit. First, we take the limit at

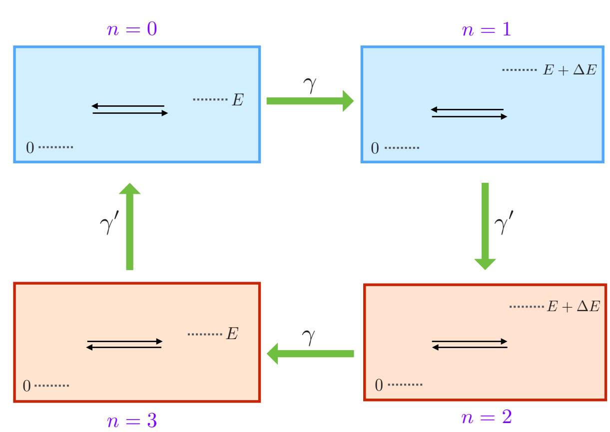

FIG. 2. Model for a heat engine. The temperature is cold for $n = 0,1$ and hot for $n = 2,3$. The transition rate from the state with energy 0 to the states with energy E^n is set to $ke^{-\beta^n E^n/2}$, while the reversed transition rate is $ke^{\beta^n E^n/2}$. The transition rate associated with isothermal changes is γ, whereas the transition rate associated with temperature changes is γ'.

which temperature changes are instantaneous, leading to $\gamma' \gg \gamma, k$. Second, we consider that the system equilibrates before an isothermal step, i.e., $k \gg \gamma$. Within this limit, calculating the stationary distribution of the full bipartite system, we obtain the following simple expressions:

$$-J_e = \gamma \frac{e^{\beta_c E} - e^{\beta_h (E+\Delta E)}}{2(1+e^{\beta_h (E+\Delta E)})(1+e^{\beta_c E})} \tag{15}$$

and

$$J_q = \gamma \beta_c (E+\Delta E) \frac{e^{\beta_c E} - e^{\beta_h (E+\Delta E)}}{2(1+e^{\beta_h (E+\Delta E)})(1+e^{\beta_c E})}, \tag{16}$$

which leads to the entropy production

$$\sigma = \gamma[\beta_c E - \beta_h (E+\Delta E)] \frac{e^{\beta_c E} - e^{\beta_h (E+\Delta E)}}{2(1+e^{\beta_h (E+\Delta E)})(1+e^{\beta_c E})} \geqslant 0. \tag{17}$$

Hence, for $\beta_h/\beta_c \leqslant E/(E+\Delta E)$ this machine operates as a heat engine that uses part of the heat taken from the hot reservoir to extract work. Interestingly, the efficiency of the heat engine in this regime is independent of the temperature difference, i.e.,

$$\eta \equiv \frac{-\mathcal{F}_e J_e}{J_q} = \frac{\Delta E}{E+\Delta E} \leqslant 1 - \frac{\beta_h}{\beta_c}. \tag{18}$$

The second inequality, which follows from the second law in Eq. (17), tells us that the efficiency of the heat engine is bounded by the Carnot efficiency.

2. *Molecular pump*

We consider a model for a molecular pump shown in Fig. 3, which has a protocol with $N = 3$ states and $\Omega = 3$ internal states. This model has been analyzed in [35,47]. The temperature is fixed and set to $\beta^n = 1$. The energy is set to $E_i^n = \mathcal{F}_e \delta_{i,n+1}$, i.e., the green state in Fig. 3 has energy $\mathcal{F}_e$ and the other two states have energy 0. The dotted line in Fig. 3 represents an energy barrier B. The transition rates for a change in the external protocol are all $\gamma^n = \gamma$. The internal transition rates fulfilling the generalized detailed balance relation in Eq. (4) are given in the caption of Fig. 3.

The clockwise rotation of both this energy barrier and the state with higher energy can lead to an internal current in the clockwise direction that goes against an internal load $\mathcal{F}$ in the anticlockwise direction. For such a molecular pump, the entropy production in Eq. (13) takes the form

$$\sigma = J_e \mathcal{F}_e + J_\alpha \mathcal{F}, \tag{19}$$

where J_α is the internal current defined in Eq. (9), with $d_{ij}^\alpha = 1/3$ for a clockwise transition and $d_{ij}^\alpha = -1/3$ for an anticlockwise transition. The work exerted on the system $J_e \mathcal{F}_e$ can lead to work done against the internal force $-J_\alpha \mathcal{F}$, with an efficiency $\eta \equiv (-J_\alpha \mathcal{F})/(J_e \mathcal{F}_e)$. In the limit of an infinite energy barrier B and for internal transitions that are much faster than changes in the external protocol ($k \gg \gamma$), we obtain the following expressions for the currents:

$$-J_\alpha = \gamma \frac{e^{\mathcal{F}/3+\mathcal{F}_e} + e^{\mathcal{F}_e} - 2e^{2\mathcal{F}/3}}{3(e^{\mathcal{F}/3+\mathcal{F}_e} + e^{\mathcal{F}_e} + e^{2\mathcal{F}/3})} \tag{20}$$

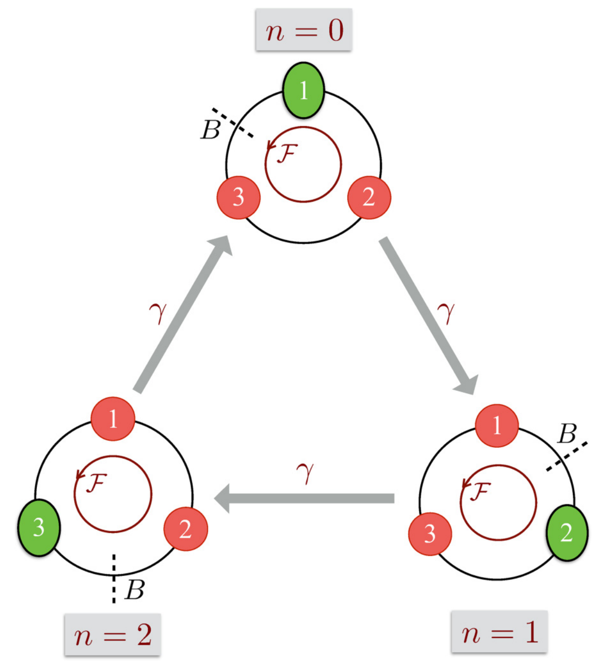

FIG. 3. Model for a molecular pump. The ellipse in green represents a state with energy $\mathcal{F}_e$, and the red circles represent states with energy 0. The transition rates for $n = 0$ are $w_{12}^0 = k e^{\mathcal{F}_e - \mathcal{F}/3}$, $w_{13}^0 = k e^{\mathcal{F}_e - B}$, $w_{23}^0 = k e^{-\mathcal{F}/3}$, $w_{21}^0 = k$, $w_{31}^0 = k e^{-B-\mathcal{F}/3}$, and $w_{32}^0 = k$, where $\beta_c = 1$. Changing n leads to a rotation in the clockwise direction of the transition rates. For example, $w_{12}^0 = w_{23}^0 = w_{31}^0$.

and

$$J_e = \gamma \frac{e^{\mathcal{F}/3}(e^{\mathcal{F}_e} - e^{\mathcal{F}/3})}{3(e^{\mathcal{F}/3+\mathcal{F}_e} + e^{\mathcal{F}_e} + e^{2\mathcal{F}/3})}. \tag{21}$$

Therefore, for a fixed positive $\mathcal{F}_e$, this model operates as a molecular pump that does work against the internal force $0 \leqslant \mathcal{F} \leqslant \mathcal{F}^*$, where $\mathcal{F}^*$ is the solution of the equation $J_\alpha = 0$.

D. Reversed protocol

Our results in the next section are obtained in terms of the original bipartite Markov process and another bipartite Markov process that corresponds to reversal of the external protocol, which is represented in Fig. 4. The transition rates for the original bipartite process are given by

$$w_{ij}^{nn'} \equiv \begin{cases} w_{ij}^n & \text{if } i \neq j \text{ and } n' = n, \\ \gamma^n & \text{if } i = j \text{ and } n' = n+1, \\ 0 & \text{otherwise.} \end{cases} \tag{22}$$

The transition rates for the bipartite Markov process that corresponds to reversal of the protocol are

$$v_{ij}^{nn'} \equiv \begin{cases} w_{ij}^n & \text{if } i \neq j \text{ and } n' = n, \\ \gamma^n & \text{if } i = j \text{ and } n' = n-1, \\ 0 & \text{otherwise.} \end{cases} \tag{23}$$

For a symmetric protocol, the bipartite Markov processes defined in Eqs. (22) and (23) become equivalent. Such a symmetric protocol fulfills the conditions $w_{ij}^n = w_{ij}^{N-1-n}$ and $\gamma^n = \gamma^{N-1-n}$.

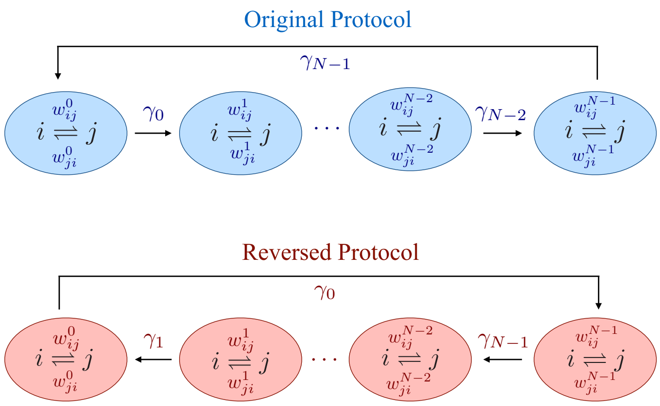

FIG. 4. Illustration of the comparison between the original bipartite Markov process with rates in Eq. (22) and the one corresponding to reversal of the protocol with rates in Eq. (23).

III. FLUCTUATION THEOREM FOR CURRENTS

A. Fluctuating currents

A fluctuating elementary current X_{ij}^n is a functional of the stochastic trajectory from time 0 to time t that counts transitions between states (i,n) and (j,n). For compact notation, we omit the dependence of X_{ij}^n on the time interval t. If a transition from (i,n) to (j,n) happens, this random variable increases by 1, and if a transition from (j,n) to (i,n) happens, this random variable decreases by 1. The average of this fluctuating current is

$$\lim_{t\to\infty} \frac{\langle X_{ij}^n \rangle}{t} = J_{ij}^n, \tag{24}$$

where the angular brackets indicate an average over stochastic trajectories. Similar to Eq. (9), the fluctuating currents X_α are given by

$$X_\alpha \equiv \sum_n \sum_{i<j} (\beta_c)^{-1} \beta^n X_{ij}^n d_{ij}^{(\alpha)}. \tag{25}$$

Furthermore, from Eq. (11) we define

$$X_q \equiv \sum_n \sum_{i<j} X_{ij}^n h^n \beta_c \big(E_j^n - E_i^n\big), \tag{26}$$

and from Eq. (12) we define

$$X_e \equiv \sum_n \sum_{i<j} X_{ij}^n \big(f_i^n - f_j^n\big). \tag{27}$$

The fluctuating entropy production X_s reads

$$X_s \equiv \mathcal{F}_q X_q + \mathcal{F}_e X_e + \sum_\alpha \mathcal{F}_\alpha X_\alpha = \sum_a \mathcal{F}_a X_a, \tag{28}$$

where the sum $\sum_a$ represents a sum over all currents and affinities including $a = q$, $a = e$, and $a = \alpha$.

The scaled cumulant-generating function associated with the vector of currents $\mathbf{X} = (X_a)$ is defined as

$$G(\mathbf{z}) \equiv \lim_{t\to\infty} \frac{1}{t} \ln\langle \exp(\mathbf{z}\cdot\mathbf{X})\rangle, \tag{29}$$

where $\mathbf{z} = (z_a)$ is a vector of real numbers $\mathbf{z}\cdot\mathbf{X} \equiv \sum_a z_a X_a$. This quantity is related to the rate function $I(\mathbf{x})$ from large deviation theory [48], which is defined as

$$\text{Prob}(\mathbf{X}) \sim \exp[-tI(\mathbf{x})], \tag{30}$$

where $\mathbf{x} \equiv \mathbf{X}/t$, and the symbol $\sim$ indicates asymptotic behavior in the limit $t \to \infty$. Specifically, $I(\mathbf{x})$ is a Legendre-Fenchel transform of $G(\mathbf{z})$, i.e.,

$$I(\mathbf{x}) = \max_{\mathbf{z}}[\mathbf{x}\cdot\mathbf{z} - G(\mathbf{z})]. \tag{31}$$

B. Fluctuation theorem

We now prove the fluctuation theorem for the currents, which is a symmetry in the scaled cumulant-generating function $G(\mathbf{z})$. The modified generator $\mathcal{L}(\mathbf{z})$ is a quadratic matrix with dimension $\Omega \times N$. Its elements are identified by a state of the bipartite process i,n. These elements are defined as

$$[\mathcal{L}(\mathbf{z})]_{j,n';i,n} \equiv \begin{cases} w_{ij}^n e^{\sum_a d_{ij}^{n(a)} z_a} & \text{if } j \neq i \text{ and } n' = n, \\ \gamma^n & \text{if } j = i \text{ and } n' = n+1, \\ -\gamma^n - \sum_k w_{ik}^n & \text{if } j = i \text{ and } n' = n, \\ 0 & \text{otherwise}, \end{cases} \tag{32}$$

where $d_{ij}^{n(\alpha)} \equiv (\beta_c)^{-1}\beta^n d_{ij}^{(\alpha)}$, $d_{ij}^{n(q)} \equiv h^n \beta_c (E_j^n - E_i^n)$, and $d_{ij}^{n(e)} \equiv (f_i^n - f_j^n)$. This matrix can be written in the form

$$\mathcal{L}(\mathbf{z}) = \begin{pmatrix} \mathcal{L}_0(\mathbf{z}) - \mathbf{\Gamma}_0 & 0 & \cdots & \mathbf{\Gamma}_{N-1} \\ \mathbf{\Gamma}_0 & \mathcal{L}_1(\mathbf{z}) - \mathbf{\Gamma}_1 & \cdots & 0 \\ 0 & \mathbf{\Gamma}_1 & \cdots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \cdots & \mathcal{L}_{N-1}(\mathbf{z}) - \mathbf{\Gamma}_{N-1} \end{pmatrix}, \tag{33}$$

where

$$[\mathcal{L}_n(\mathbf{z})]_{j;i} \equiv \begin{cases} w_{ij}^n e^{\sum_a d_{ij}^{n(a)} z_a} & \text{if } i \neq j, \\ -\sum_k w_{ik}^n & \text{if } i = j, \end{cases} \tag{34}$$

and $\mathbf{\Gamma}_n = \gamma^n \mathbf{I}$, with $\mathbf{I}$ as the identity matrix with dimension Ω. This modified generator is a Perron-Frobenius matrix, and its maximum eigenvalue is the scaled cumulant-generating function $G(\mathbf{z})$ [37].

The scaled cumulant-generating function associated with the reversed bipartite process, with transition rates given by Eq. (23), is denoted $G^R(\mathbf{z})$. The modified generator related to it is

$$[\mathcal{L}^R(\mathbf{z})]_{j,n';i,n} \equiv \begin{cases} w_{ij}^n \mathrm{e}^{\sum_a d_{ij}^{n(a)} z_a} & \text{if } j \neq i \text{ and } n' = n, \\ \gamma^n & \text{if } j = i \text{ and } n' = n-1, \\ -\gamma^n - \sum_k w_{ik}^n & \text{if } j = i \text{ and } n' = n, \\ 0 & \text{otherwise.} \end{cases} \quad (35)$$

This matrix can be written in the form

$$\mathcal{L}^R(\mathbf{z}) = \begin{pmatrix} \mathcal{L}_0(\mathbf{z}) - \mathbf{\Gamma}_0 & \mathbf{\Gamma}_1 & \cdots & 0 \\ 0 & \mathcal{L}_1(\mathbf{z}) - \mathbf{\Gamma}_1 & \cdots & 0 \\ 0 & 0 & \cdots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ \mathbf{\Gamma}_0 & 0 & \cdots & \mathcal{L}_{N-1}(\mathbf{z}) - \mathbf{\Gamma}_{N-1} \end{pmatrix}. \quad (36)$$

From Eqs. (2)–(4), and (34), we obtain the following symmetry:

$$[\mathcal{L}_n(\mathbf{z})]_{j;i} = [\mathcal{L}_n(-\mathbf{F} - \mathbf{z})]_{i;j} \mathrm{e}^{\beta_c (E_i - E_j)}, \quad (37)$$

where $\mathbf{F} = (\mathcal{F}_a)$, and E_i is the part of the energy E_i^n that does not depend on the external protocol. For the case $\gamma^n = \gamma$, with a matrix $\mathcal{D}$ that is a diagonal matrix with components $[\mathcal{D}]_{i,n;j,n'} = \delta_{nn'}\delta_{ij}\mathrm{e}^{\beta_c E_i}$, we obtain

$$\mathcal{L}(\mathbf{z}) = [\mathcal{D}\mathcal{L}^R(-\mathbf{F} - \mathbf{z})\mathcal{D}^{-1}]^T, \quad (38)$$

where the superscript T denotes transpose. This similarity transformation proves that $\mathcal{L}(\mathbf{z})$ and $\mathcal{L}^R(-\mathbf{F} - \mathbf{z})$ have the same characteristic polynomial. A similar similarity transformation appears in the proof of a transient fluctuation theorem for the currents [39].

For general γ^n, Eq. (38) does not hold; however, as shown in Appendix B, the characteristic polynomials of $\mathcal{L}(\mathbf{z})$ and $\mathcal{L}^R(-\mathbf{F} - \mathbf{z})$ are the same. Since the scaled cumulant-generating function is the maximum eigenvalue of the modified generator, this equality between characteristic polynomials implies the symmetry

$$G(\mathbf{z}) = G^R(-\mathbf{F} - \mathbf{z}). \quad (39)$$

This fluctuation theorem for the currents for periodically driven systems is the most general result of this paper. It is a generalization of the fluctuation theorem for the currents for nonequilibrium steady states [37,40] to periodically driven systems. For the case of a symmetric protocol, this relation becomes $G(\mathbf{z}) = G(-\mathbf{F} - \mathbf{z})$, which is the exact same form of the fluctuation theorem for the currents for nonequilibrium steady states. In spite of this same form and a similar mathematical derivation, the relation $G(\mathbf{z}) = G(-\mathbf{F} - \mathbf{z})$ for symmetric protocols is a different mathematical result, which applies to a different class of Markov processes, in relation to the fluctuation theorem for the currents for nonequilibrium steady states. We point out that our results should also be valid for deterministic protocols that are continuous, since there is strong evidence that such protocols can be obtained as a limit of a stochastic protocol with infinitely many jumps, as discussed in Appendix A.

It is worth mentioning that a fluctuation theorem for currents for a system driven by periodic and deterministic protocols has been obtained in [46]. Their derivation, however, relies on assumptions that restrict the time dependence of transitions rates. In particular, they cannot have a situation in which both energies and energies barriers are varied in time, which is a necessary condition for a molecular pump to generate an internal current [26,27]. Hence, the fluctuation theorem from [46] cannot be used to derive the response relations from Sec. IV that are valid for both heat engines and molecular pumps.

The scaled cumulant-generating function associated with the entropy current X_s is obtained by setting the real vector to $\mathbf{z} = (\mathcal{F}_a z)$, i.e.,

$$G_s(z) = G(z\mathbf{F}). \quad (40)$$

The fluctuation theorem for the currents implies

$$G_s(z) = G_s^R(-1 - z). \quad (41)$$

This equation is a generalization of the Gallavotti-Cohen symmetry [37] to periodically driven systems. In Fig. 5 we plot $G_s(z)$ for the models explained in Appendix B. As illustrated in Fig. 5(a), the function $G_s(z)$ is symmetric for the case of a symmetric protocol. Furthermore, as shown in Fig. 5(b), for a nonsymmetric protocol $G_s(z)$ fulfills the property $G_s(0) = G_s(-1) = 0$, which is a consequence of Eq. (41). This property, which is also valid for $G(\mathbf{z})$, is important for the derivations in the next section. We note that in terms of the rate function $I(\mathbf{x})$, the fluctuation theorem for the currents in Eq. (39) becomes

$$I(\mathbf{x}) - I^R(-\mathbf{F} - \mathbf{x}) = -\mathbf{F} \cdot \mathbf{x}, \quad (42)$$

where we have used Eq. (31).

IV. RESPONSE COEFFICIENTS

A. Fluctuation dissipation relation

In this section, we write the scaled cumulant-generating function as $G(\mathbf{z},\mathbf{F})$, keeping the dependence on the affinities explicit. An average current J_a can be obtained from $G(\mathbf{z},\mathbf{F})$ with the equation

$$J_a(\mathbf{F}) = \left.\frac{\partial G}{\partial z_a}\right|_{\mathbf{z}=0}. \quad (43)$$

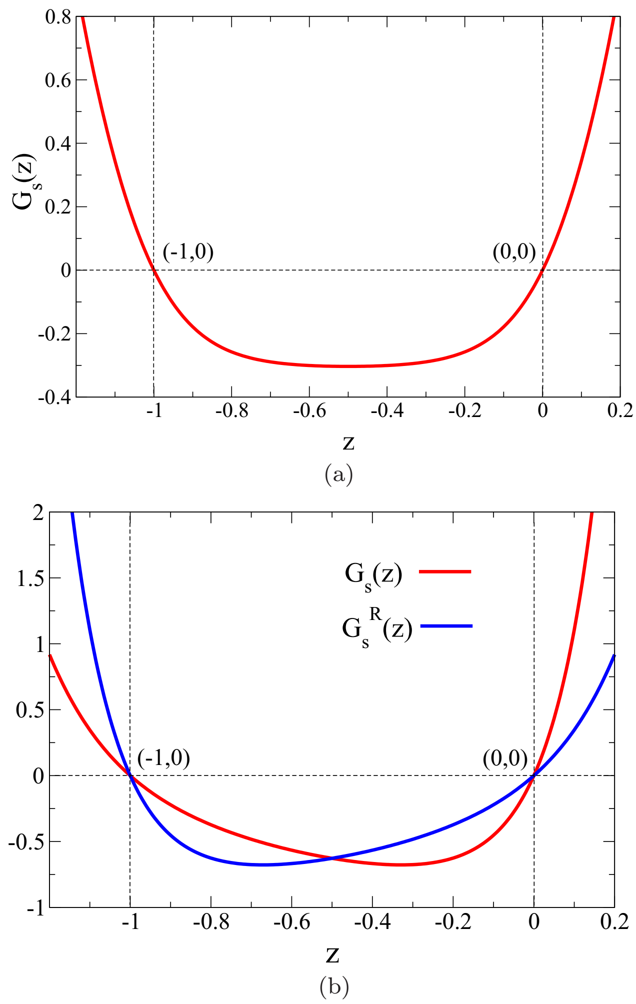

FIG. 5. Scaled cumulant-generating function associated with the entropy current $G_s(z)$. (a) Symmetric protocol for the model depicted in Fig. 6. Parameters were set to $k = \mathcal{F}_e = 10$, $\gamma^0 = 1$, $\gamma^1 = 2.5$, $\gamma^2 = 4$, and $\gamma^3 = 3$. (b) Nonsymmetric protocol for the molecular pump depicted in Fig. 3. Parameters were set to $k = 10$, $\gamma = 1$, $\mathcal{F}_e = B = 10$, and $\mathcal{F} = 5$.

Furthermore, the diffusion coefficient is defined as

$$D_{ab}(\mathbf{F}) \equiv \frac{\langle (X_a - \langle X_a \rangle)(X_b - \langle X_b \rangle)\rangle}{t} = \left.\frac{\partial^2 G}{\partial z_a z_b}\right|_{\mathbf{z}=\mathbf{0}}. \quad (44)$$

In the linear-response regime, the current in Eq. (43) becomes

$$J_a = \sum_b L_{ab}\mathcal{F}_b + O(\mathcal{F}^2), \quad (45)$$

where

$$L_{ab} \equiv \left.\frac{\partial^2 G}{\partial z_a \partial \mathcal{F}_b}\right|_{\mathbf{z}=\mathbf{0},\mathbf{F}=\mathbf{0}} \quad (46)$$

are the Onsager coefficients. We now derive a fluctuation dissipation relation for periodically driven systems that relates the response coefficients L_{ab} with fluctuations in equilibrium, as quantified by $D^{\mathrm{eq}}_{ab} \equiv D_{ab}(\mathbf{F} = \mathbf{0})$.

The fluctuation theorem for the currents (39) implies the relation

$$G(0,\mathbf{F}) = G(-\mathbf{F},\mathbf{F}) = 0. \quad (47)$$

A Taylor expansion around $\mathbf{z} = \mathbf{F} = 0$ of the scaled cumulant-generating function leads to

$$G(\mathbf{z}^*,\mathbf{F}^*) = \sum_{\mathbf{kl}} g_{\mathbf{k},\mathbf{l}} \prod_a \frac{(z_a^*)^{k_a}(\mathcal{F}_a^*)^{l_a}}{k_a!\,l_a!}, \quad (48)$$

where

$$g_{\mathbf{k},\mathbf{l}} \equiv \left.\frac{\partial^{k+l} G}{\prod_a \partial^{k_a} z_a \partial^{l_a} \mathcal{F}_a}\right|_{\mathbf{z}=0,\mathbf{F}=0}, \quad (49)$$

$\mathbf{k} \equiv (k_a)$, $\mathbf{l} \equiv (l_a)$, $k = \sum_a k_a$, and $l = \sum_a l_a$. The sum $\sum_{\mathbf{kl}}$ is over all possible vectors with each component taking the values $k_a = 0,1,\ldots,\infty$ and $l_a = 0,1,\ldots,\infty$. With a Taylor expansion around $-\mathbf{z}^* - \mathbf{F}^*$, we obtain

$$G(-\mathbf{F}^* - \mathbf{z}^*,\mathbf{F}^*) = \sum_{\mathbf{kl}} g_{\mathbf{k},\mathbf{l}} \prod_a \frac{(-z_a^* - \mathcal{F}_a^*)^{k_a}(\mathcal{F}_a^*)^{l_a}}{k_a!\,l_a!}$$
$$= \sum_{\mathbf{kl}} \tilde{g}_{\mathbf{k},\mathbf{l}} \prod_a \frac{(-z_a^*)^{k_a}(\mathcal{F}_a^*)^{l_a}}{k_a!\,l_a!}, \quad (50)$$

where

$$\tilde{g}_{\mathbf{k},\mathbf{l}} \equiv \left.\frac{\partial^{k+l} G}{\prod_a \partial^{k_a} z_a \partial^{l_a} \mathcal{F}_a}\right|_{\mathbf{z}=-\mathbf{F}^*,\mathbf{F}=0}. \quad (51)$$

Equation (50) implies

$$\tilde{g}_{\mathbf{k},\mathbf{l}} = \sum_{\mathbf{n}} g_{\mathbf{k}+\mathbf{n},\mathbf{l}-\mathbf{n}} \prod_a (-1)^{n_a} \frac{l_a!}{(l_a - n_a)!\,n_a!}, \quad (52)$$

where $\mathbf{n} \equiv (n_a)$ and $n_a = 0,1,\ldots,l_a$ in the sum $\sum_{\mathbf{n}}$. The zeros of $G(\mathbf{z},\mathbf{F})$ in Eq. (47), combined with Eqs. (48) and (50), lead to $g_{0,\mathbf{l}} = \tilde{g}_{0,\mathbf{l}} = 0$ for all vectors $\mathbf{l}$. Hence, setting $\mathbf{k} = \mathbf{0}$ in Eq. (52), we obtain

$$g_{\mathbf{l},0} = -\sum_{\mathbf{n}}{}' g_{\mathbf{n},\mathbf{l}-\mathbf{n}} \prod_a (-1)^{n_a} \frac{l_a!}{(l_a - n_a)!\,n_a!}, \quad (53)$$

where the sum $\sum'_{\mathbf{n}}$ is over all $n_a = 0,1,\ldots,l_a$ apart from the term $n_a = l_a$ for all a. A similar mathematical derivation of Eq. (53) from the condition in Eq. (47) has been used in [49] for the case of nonlinear transport in a conductor.

If we set the vector $\mathbf{l}$ to 1 for components a and b, and to 0 for all other components, Eq. (53) becomes

$$D^{\mathrm{eq}}_{ab} = L_{ab} + L_{ba}, \quad (54)$$

which is the fluctuation-dissipation relation for periodically driven systems. This equation relates fluctuations in equilibrium, as quantified by D^{eq}_{ab}, with nonequilibrium response functions, as quantified by the Onsager coefficients. For the case $a = b$, we obtain $D^{\mathrm{eq}}_{aa} = 2L_{aa}$ by setting the component a of the vector $\mathbf{l}$ to 2 and the other components to 0 in Eq. (53).

B. Symmetry for Onsager coefficients

For the reciprocity relation for periodically driven systems, we also have to consider the bipartite Markov process corresponding to reversal of the protocol. From the fluctuation theorem for currents in Eq. (39), we obtain

$$\left.\frac{\partial^2 G}{\partial z_a \partial \mathcal{F}_b}\right|_{\mathbf{z}=\mathbf{z}^*,\mathbf{F}=\mathbf{F}^*} = \left.\frac{\partial^2 G^R}{\partial z_a \partial z_b}\right|_{\mathbf{z}=-\mathbf{z}^*-\mathbf{F}^*,\mathbf{F}=\mathbf{F}^*} - \left.\frac{\partial^2 G^R}{\partial z_a \partial \mathcal{F}_b}\right|_{\mathbf{z}=-\mathbf{z}^*-\mathbf{F}^*,\mathbf{F}=\mathbf{F}^*}. \quad (55)$$

Setting $\mathbf{z}^* = \mathbf{F}^* = \mathbf{0}$, Eq. (55) becomes

$$L_{ab} = D_{ab}^{\text{eq}} - L_{ab}^R. \quad (56)$$

This equation, together with the fluctuation-dissipation relation in Eq. (54), gives the symmetry of the Onsager coefficients,

$$L_{ab}^R = L_{ba}. \quad (57)$$

This symmetry relation is a generalization of the symmetry derived in [16], since our framework also accounts for the case of nonzero fixed thermodynamic affinities $\mathcal{F}_\alpha$.

We note that this method of taking derivatives of the fluctuation theorem for the currents to derive relations for response coefficients as in Eq. (55) has been used in [40] for the case of nonequilibrium steady states. The main difference between the derivations in this reference and the present derivation is that for periodically driven systems, we have to consider two scaled cumulant-generating functions, and, therefore, Eq. (55) alone is not enough to get the symmetry of Onsager coefficients; we also need Eq. (54).

C. Nonlinear coefficients

We now show that the fluctuation theorem for the currents also implies relations between the nonlinear-response coefficients. Expanding the current up to second order in the affinity, we obtain

$$J_a = \sum_b L_{ab}\mathcal{F}_b + \frac{1}{2}\sum_{bc} M_{a,bc}\mathcal{F}_b\mathcal{F}_c + O(\mathcal{F}^3), \quad (58)$$

where

$$M_{a,bc} \equiv \left.\frac{\partial^3 G}{\partial z_a \partial \mathcal{F}_b \partial \mathcal{F}_c}\right|_{\mathbf{z}=0,\mathbf{F}=0}. \quad (59)$$

The diffusion coefficient is expanded up to first order,

$$D_{ab} = D_{ab}^{\text{eq}} + \sum_c N_{ab,c}\mathcal{F}_c + O(\mathcal{F}^2), \quad (60)$$

where

$$N_{ab,c} \equiv \left.\frac{\partial^3 G}{\partial z_a \partial z_b \partial \mathcal{F}_c}\right|_{\mathbf{z}=0,\mathbf{F}=0}. \quad (61)$$

From the fluctuation theorem for the currents in Eq. (39), we see that the scaled cumulant-generating function in equilibrium is symmetric and, hence, the odd cumulants associated with the currents in equilibrium are zero. In particular, using the fact that the third cumulant in equilibrium is zero, from Eq. (53) we obtain

$$M_{a,bc} + M_{b,ac} + M_{c,ab} = N_{ab,c} + N_{ac,b} + N_{bc,a}. \quad (62)$$

Hence, the second-order coefficients of the current can be expressed as first-order coefficients of the diffusion coefficient. Furthermore, taking a further derivative with respect to $\mathcal{F}_c$ in Eq. (55), we obtain

$$M_{a,bc} + M_{a,bc}^R = N_{ab,c} + N_{ac,b} = N_{ab,c}^R + N_{ac,b}^R, \quad (63)$$

where the second equality comes from the fact that we can interchange the roles of original and reversed protocol in Eq. (55). From Eqs. (62) and (63), the following relation for the second-order coefficient of the current is obtained:

$$M_{a,bc} + M_{b,ac} + M_{c,ab} = M_{a,bc}^R + M_{b,ac}^R + M_{c,ab}^R. \quad (64)$$

In general, relation (53) shows that higher-order cumulants at equilibrium can be expressed as response functions associated with lower-order cumulants. Considering higher orders in Eq. (53) and taking further derivatives in Eq. (55) lead to relations between higher-order response coefficients. For the case of a symmetric protocol, all relations for nonlinear-response coefficients derived in [40] hold true, since their derivation relies on the relation $G(\mathbf{z},\mathbf{F}) = G(-\mathbf{z}-\mathbf{F},\mathbf{F})$ that is valid for a symmetric protocol.

V. CONCLUSION

We have proven a fluctuation theorem for the currents for periodically driven systems. This result generalizes the symmetry of the Onsager coefficients for periodically driven systems obtained in [16]: our fluctuation theorem implies this symmetry, a fluctuation dissipation relation, and further relations for nonlinear-response coefficients. This situation is akin to the previously known fluctuation theorem for the currents for steady states that implies response relations.

Our results also provide a unifying framework that includes two different classes of periodically driven systems that have hitherto been analyzed separately in the literature and that have been realized experimentally. These two classes are small heat engines operated with periodic temperature variation and molecular pumps that can have fixed thermodynamic forces and, therefore, would be out of equilibrium even without periodic driving.

Several universal features of nonequilibrium steady states have been obtained within the framework of stochastic thermodynamics [2]. The fluctuation theorem for currents is one such universal feature that is now generalized to the case of periodically driven systems. Generalizing other results that have been established for nonequilibrium steady states, e.g., fluctuation dissipation relations far from equilibrium [50–52] and the thermodynamic uncertainty relation [35,53], to periodically driven systems constitutes an interesting direction for future work.

ACKNOWLEDGMENTS

We thank Udo Seifert for helpful discussions and Matteo Polettini for pointing out a mistake in a previous version.

APPENDIX A: DETERMINISTIC PROTOCOL AS A LIMIT OF A STOCHASTIC PROTOCOL

In this appendix, we explain how a continuous deterministic protocol can be obtained as a stochastic protocol with infinitely many jumps. We also write down the expression of the entropy production for this case of a deterministic protocol.

1. Average entropy production

The stochastic protocol alone is a Markov process that follows the master equation

$$\frac{d}{dt}P^n = \gamma P^{n-1} - \gamma P^n, \tag{A1}$$

where $P^n = \sum_i P_i^n$, and we set $\gamma^n = \gamma$ for $n = 0,1,\ldots,N-1$. If we consider a random variable X_{ext} that counts the number of jumps of the external protocol, a standard calculation gives

$$v_{\mathrm{ext}} \equiv \langle X_{\mathrm{ext}}\rangle/t = \gamma/N \tag{A2}$$

and

$$D_{\mathrm{ext}} \equiv \langle (X_{\mathrm{ext}} - \langle X_{\mathrm{ext}}\rangle)^2\rangle/t = \gamma/N^2. \tag{A3}$$

By setting $\gamma = N/\tau$ and taking the limit $N \to \infty$, the stochastic protocol becomes deterministic with a speed $v_{\mathrm{ext}} = \tau^{-1}$ and a dispersion $D_{\mathrm{ext}} = (\tau N)^{-1} \to 0$. In this limit, the transition rates w_{ij}^n become $w_{ij}(t)$, where $t = n\tau/N$. The periodicity condition $w_i^n = w_i^{n+N}$ changes to $w_{ij}(t) = w_{ij}(t+\tau)$.

The master equation in this limit then becomes

$$\frac{d}{dt}R_i(t) = \sum_j [R_j(t)w_{ji}(t) - R_i(t)w_{ij}(t)], \tag{A4}$$

where $R_i(t)$ is the probability to be in state i at time t. The generalized detailed balance relation in Eq. (4) changes to

$$\ln\frac{w_{ij}(t)}{w_{ji}(t)} = \beta(t)\big[E_i(t) - E_j(t) + (\beta_c)^{-1}\mathcal{F}_\alpha d_{ij}^{(\alpha)}\big], \tag{A5}$$

where $\beta(t) = \beta_c[1 - \mathcal{F}_q h(t)]$ and $E_i(t) = E_i + \Delta E f_i(t)$. Comparing with the stochastic protocol, the functions $h(t)$ and $E_i(t)$ fulfill the relations $h(t = \tau n/N) = h^n$ and $E_i(t = \tau n/N) = E_i^n$, where E_i^n is given in Eq. (2) and h^n is given in Eq. (3)

In the long-time limit, the system reaches a periodic steady state characterized by the probability $R_i^*(t) = R_i^*(t+\tau)$. For the comparison of this probability with the stationary probability of the bipartite process P_i^n, we define the conditional stationary probability of the system being in state i given the protocol is in state n, $P(i|n) \equiv P_i^n/P^n$, where the stationary probability of the protocol is $P^n = 1/N$. It can be shown that the conditional probability of the bipartite Markov process $P(i|n)$ tends to $R_i^*(t = n\tau/N)$ in the limit $N \to \infty$ [35].

The elementary current X_{ij}^*, analogous to $\sum_n X_{ij}^n$ for a stochastic protocol, is a random variable that increases by 1 if a jump from i to j takes place and that decreases by 1 if a jump from j to i takes place. The average current,

$$J_{ij}^* \equiv \lim_{t\to\infty}\frac{\langle X_{ij}^*\rangle}{t}, \tag{A6}$$

is given by

$$J_{ij}^* = \frac{1}{\tau}\int_0^\tau [R_i^*(t)w_{ij}(t) - R_j^*(t)w_{ji}(t)]dt \equiv \frac{1}{\tau}\int_0^\tau J_{ij}(t)dt. \tag{A7}$$

Using Eq. (6), this expression can be compared to the following expression for the stochastic protocol:

$$J_{ij} \equiv \sum_n J_{ij}^n = \frac{1}{N}\sum_n \big[P(i|n)w_{ij}^n - P(j|n)w_{ji}^n\big]. \tag{A8}$$

Comparing with J_{ij}^*, we obtain that the convergence $P(i|n) \to R_i^*(t = n\tau/N)$ in the limit $N \to \infty$ implies $J_{ij} \to J_{ij}^*$.

The entropy production in Eq. (5) changes to

$$\begin{aligned}\sigma^* &\equiv \frac{1}{\tau}\int_0^\tau \sum_{ij} R_i^*(t)w_{ij}(t)\ln\frac{w_{ij}(t)}{w_{ji}(t)} \\ &= \mathcal{F}_q J_q^* + \mathcal{F}_e J_e^* + \sum_\alpha \mathcal{F}_\alpha J_\alpha^* \geqslant 0,\end{aligned} \tag{A9}$$

where

$$J_\alpha^* \equiv \frac{1}{\tau}\int_0^\tau \sum_{i<j}(\beta_c)^{-1}\beta(t)J_{ij}(t)d_{ij}^{(\alpha)}dt, \tag{A10}$$

$$J_q^* \equiv \frac{1}{\tau}\int_0^\tau \sum_{i<j} J_{ij}(t)h(t)\beta_c[E_j(t) - E_i(t)]dt, \tag{A11}$$

and

$$J_e^* \equiv \frac{1}{\tau}\int_0^\tau \sum_{i<j} J_{ij}(t)[f_i(t) - f_j(t)]dt. \tag{A12}$$

The fact that the stationary probability of the bipartite process converges to $R_i^*(t)$ suggests that such convergence should also take place for current fluctuations, as characterized by the scaled cumulant-generating function. Furthermore, an expression for the large deviation function characterizing fluctuations of currents in periodically driven systems with a deterministic protocol in terms of $R_i^*(t)$ has been recently proposed in [36]. Such an expression provides further evidence for this convergence for current fluctuations. We now illustrate the convergence of the scaled cumulant-generating function for a specific model analyzed in [35].

2. Current fluctuations

The model with a symmetric protocol illustrated in Fig. 6 is defined as follows. The system has two states, one with energy zero and the other with energy $E^n = \mathcal{F}_e\cos(2\pi n/N)$. The temperature is constant and set to $\beta^n = 1$. The transition rates

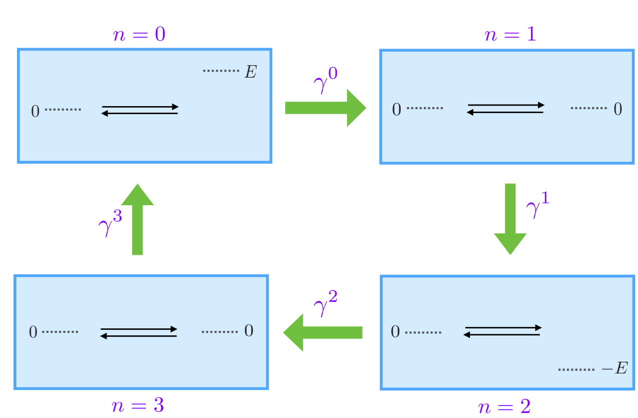

FIG. 6. Model with a symmetric protocol for $N = 4$.

of the protocol are γ^n. For the comparison with a deterministic protocol, we set $\gamma^n = \gamma$. The transition rate from the state with energy 0 to the state with energy E^n is set to $k e^{-E^n/2}$, while the reversed transition rate is $k e^{E^n/2}$. The scaled cumulant-generating function $G_s(z)$ can be obtained by calculating the eigenvalue of the modified generator from Sec. III.

We now consider the deterministic version of the model. The probability vector $\mathbf{R}(t)$ has two components, with the first component as the probability that the system is in the state with energy 0 and the second as the probability that the system is in the state with energy $E(t) = \mathcal{F}_e \cos(t)$. The transition rate from the state with energy 0 to the states with energy $E(t)$ is $k e^{-E(t)/2}$, whereas the reversed transition rate is $k e^{E(t)/2}$.

The probability vector $\mathbf{R}(X_s^*,t)$ gives the probabilities that the system is in a certain state with the entropy current given by X_s^*. Defining the Laplace transform $\mathbf{R}(z,t) = \sum_{X_s^*} \mathbf{R}(X_s^*,t) e^{z X_s^*}$ and using the master equation (A4), we obtain

$$\frac{d}{dt}\mathbf{R}(z,t) = \mathcal{L}(z,t)\mathbf{R}(z,t), \tag{A13}$$

where

$$\mathcal{L}(\mathbf{z},t) = \begin{pmatrix} -k e^{E(t)/2} & k e^{-E(t)/2} e^{-zE(t)} \\ k e^{E(t)/2} e^{zE(t)} & -k e^{-E(t)/2} \end{pmatrix}. \tag{A14}$$

The scaled cumulant-generating function is given by

$$\begin{aligned} G_s^*(z) &\equiv \lim_{t\to\infty} \frac{1}{t} \ln\langle \exp(z X_s^*)\rangle \\ &= \lim_{t\to\infty} \frac{1}{t} \ln[R_1(z,t) + R_2(z,t)], \end{aligned} \tag{A15}$$

where $R_i(z,t)$ is the component of the vector $\mathbf{R}(z,t)$. Using Floquet theory [54], the scaled cumulant-generating function $G_s^*(z)$ is given by the maximal Floquet exponent associated with $\mathcal{L}(\mathbf{z},t)$. We have calculated this maximal Floquet exponent following the numerical method explained in [54]. In Fig. 7, we show the convergence of the scaled cumulant-generating function obtained with the stochastic protocol with increasing N to $G_s^*(z)$. We note that, to our knowledge, a rigorous proof of the large deviation principle for arbitrary currents in periodically driven systems with deterministic protocols is still lacking. However, it is reasonable to expect that beyond the example analyzed here, this scaled cumulant-generating function is given by a maximal Floquet exponent.

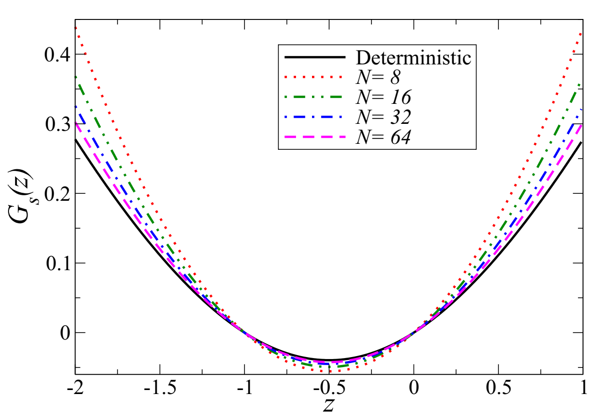

FIG. 7. Scaled cumulant-generating functions for a deterministic protocol and for a stochastic protocol. The scaled cumulant-generating function for a stochastic protocol tends to the scaled cumulant-generating function for the deterministic protocol with increasing N. The parameters of the model with a symmetric protocol are set to $\gamma = 2\pi/N$, $k = 1$, and $\mathcal{F}_e = 2$, where the parameter γ is valid only for the stochastic protocol.

APPENDIX B: EQUALITY BETWEEN CHARACTERISTIC POLYNOMIALS

The scaled cumulant-generating function $G(\mathbf{z})$ is a root of the characteristic polynomial associated with $\mathcal{L}(\mathbf{z})$. This polynomial is given by the determinant of the matrix $\mathcal{L}(\mathbf{z}) - \mathcal{I}x$, where $\mathcal{I}$ is the identity matrix with dimension $\Omega \times N$ and x is the variable of the polynomial. From Eq. (33), this matrix takes the form

$$\begin{pmatrix} \mathcal{L}_0(\mathbf{z}) - \mathbf{D}_0 & 0 & \cdots & \mathbf{\Gamma}_{N-1} \\ \mathbf{\Gamma}_0 & \mathcal{L}_1(\mathbf{z}) - \mathbf{D}_1 & \cdots & 0 \\ 0 & \mathbf{\Gamma}_1 & \cdots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \cdots & \mathcal{L}_{N-1}(\mathbf{z}) - \mathbf{D}_{N-1} \end{pmatrix}, \tag{B1}$$

where $\mathbf{D}_n = \mathbf{I}(\gamma^n + x)$. Furthermore, from Eqs. (36) and (37), the transpose of the matrix $\mathcal{D}\mathcal{L}^R(-\mathbf{F}-\mathbf{z})\mathcal{D}^{-1} - \mathcal{I}x$, where $\mathcal{D}$ is the diagonal matrix from Eq. (38), reads

$$\begin{pmatrix} \mathcal{L}_0(\mathbf{z}) - \mathbf{D}_0 & 0 & \cdots & \mathbf{\Gamma}_0 \\ \mathbf{\Gamma}_1 & \mathcal{L}_1(\mathbf{z}) - \mathbf{D}_1 & \cdots & 0 \\ 0 & \mathbf{\Gamma}_2 & \cdots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \cdots & \mathcal{L}_{N-1}(\mathbf{z}) - \mathbf{D}_{N-1} \end{pmatrix}. \tag{B2}$$

To show that the matrices in Eqs. (B1) and (B2) have the same determinant, we consider the Leibniz formula for determinants (Eq. 0.3.2.1 in [55]), where the determinant is written as a sum over all $(\Omega \times N)!$ permutations of the elements. In a graphical representation of these terms, where the states of the bipartite process (i,n) are vertices and nonzero transition rates are edges, there are diagonal terms and cyclic permutations with sizes that range from 2 up to $\Omega \times N$ (see [38,56]). For the case of the matrices in Eqs. (B1) and (B2), there are two kinds of cycles. First there are cycles that do not contain external jumps that lead to a change in the external protocol. In this case, since the diagonal blocks in Eqs. (B1) and (B2) are identical, the contribution to the determinants coming from these cycles must be the same for both matrices. Second, there are cycles that contain external jumps. In this case, since the external jumps are irreversible, all such cycles must go through all external states in order to close the cycle. For both matrices, the contribution to these cycles due to the external jumps is the same and given by $\prod_{n=0}^{N-1} \gamma^n$. We thus conclude that all terms contributing to the determinant, namely diagonal terms, cycles containing only internal jumps, and cycles containing external jumps, are exactly the same for the matrices in Eqs. (B1) and (B2). Hence, the determinants of these matrices are identical, which leads to the symmetry $G(\mathbf{z}) = G^R(-\mathbf{F}-\mathbf{z})$.

[1] H. B. Callen, *Thermodynamics and an Introduction to Thermostatistics*, 2nd ed. (Wiley, New York, 1985).
[2] U. Seifert, Rep. Prog. Phys. **75**, 126001 (2012).
[3] P. Steeneken, K. Le Phan, M. Goossens, G. Koops, G. Brom, C. Van der Avoort, and J. Van Beek, Nat. Phys. **7**, 354 (2011).
[4] V. Blickle and C. Bechinger, Nat. Phys. **8**, 143 (2012).
[5] I. A. Martínez, E. Roldán, L. Dinis, D. Petrov, and R. A. Rica, Phys. Rev. Lett. **114**, 120601 (2015).
[6] I. A. Martínez, E. Roldán, L. Dinis, J. M. R. Parrondo, D. Petrov, and R. A. Rica, Nat. Phys. **12**, 67 (2016).
[7] I. A. Martínez, E. Roldán, L. Dinis, and R. A. Rica, Soft Matter **13**, 22 (2017).
[8] D. A. Leigh, J. K. Wong, F. Dehez, and F. Zerbetto, Nature (London) **424**, 174 (2003).
[9] R. Eelkema, M. M. Pollard, J. Vicario, N. Katsonis, B. S. Ramon, C. W. Bastiaansen, D. J. Broer, and B. L. Feringa, Nature (London) **440**, 163 (2006).
[10] Q. Li, G. Fuks, E. Moulin, M. Maaloum, M. Rawiso, I. Kulic, J. T. Foy, and N. Giuseppone, Nat. Nanotechnol. **10**, 161 (2015).
[11] S. Erbas-Cakmak, D. A. Leigh, C. T. McTernan, and A. L. Nussbaumer, Chem. Rev. **115**, 10081 (2015).
[12] J. Schnakenberg, Rev. Mod. Phys. **48**, 571 (1976).
[13] L. Onsager, Phys. Rev. **37**, 405 (1931).
[14] L. Onsager, Phys. Rev. **38**, 2265 (1931).
[15] S. R. De Groot and P. Mazur, *Non-equilibrium Thermodynamics* (Courier, New York, 2013).
[16] K. Brandner, K. Saito, and U. Seifert, Phys. Rev. X **5**, 031019 (2015).
[17] K. Proesmans and C. Van den Broeck, Phys. Rev. Lett. **115**, 090601 (2015).
[18] K. Proesmans, B. Cleuren, and C. Van den Broeck, J. Stat. Mech. (2016) 023202.
[19] Y. Izumida and K. Okuda, Phys. Rev. E **80**, 021121 (2009).
[20] Y. Izumida and K. Okuda, Eur. Phys. J. B **77**, 499 (2010).
[21] Y. Izumida and K. Okuda, New J. Phys. **17**, 085011 (2015).
[22] T. Schmiedl and U. Seifert, Europhys. Lett. **81**, 20003 (2008).
[23] M. Esposito, R. Kawai, K. Lindenberg, and C. Van den Broeck, Phys. Rev. E **81**, 041106 (2010).
[24] Z. C. Tu, Phys. Rev. E **89**, 052148 (2014).
[25] R. D. Astumian, Ann. Rev. Biophys. **40**, 289 (2011).
[26] S. Rahav, J. Horowitz, and C. Jarzynski, Phys. Rev. Lett. **101**, 140602 (2008).
[27] V. Y. Chernyak and N. A. Sinitsyn, Phys. Rev. Lett. **101**, 160601 (2008).
[28] C. Maes, K. Netočný, and S. R. Thomas, J. Chem. Phys. **132**, 234116 (2010).
[29] S. Rahav, J. Stat. Mech.: Theor. Exp. (2011) P09020.
[30] D. Mandal, Europhys. Lett. **108**, 50001 (2014).
[31] G. Verley, C. V. den Broeck, and M. Esposito, New J. Phys. **16**, 095001 (2014).
[32] S. Asban and S. Rahav, Phys. Rev. Lett. **112**, 050601 (2014).
[33] M. Esposito and J. M. R. Parrondo, Phys. Rev. E **91**, 052114 (2015).
[34] O. Raz, Y. Subaşı, and C. Jarzynski, Phys. Rev. X **6**, 021022 (2016).
[35] A. C. Barato and U. Seifert, Phys. Rev. X **6**, 041053 (2016).
[36] G. M. Rotskoff, Phys. Rev. E **95**, 030101 (2017).
[37] J. L. Lebowitz and H. Spohn, J. Stat. Phys. **95**, 333 (1999).
[38] D. Andrieux and P. Gaspard, J. Stat. Phys. **127**, 107 (2007).
[39] M. Polettini and M. Esposito, J. Stat. Mech.: Theor. and Exp. (2014) P10033.
[40] D. Andrieux and P. Gaspard, J. Stat. Mech. (2007) P02006.
[41] J. R. Gomez-Solano, L. Bellon, A. Petrosyan, and S. Ciliberto, Europhys. Lett. **89**, 60003 (2010).
[42] E. Dieterich, J. Camunas-Soler, M. Ribezzi-Crivellari, U. Seifert, and F. Ritort, Nat. Phys. **11**, 971 (2015).
[43] D. Hartich, A. C. Barato, and U. Seifert, J. Stat. Mech. (2014) P02016.
[44] A. C. Barato, D. Hartich, and U. Seifert, New J. Phys. **16**, 103024 (2014).
[45] J. M. Horowitz and M. Esposito, Phys. Rev. X **4**, 031015 (2014).
[46] N. A. Sinitsyn, A. Akimov, and V. Y. Chernyak, Phys. Rev. E **83**, 021107 (2011).
[47] A. C. Barato and U. Seifert, New J. Phys. **19**, 073021 (2017).
[48] H. Touchette, Phys. Rep. **478**, 1 (2009).
[49] H. Förster and M. Büttiker, Phys. Rev. Lett. **101**, 136805 (2008).
[50] U. Seifert and T. Speck, Europhys. Lett. **89**, 10007 (2010).
[51] M. Baiesi, C. Maes, and B. Wynants, Phys. Rev. Lett. **103**, 010602 (2009).
[52] B. Altaner, M. Polettini, and M. Esposito, Phys. Rev. Lett. **117**, 180601 (2016).
[53] A. C. Barato and U. Seifert, Phys. Rev. Lett. **114**, 158101 (2015).
[54] C. A. Klausmeier, Theor. Ecol. **1**, 153 (2008).
[55] R. A. Horn and C. R. Johnson, *Matrix Analysis* (Cambridge University Press, New York, 2013).
[56] A. C. Barato and R. Chétrite, J. Phys. A **45**, 485002 (2012).