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Fluctuation theorem for currents in semi-Markov processes

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The fluctuation theorem for currents is proved in semi-Markov processes satisfying the condition of direction-time independence. The thermodynamic affinities as well as the corresponding fluctuating currents are defined using graph theory and the cyclic representation of the process. The fluctuation theorem is obtained by demonstrating a fundamental symmetry property for the evolution operator of the process. This fundamental symmetry of the evolution operator is also proved in the Markovian case. The results are illustrated with a semi-Markov process describing ion currents through a membrane.

I. INTRODUCTION

Random processes are of great importance in nanosciences. At these small scales, the degrees of freedom of the atoms and molecules composing the systems of interest play an important role and cannot be averaged out as it is the case for macroscopic systems. Accordingly, systems evolving over time scales longer than the intercollisional time are described at the mesoscopic level in terms of stochastic processes. If the successive random events are statistically independent, the stochastic process is Markovian. However, there exist several classes of systems exhibiting memory effects or even long-range temporal correlations. This is the case in particular for the single-molecule kinetics of proteins or DNA [1–5] and the transport of ions through membranes [6]. Other examples are strongly interacting quantum systems where non-Markovian effects are often present, such as single-level quantum dots or metallic single-electron transistors [7, 8].

Small systems are often out of equilibrium as they are in contact with several larger systems at different temperatures or electric or chemical potentials. In such environments, they sustain transports of heat, matter, or electric charges. By their smallness, the currents crossing these systems are fluctuating. Although their mean values obey the macroscopic laws of thermodynamics, recent advances have shown that their fluctuations also satisfy general relationships called fluctuation theorems [9–16]. A fluctuation theorem is a large-deviation relationship between the probabilities of positive versus negative fluctuations of the dissipation. At equilibrium, the fluctuation theorem reduces to the expression of detailed balance arising from microreversibility. Fluctuation theorems have been derived in various contexts, either deterministic [9, 10] or stochastic [13, 14], and for different properties such as the global dissipation related to the entropy production or the multiple fluctuating currents generated by the thermodynamic forces driving the system out of equilibrium [17–19]. More recently, fluctuation theorems have begun to be considered in non-Markovian stochastic processes described by baths with memory [20–22], by time-dependent transition rates [23], or as continuous-time random walks [24]. In this latter work, a fluctuation theorem has been obtained for energy and matter exchanges in systems where the ratios of forward and backward transition rates are assumed to depend on the changes of energy and particle numbers in each reservoir [24].

The purpose of the present work is to establish the fluctuation theorem for currents in semi-Markov processes by identifying the thermodynamic forces – also called affinities – thanks to the cyclic representation of the process in graph theory [25–27]. This method allows us to obtain with great generality the fluctuation theorem for currents directly in terms of the global thermodynamic forces driving the system at its boundaries. Moreover, the fluctuation theorem we here demonstrate holds for nonequilibrium steady states. In order to construct in a consistent way the stationary realizations of a semi-Markov process, it turns out that its transition probabilities should be time independent and statistically independent from the residence time distributions [28]. This condition has been called direction-time independence [4, 5] and shown to be essential together with detailed balance for the time reversibility of the semi-Markov process at equilibrium [5, 29]. The importance of this condition has also been discussed in Ref. [24]. Here, we also use this condition for our purpose. Furthermore, the fluctuation theorem for currents is here obtained by proving a symmetry relation for the evolution operator of the semi-Markov process.

The paper is organized as follows. In Sec. II, the semi-Markov processes are defined together with their cyclic representation and the fluctuation theorem for currents is stated. The demonstration of the fluctuation theorem is carried out in Sec. III. The Markovian case is presented in Sec. IV. In Sec. V, the fluctuation theorem is applied to the ion current through a membrane. Conclusions are drawn in Sec. VI.

II. NON-MARKOVIAN STOCHASTIC PROCESSES

A. Semi-Markov processes

We are here concerned with systems presenting a discrete set of configurations, or states, labeled ω. The stochastic dynamics is assumed to be a non-Markovian renewal process which is fully described by the set of probability densities $\psi_{\omega'\omega}(\tau)$ for making random transitions within the time interval $[\tau, \tau + d\tau]$ from the state ω to the state ω'. These probability densities are necessarily positive and obey the normalization conditions

$$\sum_{\omega'=1}^{N} \int_0^\infty \psi_{\omega'\omega}(\tau) d\tau = 1 \tag{1}$$

for all $\omega = 1, 2, ..., N$. The subsequent residence times (also called waiting times) between the random jumps are assumed to be mutually uncorrelated. The residence time distribution (RTD) $\psi_\omega(\tau)$ in the state ω reads

$$\psi_\omega(\tau) = \sum_{\omega'} \psi_{\omega'\omega}(\tau) = -\frac{d\phi_\omega(\tau)}{d\tau} \tag{2}$$

where $\phi_\omega(\tau)$ is the survival probability of the state ω obtained as

$$\phi_\omega(\tau) = \int_\tau^\infty \psi_\omega(t) dt\,. \tag{3}$$

This constitutes the general scheme for continuous time random walk (CTRW) theory [30].

Several descriptions used for such non-Markovian processes of the renewal type have been developed. The approach of Ref. [31] in terms of time-dependent aging rates $k_{\omega'\omega}(t)$ for the transitions from state ω to state ω' corresponds to a particular choice, while a different scheme was proposed in Ref. [32]. In our case, we will consider the description introduced by Goychuk who also discussed the equivalence between all these theoretical schemes [28]. In this framework, the probability densities are given by

$$\psi_{\omega'\omega}(\tau) = p_{\omega'\omega} \psi_\omega(\tau) \tag{4}$$

with *time-independent* transition probabilities $p_{\omega'\omega}$. In this case, the normalization conditions (1) become

$$\sum_{\omega'} p_{\omega'\omega} = 1, \quad \int_0^\infty \psi_\omega(\tau) d\tau = 1\,. \tag{5}$$

This approach has several advantages. The RTD $\psi_\omega(\tau)$ and the transition probabilities $p_{\omega'\omega}$ can be directly deduced from measured sample trajectories in an actual experiment although it appears difficult to obtain time-dependent aging rates $k_{\omega'\omega}(\tau)$ from an observed random process. The study of the statistics of the residence times allows one to obtain the corresponding probability densities $\psi_\omega(\tau)$ and, hence, the survival probabilities $\phi_\omega(\tau)$. Furthermore, the statistics of the transitions from one state into all other states allows one to derive the corresponding conditional probabilities $p_{\omega'\omega}$. Moreover, the description with a constant set $p_{\omega'\omega}$ provides a consistent approach to describe stationary realizations of the random process, and consequently to find the corresponding averaged stationary evolution [28]. On the other hand, it was shown that the semi-Markov process is reversible if and only if the condition (4) is satisfied and the embedded Markov chain of transition probabilities $p_{\omega'\omega}$ obeys the condition of detailed balance, as it should be the case at the thermodynamic equilibrium [4, 5, 29]. For this reason, the condition (4) is called the direction-time independence [4, 5].

A stochastic trajectory consists of random jumps at random times

$$\omega_0 \overset{t_1}{\to} \omega_1 \overset{t_2}{\to} \cdots \overset{t_n}{\to} \omega_n \tag{6}$$

where this trajectory begins in state ω_0 just after his arrival in this initial state at time t_0. The probability of this path ending at time t is given by

$$\phi_{\omega_n}(t - t_n)\ \psi_{\omega_n\omega_{n-1}}(t_n - t_{n-1})\ \cdots\ \psi_{\omega_2\omega_1}(t_2 - t_1)\ \psi_{\omega_1\omega_0}(t_1 - t_0)\,. \tag{7}$$

With these probabilities, one can derive various quantities of interest such as the probability to be in a state ω after a time t having started in the state ω_0 at the time t_0. It is given by

$$P_{\omega\omega_0}(t) = \delta_{\omega\omega_0}\phi_{\omega_0}(t - t_0) + \sum_{n=1}^{\infty} \int_{t_0}^{t} dt_1 \int_{t_1}^{t} dt_2 \cdots \int_{t_{n-1}}^{t} dt_n \sum_{\omega_1,\cdots,\omega_n} \delta_{\omega\omega_n} \times \text{Eq. (7)} \tag{8}$$

where the integration is subject to the condition $t_0 < t_1 < t_2 < \cdots < t_n < t$.

B. Cycle representation

At the macroscopic level, nonequilibrium constraints are imposed to a system if the reservoirs surrounding the system have different temperatures, pressures, or chemical potentials. These constraints are characterized by the global thermodynamic forces or affinities defined by the differences of the temperatures, pressures, or chemical potentials in the reservoirs. The global affinities $\{A_\alpha\}$ are thus independent of the particular states ω or ω'. In this regard, the global affinities are macroscopic. Here below, we show how the cyclic representation of the stochastic process connects in a fundamental way the transition probabilities of the stochastic process to the thermodynamic description.

We now introduce the cycle analysis of the random process [25–27]. A graph G is associated as follows: Each state ω of the system corresponds to a vertex or node while the edges represent the different transitions $\omega \overset{\rho}{\rightleftharpoons} \omega'$ allowed between the states. Accordingly, two states are connected by several edges if several elementary processes ρ allow transitions between them. An example will be detailed in Sec. V.

An orientation is given to each edge of the graph G. The directed edges are thus defined by

$$e \equiv \omega \xrightarrow{\rho} \omega' \,. \tag{9}$$

Let f be a directed subgraph of G. The orientation of the subgraph f with respect to its edges $\{e\}$ is described by introducing the quantity

$$S_e(f) \equiv \begin{cases} +1 & \text{if } e \text{ and } f \text{ are parallel,} \\ -1 & \text{if } e \text{ and } f \text{ are antiparallel,} \\ 0 & \text{if } e \text{ is not in } f, \end{cases} \tag{10}$$

where e and f are said to be parallel (respectively antiparallel) if f contains the edge e in its reference (respectively opposite) orientation.

A graph G usually presents a huge number of cyclic paths c. However, all cyclic paths are not independent. They can be expressed by a linear combination of a smaller subset of cycles, called the *fundamental set*, which plays the role of a basis in the space of cycles. The fundamental set generalizes the concept of mesh currents introduced in the analysis of planar electrical circuits [33]. A method has been provided by Schnakenberg to identify all the independent cycles of a graph [26]. Formally, the method is based on the definition of a *maximal tree* $T(G)$, which is a subgraph of the graph G satisfying the following properties:

- T contains all the vertices of G;
- T is connected;
- T contains no circuit, i.e., no cyclic sequence of edges.

In general a given graph G has several maximal trees.

The edges l of G which do not belong to T are called the *chords* of T. If we add to T one of its chords l, the resulting subgraph $T + l$ contains exactly one circuit, c_l, which is obtained from $T + l$ by removing all the edges which are not part of the circuit. Each chord l thus defines a unique cycle c_l called a *fundamental cycle*. Henceforth, we will use the convention that the orientation is such that $S_l(c_l) = 1$, i.e., the cycles are oriented as the chords l. Note that, for a graph with N vertex and E edges, there exist $E - N + 1$ chords.

We can now formulate many important thermodynamic concepts in terms of cycles. The affinity of a cycle $c = (\omega_1, \ldots, \omega_n)$ is defined as

$$A(c) = \ln \frac{p_{\omega_1\omega_n} \cdots p_{\omega_3\omega_2} p_{\omega_2\omega_1}}{p_{\omega_n\omega_1} p_{\omega_1\omega_2} \cdots p_{\omega_{n-1}\omega_n}} \,. \tag{11}$$

Each cycle can now be decomposed in terms of the fundamental cycles c_l [26]. For instance, the affinity of an arbitrary cycle c can be expressed as

$$A(c) = \sum_l S_l(c) A(c_l) \tag{12}$$

where the sum extends over all the chords. This shows in particular that the affinity of an arbitrary cycle is a linear combination of the affinities of a fundamental set [26]. Accordingly, the maximal tree T can be chosen arbitrarily

because each cycle c_l can be redefined by linear combinations of the fundamental cycles. The fundamental cycles constitute a basis identifying the *independent* contributions to the stochastic process.

These observations led Hill [25] and Schnakenberg [26] to identify the macroscopic nonequilibrium constraints of a system to the affinities of the fundamental cycles c_l of the graph. This identification is verified in a large class of processes including diffusion processes in lattice gases, nonequilibrium chemical reactions, and electronic transport in mesoscopic conductors [17, 18]. These conditions are weaker than in systems with external mechanical forces where the affinities can be directly identified at the level of the transition rates themselves.

We notice that there can still exist more cycles c_l than macroscopic processes α. The reason is that the graph describes all the possible states and transitions at the mesoscopic level while the currents α are typically macroscopic and fewer than the mesoscopic states. The affinities or thermodynamic forces $A(c_l)$ associated with the various cycles c_l of a graph G may thus take the same value for all cycles corresponding to the same current α: $A(c_l) = A_\alpha$ for all $c_l \in \alpha$ [25, 26].

C. Fluctuation theorem for the currents

The observables we are interested in are the independent currents. The instantaneous current on the chord l is defined by

$$j_l(t) \equiv \sum_{n=-\infty}^{+\infty} S_l(e_n)\, \delta(t - t_n) \tag{13}$$

where t_n is the time of the random transition e_n during a path of the stochastic process. We use the convention that j_l is oriented as the graph G since $S_l(e_n)$ is equal to $(-)1$ if the transition e_n is (anti)parallel to the chord l. The current (13) is a fluctuating random variable. We can now regroup the different microscopic currents corresponding to a given macroscopic process α:

$$j_\alpha(t) \equiv \sum_{l\in\alpha} \sum_{n=-\infty}^{+\infty} S_l(e_n)\, \delta(t - t_n)\,. \tag{14}$$

In the next section we shall demonstrate the

Theorem. *For semi-Markov processes satisfying the condition (4), the generating function of the macroscopic currents*

$$\bar{Q}(\boldsymbol{\lambda}) \equiv \lim_{t\to\infty} -\frac{1}{t} \ln \left\langle \mathrm{e}^{-\sum_\alpha \lambda_\alpha \int_0^t dt' j_\alpha(t')} \right\rangle \tag{15}$$

with the average $\langle\cdot\rangle$ taken over all the possible paths weighted by their respective probabilities (7), obeys the symmetry relation

$$\bar{Q}(\boldsymbol{\lambda}) = \bar{Q}(\boldsymbol{A} - \boldsymbol{\lambda}) \tag{16}$$

in terms of the affinities (11).

We notice that this result is known for Markovian processes [19] where it has been shown to imply symmetries for the nonlinear response coefficients at all orders [34]. We point out that the symmetry property (16) involves the ensemble of currents in the system. In Ref. [35], we derived the necessary and sufficient conditions under which a fluctuation theorem will hold for a *single* macroscopic current. These conditions are expressed in terms of geometric and thermodynamic conditions on the graph. In such a situation, a given current j_α satisfies a fluctuation symmetry regardless of the other thermodynamic processes at stake [35].

The generating function is closely related to the properties of large fluctuations. Large-deviation theory indeed shows that, asymptotically,

$$\mathrm{Prob}\left[\boldsymbol{G}(t)/t \simeq \boldsymbol{\xi}\right] \sim \mathrm{e}^{-I(\boldsymbol{\xi})t} \qquad \text{for} \quad t \to \infty\,, \tag{17}$$

where $\boldsymbol{G}(t)$ regroups the Helfand moments

$$G_l(t) \equiv \int_0^t j_l(t')dt' \tag{18}$$

and I is the Legendre transform of $\bar{Q}$. Hence, the fluctuation symmetry (16) is reflected on the rate function $I(\boldsymbol{\xi})$ as follows:

$$\begin{aligned} I(\boldsymbol{\xi}) &= \max_{\boldsymbol{\lambda}}\{\bar{Q}(\boldsymbol{\lambda}) - \boldsymbol{\lambda}\cdot\boldsymbol{\xi}\} \\ &= \max_{\boldsymbol{\lambda}}\{\bar{Q}(\boldsymbol{A}-\boldsymbol{\lambda}) - \boldsymbol{\lambda}\cdot\boldsymbol{\xi}\} \\ &= \max_{\boldsymbol{\lambda}}\{\bar{Q}(\boldsymbol{\lambda}) - (\boldsymbol{A}-\boldsymbol{\lambda})\cdot\boldsymbol{\xi}\} \\ &= I(-\boldsymbol{\xi}) - \boldsymbol{A}\cdot\boldsymbol{\xi} \end{aligned} \tag{19}$$

or, equivalently,

$$\text{Prob}\left[\boldsymbol{G}(t)/t \simeq \boldsymbol{\xi}\right] \simeq \mathrm{e}^{\boldsymbol{A}\cdot\boldsymbol{\xi}t}\ \text{Prob}\left[\boldsymbol{G}(t)/t \simeq -\boldsymbol{\xi}\right] \tag{20}$$

in the limit $t \to \infty$. This relation shows that the probability to observe a fluctuation of the currents in the direction of the affinities is exponentially more likely than the probability to observe the opposite one. This exponential dependence is proportional to time as well as to the affinities driving the systems out of equilibrium.

III. DEMONSTRATION OF THE FLUCTUATION THEOREM

In this section, we shall derive the fluctuation theorem for semi-Markov processes. The generating function can be expressed in terms of the quantities $F_\omega(t) \equiv \langle e^{-\sum_l \lambda_l G_l(t)}\rangle_\omega$, where the system starts in the state ω at the time $t_0 = 0$ and ends in any state after the time t. They can be obtained from

$$F_\omega(t) = \phi_\omega(t) + \sum_{n=1}^{\infty}\int_0^t dt_1 \int_{t_1}^t dt_2 \cdots \int_{t_{n-1}}^t dt_n \sum_{\omega_1\cdots\omega_n} \phi_{\omega_n}(t-t_n)\ \gamma_{\omega_n\omega_{n-1}}(t_n - t_{n-1})\ \cdots\ \gamma_{\omega_2\omega_1}(t_2-t_1)\ \gamma_{\omega_1\omega}(t_1) \tag{21}$$

with

$$\gamma_{\omega'\omega}(t) \equiv \mathrm{e}^{-z_{\omega'\omega}} p_{\omega'\omega}\psi_\omega(t) \tag{22}$$

where the quantities

$$z_{\omega'\omega} \equiv \sum_l S_l(\omega\to\omega')\lambda_l\,, \tag{23}$$

are expressed in terms of the orientation numbers (10) and a sum over all the chords $\{l\}$. These quantities take into account the contributions of the currents to the generating function [19].

To further study the quantities $F_\omega(t)$, we introduce the Laplace transform of the residence time distributions:

$$\tilde{\phi}_\omega(s) \equiv \int_0^\infty dt\ e^{-st}\ \phi_\omega(t) \tag{24}$$

and similarly for the other distributions $\tilde{\psi}_{\omega'\omega}(s)$ and $\tilde{\gamma}_{\omega'\omega}(s)$. These functions can be regrouped in matrix form as

$$\left[\tilde{\boldsymbol{\Phi}}(s)\right]_{\omega'\omega} \equiv \delta_{\omega'\omega}\tilde{\phi}_\omega(s)\,, \tag{25}$$

$$\left[\tilde{\boldsymbol{\Psi}}(s)\right]_{\omega'\omega} \equiv \tilde{\psi}_{\omega'\omega}(s)\,, \tag{26}$$

$$\left[\tilde{\boldsymbol{\Gamma}}(s)\right]_{\omega'\omega} \equiv \tilde{\gamma}_{\omega'\omega}(s)\,. \tag{27}$$

Using Eq. (21), the Laplace transform of the quantity $F_\omega(t)$ is then given by

$$\tilde{F}_\omega(s) = \sum_{\omega'}\left[\tilde{\boldsymbol{\Phi}}(s) + \sum_{n=1}^{\infty}\tilde{\boldsymbol{\Phi}}(s)\cdot\tilde{\boldsymbol{\Gamma}}^n(s)\right]_{\omega'\omega} = \sum_{\omega'}\left[\tilde{\boldsymbol{\Phi}}(s)\cdot\frac{\mathbf{1}}{\mathbf{1}-\tilde{\boldsymbol{\Gamma}}(s)}\right]_{\omega'\omega}. \tag{28}$$

We introduce the matrix

$$\tilde{\boldsymbol{M}}(s) \equiv \mathbf{1} - \tilde{\boldsymbol{\Gamma}}(s)\,, \tag{29}$$

the inverse of which can be written as

$$\tilde{\boldsymbol{M}}(s)^{-1} \equiv \frac{1}{\det \tilde{\boldsymbol{M}}(s)} \tilde{\boldsymbol{Y}}(s) \tag{30}$$

where $\tilde{\boldsymbol{Y}}$ is the transpose of the matrix of cofactors of $\tilde{\boldsymbol{M}}$.

If we want to obtain the long-time exponential behavior as defined in Eq. (15), we must find the largest pole of $\tilde{F}_\omega(s)$. Because of Eq. (28), the different poles are in turn given by the zeros of the determinant $\det \tilde{\boldsymbol{M}}(s) = \det[\mathbf{1} - \tilde{\boldsymbol{\Gamma}}(s)]$. We notice that, in order to obtain a truly stationary process, we should consider the quantities $\tilde{F}_\omega(s)$ averaged over the stationary probabilities $p_\omega^{(\mathrm{st})}$ as well as over the first residence time [28]. This amount to weight differently the terms occurring in $\tilde{\boldsymbol{\Phi}}(s)$ but it does not change the long-time behavior given by the poles of the matrix $\tilde{\boldsymbol{M}}(s)^{-1}$.

To achieve our goal of demonstrating the fluctuation theorem, our strategy will be to construct a special transformation that will change the evolution operator $\tilde{\boldsymbol{M}}$ in a form that satisfies

$$\tilde{\boldsymbol{M}}'_{\boldsymbol{\lambda}} = \tilde{\boldsymbol{M}}'^{\mathrm{T}}_{\boldsymbol{A}-\boldsymbol{\lambda}} \tag{31}$$

where $^{\mathrm{T}}$ denotes the transpose. As a consequence, all the eigenvalues of $\tilde{\boldsymbol{M}}'$ – and thus also of $\tilde{\boldsymbol{M}}$ – will present the symmetry of the fluctuation theorem.

Now, the equations for the eigenvalues Λ of $\tilde{\boldsymbol{M}}$ are given by

$$(1-\Lambda) g_{\omega'} + \sum_{\omega(\neq\omega')} \tilde{\gamma}_{\omega'\omega}(s)\; g_\omega = 0 \tag{32}$$

where g_ω are the components of the corresponding eigenvectors. The linear transformation $g_\omega = g'_\omega u_\omega$ yields

$$(1-\Lambda) g'_{\omega'} + \sum_{\omega(\neq\omega')} \frac{u_\omega}{u_{\omega'}}\; \tilde{\gamma}_{\omega'\omega}(s)\; g'_\omega = 0\,. \tag{33}$$

According to Eq. (29), the new quantities g'_ω are the components of the eigenvectors of the transformed matrix

$$\tilde{M}'_{\omega'\omega} = \tilde{M}_{\omega'\omega} \frac{u_\omega}{u_{\omega'}} \tag{34}$$

or, equivalently,

$$\tilde{\boldsymbol{M}}'_{\boldsymbol{\lambda}} = \boldsymbol{U}^{-1} \cdot \tilde{\boldsymbol{M}}_{\boldsymbol{\lambda}} \cdot \boldsymbol{U} \tag{35}$$

with

$$U_{\omega'\omega} = \delta_{\omega'\omega} u_\omega\,. \tag{36}$$

We now proceed to determine the elements u_ω. For all the transitions $\omega \to \omega'$ which do not correspond to a chord [so that $z_{\omega'\omega} = 0$ in Eq. (22)], we impose that the ratios $u_\omega/u_{\omega'}$ satisfy

$$\frac{u_\omega}{u_{\omega'}} p_{\omega'\omega} \tilde{\psi}_\omega = p_{\omega\omega'} \tilde{\psi}_{\omega'} \frac{u_{\omega'}}{u_\omega} \tag{37}$$

or

$$\frac{u_\omega}{u_{\omega'}} = \left(\frac{p_{\omega\omega'} \tilde{\psi}_{\omega'}}{p_{\omega'\omega} \tilde{\psi}_\omega} \right)^{\frac{1}{2}}\,. \tag{38}$$

This implies that the elements of $\tilde{M}'_{\omega'\omega}$ now take the values

$$\tilde{M}'_{\omega'\omega}(s) = \delta_{\omega'\omega} - \sqrt{p_{\omega'\omega} \tilde{\psi}_\omega p_{\omega\omega'} \tilde{\psi}_{\omega'}} = \tilde{M}'_{\omega\omega'}(s)\,, \tag{39}$$

if the transition $\omega' \to \omega$ is not a chord and $z_{\omega'\omega} = 0$. These elements of $\tilde{\boldsymbol{M}}'$ are now symmetric.

At this point, we have fixed the value of $N-1$ ratios of the form (37). Indeed, if there are E edges in the graph and N states, there exist $E-N+1$ chords in the graph so that we have fixed $E-(E-N+1) = N-1$ ratios. This

is precisely the number of independent variables we can specify. The remaining elements of $\tilde{\boldsymbol{M}}'$ corresponding to the chords are now obtained as follows. For a fundamental cycle $c_l = (\omega_1, \cdots, \omega_l)$, we have the identity

$$\prod_{i=1}^{l} \frac{u_{\omega_i}}{u_{\omega_{i+1}}} = \frac{u_{\omega_l}}{u_{\omega_1}} \prod_{i=1}^{l-1} \frac{u_{\omega_i}}{u_{\omega_{i+1}}} = 1 \tag{40}$$

where $\omega_{l+1} \equiv \omega_1$ and the transition $\omega_l \to \omega_1$ corresponds to the chord l in the positive direction. By construction, a fundamental cycle c_l only contains its associated chord l. Hence, using Eq. (38) as well as Eq. (11), Eq. (40) becomes

$$\frac{u_{\omega_1}}{u_{\omega_l}} = \left(\frac{p_{\omega_1\omega_l}\tilde{\psi}_{\omega_l}}{p_{\omega_l\omega_1}\tilde{\psi}_{\omega_1}}\right)^{\frac{1}{2}} \prod_{i=1}^{l} \left(\frac{p_{\omega_i\omega_{i+1}}}{p_{\omega_{i+1}\omega_i}}\right)^{\frac{1}{2}} = \left(\frac{p_{\omega_1\omega_l}\tilde{\psi}_{\omega_l}}{p_{\omega_l\omega_1}\tilde{\psi}_{\omega_1}}\right)^{\frac{1}{2}} \mathrm{e}^{-A_l/2} \,. \tag{41}$$

Consequently, we have

$$\tilde{M}'_{\omega_1\omega_l}(s,\lambda_l) = \delta_{\omega_1\omega_l} - \sqrt{p_{\omega_l\omega_1}\tilde{\psi}_{\omega_1} p_{\omega_1\omega_l}\tilde{\psi}_{\omega_l}}\; e^{A_l/2-\lambda_l} = \tilde{M}'_{\omega_l\omega_1}(s, A_l - \lambda_l) \,. \tag{42}$$

Therefore, the operator $\tilde{\boldsymbol{M}}'$ now satisfies

$$\tilde{\boldsymbol{M}}'_{\boldsymbol{\lambda}} = \tilde{\boldsymbol{M}}'^{\mathrm{T}}_{\boldsymbol{A}-\boldsymbol{\lambda}} \,, \tag{43}$$

which implies that all its eigenvalues have the symmetry

$$\lambda_l \to A_l - \lambda_l \,. \tag{44}$$

Therefore, the symmetry holds for the leading zero, $\det \boldsymbol{M}(s_0) = \det \boldsymbol{M}'(s_0) = 0$, yielding the generating function of the currents (13)

$$s_0 = -Q(\boldsymbol{\lambda}) = -Q(\boldsymbol{A} - \boldsymbol{\lambda}) \,. \tag{45}$$

The fluctuation theorem for the currents is thus related to the fundamental symmetry (43) of the evolution operator. It is also remarkable that this relation is valid arbitrarily far from equilibrium. Moreover, in its new form, the evolution operator is symmetric except for the matrix elements corresponding to the chords so that it will be much more stable when studying it numerically.

According to Eq. (14), we can now regroup the different microscopic currents corresponding to a given macroscopic process α. On the other hand, we may set $\lambda_l = \lambda_\alpha$ for all $l \in \alpha$ and define $\bar{Q}(\{\lambda_\alpha\}) \equiv Q(\{\lambda_l = \lambda_\alpha\})$. Since all the fundamental cycles contributing to a given transport process α have the same affinities, we have demonstrated the theorem in the case there is at most one edge between two states.

Furthermore, one can check that this construction can be extended to the case where there exist several edges ρ between two states so that we have

$$\psi^{(\rho)}_{\omega'\omega}(t) \equiv p^{(\rho)}_{\omega'\omega}\psi_\omega(t) \,. \tag{46}$$

The symmetry (44) is thus valid even in the more complicated case where there are several possible transitions between two states so that the corresponding characteristic equation also presents the symmetry (44). Accordingly, the fluctuation theorem (16) is proved for general semi-Markov processes in finite state space. For infinite state space, the distribution of fluctuations (20) may present long tails leading to a generalized fluctuation relation [36–38].

IV. MARKOVIAN CASE

In this section, we present the case of Markovian processes ruled by the master equation

$$\frac{d}{dt}P_\omega(t) = \sum_{\omega'} \left[W_{\omega\omega'}P_{\omega'}(t) - W_{\omega'\omega}P_\omega(t)\right] \,, \tag{47}$$

where $W_{\omega'\omega}$ is the time-independent rate of the transition $\omega \to \omega'$. Here, we consider for simplicity a process with at most one edge between two states, as it is the case in rotary molecular motors [39] and for the transfer of energy

and particles in the effusion of an ideal gas [40]. The present considerations can be extended to the general case of a process with several edges between two states [19].

The Markovian process is a particular case of semi-Markov process where the survival probabilities $\phi_\omega(\tau)$ are the following exponential functions of time:

$$\psi_\omega(\tau) = \Big(\sum_{\omega'} W_{\omega'\omega}\Big) \exp\Big(-\tau \sum_{\omega'} W_{\omega'\omega}\Big)\,, \tag{48}$$

while the transition probabilities are given by

$$p_{\omega'\omega} = \frac{W_{\omega'\omega}}{\sum_{\omega'} W_{\omega'\omega}}\,. \tag{49}$$

As in the previous section, we consider the averages $F_\omega(t) \equiv \langle e^{-\sum_l \lambda_l G_l(t)}\rangle_\omega$ which here obey the following differential equations [19]:

$$\frac{d}{dt}F_\omega(t) = [\boldsymbol{L}_{\boldsymbol{\lambda}} \cdot \mathbf{F}(t)]_\omega \equiv \sum_{\omega'} \left[W_{\omega'\omega} \mathrm{e}^{-z_{\omega'\omega}} F_{\omega'}(t) - W_{\omega\omega'} F_\omega(t)\right] \tag{50}$$

where z are given by Eq. (23). Using a similar construction as in the previous section, the evolution operator can be recast by a linear transformation $\boldsymbol{V}$ into the form $\boldsymbol{L}'_{\boldsymbol{\lambda}} = \boldsymbol{V}^{-1} \cdot \boldsymbol{L}_{\boldsymbol{\lambda}} \cdot \boldsymbol{V}$, which now satisfies the symmetry:

$$\boldsymbol{L}'_{\boldsymbol{\lambda}} = \boldsymbol{L}'^{\mathrm{T}}_{\boldsymbol{A}-\boldsymbol{\lambda}}\,. \tag{51}$$

Note that, in this case, there is no need to perform a Laplace transform. Since the leading eigenvalue of this operator gives the generating function of the currents, we recover the fluctuation theorem as the consequence of the fundamental symmetry (51) of the Markovian evolution operator [14, 15, 19].

V. EXAMPLE: ION CURRENT THROUGH A MEMBRANE

In this section, we derive the generating function of the currents for a simple example of non-Markovian system in order to illustrate the symmetry of the fluctuation theorem for currents. The system we consider is a two-state model where the residence time distributions are Gamma distributions:

$$\psi_i(t) = \frac{k_i}{\Gamma(a_i)} (k_i t)^{a_i - 1} \mathrm{e}^{-k_i t}\,, \qquad \text{with} \quad i = 1, 2\,, \tag{52}$$

where $\Gamma(z)$ is the Gamma function and where $a_i \in\,]0, \infty]$. The Markovian case is recovered when $a_i = 1$. In order to drive the system out of equilibrium, we consider the case where there exist two possible transitions between the states:

$$\psi_{21}^{(\rho)}(t) = p_{21}^{(\rho)} \psi_1(t), \quad \psi_{12}^{(\rho)}(t) = p_{12}^{(\rho)} \psi_2(t)\,, \tag{53}$$

with $\rho = \mathrm{L}, \mathrm{R}$ and

$$\sum_\rho p_{21}^{(\rho)} = \sum_\rho p_{12}^{(\rho)} = 1\,. \tag{54}$$

Accordingly, the affinity is given by

$$A \equiv \ln \frac{p_{21}^{(\mathrm{L})} p_{12}^{(\mathrm{R})}}{p_{21}^{(\mathrm{R})} p_{12}^{(\mathrm{L})}} = \ln \frac{p_{21}^{(\mathrm{L})}(1 - p_{12}^{(\mathrm{L})})}{p_{12}^{(\mathrm{L})}(1 - p_{21}^{(\mathrm{L})})}\,. \tag{55}$$

This system can model for example the transport of ion current through a membrane [6]. Such systems are known to present memory effects [41]. Here, we consider the case where the electrostatic interactions are strong enough to prevent more than one ion in the membrane channel. The state 1 represents the situation where the channel is empty while the state 2 corresponds to one ion in the channel. Ions can enter or exit the channel either from the left (transitions of type L) or from the right (transitions of type R). The cumulated current will thus be given by the

number of ions entering the channel minus the number of ions exiting the channel. In the following, we choose to measure the current in the left-hand side of the channel and with positive orientation, that is

$$j(t) = \sum_n \delta(t - t_n)\epsilon_n \tag{56}$$

with $\epsilon_n = +1$ if the transition $p_{21}^{(\mathrm{L})}$ occurs at time t_n, $\epsilon_n = -1$ if the transition $p_{12}^{(\mathrm{L})}$ occurs, and $\epsilon_n = 0$ otherwise.

The generating function of the current

$$Q(\lambda) = \lim_{t\to\infty} -\frac{1}{t}\ln\langle e^{-\lambda G(t)}\rangle, \tag{57}$$

where $G(t) = \int_0^t j(t')dt'$, is obtained by calculating the largest pole of the matrix $\tilde{\boldsymbol{M}}(s)$. With the residence time distributions (52), we have

$$\tilde{\psi}_i(s) = \frac{1}{\left(1 + \frac{s}{k_i}\right)^{a_i}} \qquad \text{for} \quad i = 1, 2\,, \tag{58}$$

and

$$\tilde{\gamma}_{21}(s) \;=\; \left(p_{21}^{(\mathrm{L})}\mathrm{e}^{-\lambda} + p_{21}^{(\mathrm{R})}\right)\tilde{\psi}_1(s)\,, \tag{59}$$

$$\tilde{\gamma}_{12}(s) \;=\; \left(p_{12}^{(\mathrm{L})}\mathrm{e}^{+\lambda} + p_{12}^{(\mathrm{R})}\right)\tilde{\psi}_2(s)\,. \tag{60}$$

The determinant of $\tilde{\boldsymbol{M}}(s)$ is given by

$$\det\tilde{\boldsymbol{M}}(s) = 1 - \tilde{\gamma}_{21}(s)\tilde{\gamma}_{12}(s)\,, \tag{61}$$

which is zero when

$$\left(1 + \frac{s}{k_1}\right)^{a_1}\left(1 + \frac{s}{k_2}\right)^{a_2} = \left(p_{21}^{(\mathrm{L})}\mathrm{e}^{-\lambda} + p_{21}^{(\mathrm{R})}\right)\left(p_{12}^{(\mathrm{L})}\mathrm{e}^{+\lambda} + p_{12}^{(\mathrm{R})}\right) \equiv f(\lambda)\,. \tag{62}$$

Since the right-hand side has the symmetry $f(\lambda) = f(A - \lambda)$, this symmetry holds for the zeros, $s_0 = -Q(\lambda) = -Q(A - \lambda)$, hence the generating function obeys the fluctuation theorem. The leading zero of Eq. (62) can be computed using the Newton-Raphson method. Figure 1 depicts the generating function of the single current for different values of the parameters of the model. We see that the symmetry of the fluctuation theorem is verified in all the cases. The case where $a_1 = k_1 = a_2 = k_2 = 1$ is Markovian with exponential residence time distributions. The two other cases are genuinely non-Markovian albeit the fluctuation theorem is still verified.

Analytic solutions of Eq. (62) can be obtained in some limiting cases. The generating function takes the analytic forms:

$$Q(\lambda) \;=\; k_2\left[1 - f(\lambda)^{\frac{1}{a_2}}\right] \qquad \text{if} \quad a_1 \to 0 \quad \text{or} \quad k_1 \to \infty\,, \tag{63}$$

$$Q(\lambda) \;=\; k_1\left[1 - f(\lambda)^{\frac{1}{a_1}}\right] \qquad \text{if} \quad a_2 \to 0 \quad \text{or} \quad k_2 \to \infty\,, \tag{64}$$

$$Q(\lambda) \;=\; k\left[1 - f(\lambda)^{\frac{1}{a_1+a_2}}\right] \qquad \text{if} \quad k_1 = k_2 = k\,, \tag{65}$$

where, again, the fluctuation theorem

$$Q(\lambda) = Q(A - \lambda) \tag{66}$$

is the consequence of the symmetry $f(\lambda) = f(A - \lambda)$ of the function defined in the left-hand side of Eq. (62).

Differentiating Eq. (62) with respect to λ, one can obtain all the cumulants of the probability distribution of the currents and, in particular, the mean current:

$$J = \lim_{t\to\infty}\frac{1}{t}\langle G(t)\rangle = \frac{dQ}{d\lambda}\Big|_{\lambda=0} = \frac{p_{21}^{(\mathrm{L})} - p_{12}^{(\mathrm{L})}}{\frac{a_1}{k_1} + \frac{a_2}{k_2}} \tag{67}$$

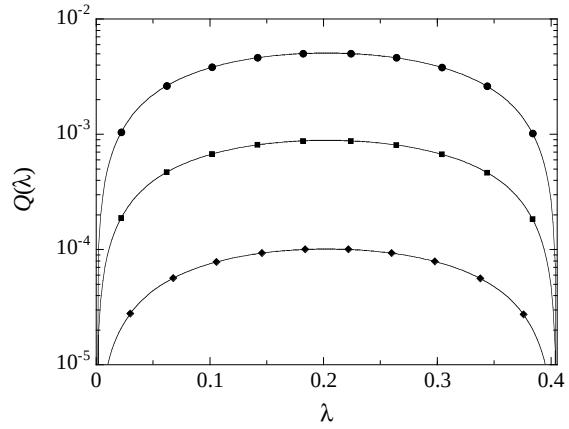

FIG. 1: Generating function of the current $Q(\lambda)$ versus λ for different values of the parameters: $a_1 = k_1 = a_2 = k_2 = 1$ (circles); $a_1 = 0.1$, $k_1 = 0.01$, $a_2 = k_2 = 1$ (squares); $a_1 = 1$, $k_1 = 0.01$, $a_2 = 0.1$, $k_2 = 1$ (diamonds). The transition probabilities are $p_{21}^{(\mathrm{L})} = 0.6$, $p_{12}^{(\mathrm{R})} = 0.4$, and $p_{21}^{(\mathrm{R})} = p_{12}^{(\mathrm{L})} = 0.5$. The affinity takes the value $A = \ln(3/2) \simeq 0.405$. The symmetry of the generating function under the transformation $\lambda \to A - \lambda$ is verified in all the cases.

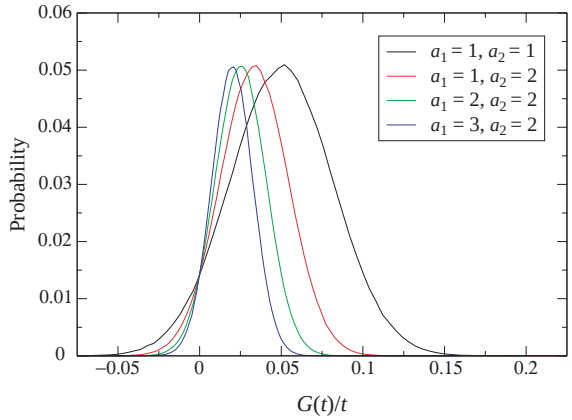

FIG. 2: Probability distribution of $G(t)/t$ for different values of the exponents a_1 and a_2 of the residence time distributions. The transition probabilities are $p_{21}^{(\mathrm{L})} = 0.6$, $p_{12}^{(\mathrm{R})} = 0.4$, and $p_{21}^{(\mathrm{R})} = p_{12}^{(\mathrm{L})} = 0.5$. The affinity takes the value $A = \ln(3/2) \simeq 0.405$.

and the coefficient of diffusivity:

$$D = \lim_{t\to\infty} \frac{1}{2t} \langle [G(t) - \langle G(t)\rangle]^2 \rangle = -\frac{1}{2} \frac{d^2 Q}{d\lambda^2}\Big|_{\lambda=0} = \frac{p_{21}^{(\mathrm{L})} p_{21}^{(\mathrm{R})} + p_{12}^{(\mathrm{L})} p_{12}^{(\mathrm{R})}}{2\left(\frac{a_1}{k_1} + \frac{a_2}{k_2}\right)} + \frac{\frac{a_1}{k_1^2} + \frac{a_2}{k_2^2}}{2\left(\frac{a_1}{k_1} + \frac{a_2}{k_2}\right)^3} \left(p_{21}^{(\mathrm{L})} - p_{12}^{(\mathrm{L})}\right)^2 . \tag{68}$$

Further differentiations would lead to cumulants of higher orders.

The analytical result (65) in the case $k_1 = k_2 = k$ can be checked in numerical simulations. For this purpose, we performed numerical simulations as follows. At each time step, the system waits a random time distributed according to the distribution (52) with parameter a_i determined by the current state of the system ($i = 1, 2$). A random number is then generated to determine whether the transition to the state $j = (i \mod 2) + 1$ occurs from the left (probability $p_{ji}^{(\mathrm{L})}$) or right (probability $p_{ji}^{(\mathrm{R})}$) reservoir.

The probability distributions of the integrated current, $\mathrm{Prob}[G(t)/t = \xi]$, are then obtained by direct sampling (Figs. 2 and 3). The generating functions (Fig. 4) are obtained from $Q(\lambda) = -(1/t) \ln \left[\sum_\xi \mathrm{Prob}(\xi) \mathrm{e}^{-\lambda\xi}\right]$.

In Fig. 2, the current probability distribution function is plotted for different values of the exponents a_1 and a_2. The mean and the variance of the distribution can be seen to be equal to the results (67) and (68). To show that indeed the symmetry (16) of the fluctuation theorem is satisfied, we plot in Fig. 3 the negative part of the distribution in comparison with the prediction of the fluctuation theorem

$$\mathrm{Prob}\left[G(t)/t \simeq -\xi\right] \simeq \mathrm{e}^{-A\xi t}\, \mathrm{Prob}\left[G(t)/t \simeq \xi\right] . \tag{69}$$

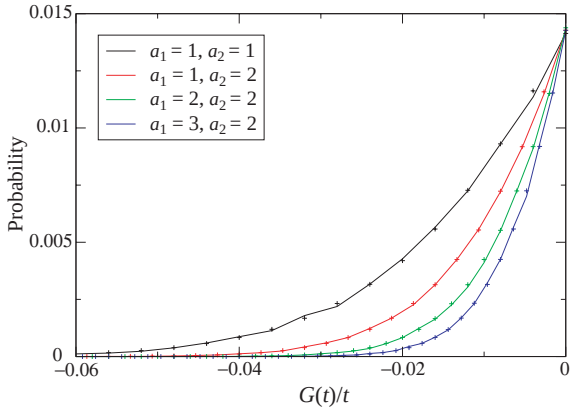

FIG. 3: Negative part of the probability distribution of $G(t)/t$ for different values of the exponents a_1 and a_2 of the residence time distributions. Comparison is made with the prediction (69) of the fluctuation theorem (crosses). The transition probabilities are $p_{21}^{(\mathrm{L})} = 0.6$, $p_{12}^{(\mathrm{R})} = 0.4$, and $p_{21}^{(\mathrm{R})} = p_{12}^{(\mathrm{L})} = 0.5$. The affinity takes the value $A = \ln(3/2) \simeq 0.405$.

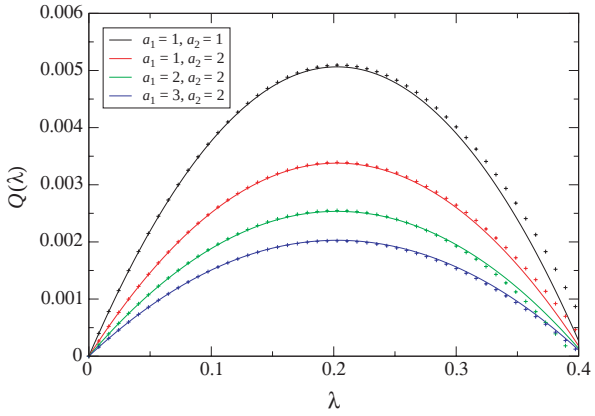

FIG. 4: Comparison between the numerical generating function (crosses) and the exact result (65) for different values of the exponents a_1 and a_2 of the residence time distributions. The transition probabilities are $p_{21}^{(\mathrm{L})} = 0.6$, $p_{12}^{(\mathrm{R})} = 0.4$, and $p_{21}^{(\mathrm{R})} = p_{12}^{(\mathrm{L})} = 0.5$. The affinity takes the value $A = \ln(3/2) \simeq 0.405$.

The agreement is excellent. One can also calculate the generating function of the distribution and compare it with the exact result (65). As seen in Fig. 4, we get a very good agreement except at values of λ close to the affinity where the generating function requires exponential statistics. The symmetry of the fluctuation theorem is thus well satisfied.

VI. CONCLUSIONS

In this paper, we have proved the fluctuation theorem for currents in semi-Markov processes satisfying the condition of direction-time independence. This condition guarantees a consistent construction of the stationary realizations of the process [28] as well as its time reversibility at equilibrium if detailed balance is satisfied by the embedded Markov chain [5]. The thermodynamic affinities as well as the corresponding fluctuating currents are defined using graph theory and the cyclic representation of the process [25–27].

The fluctuation theorem is derived by demonstrating a symmetry property for the evolution operator of the process. This evolution operator is obtained in renewal theory by taking the Laplace transform of time-dependent averages defining the large-deviation functions. The symmetry of the evolution operator is shared by its eigenvalues including the leading one which gives the generating function of the currents. In this way, the fluctuation theorem is proved for the independent currents driven by the different thermodynamic affinities applied to the system. Moreover, we show that the demonstration reduces in the Markovian case to proving the symmetry property for the evolution operator associated with the modified master equation. In this way, the fluctuation theorem for the currents is shown to find

its origins in a fundamental symmetry property of the evolution operator.

Furthermore, we have applied the results to a semi-Markov process describing ion currents through a membrane, showing that the fluctuation theorem is satisfied in this non-Markovian process as well.

The demonstration of the fluctuation theorem for currents in semi-Markov processes with direction-time independence also proves that the Onsager reciprocity relations as well as their extensions to the nonlinear response coefficients hold in these semi-Markov processes. Indeed, these further results are the direct consequences of the fluctuation theorem for currents, as we have proved elsewhere [17, 34].

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