# Fluctuation theorem for currents in open quantum systems

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A quantum-mechanical framework is set up to describe the full counting statistics of particles flowing between reservoirs in an open system under time-dependent driving. A symmetry relation is obtained which is the consequence of microreversibility for the probability of the nonequilibrium work and the transfer of particles and energy between the reservoirs. In some appropriate long-time limit, the symmetry relation leads to a steady-state quantum fluctuation theorem for the currents between the reservoirs. On this basis, relationships are deduced which extend the Onsager-Casimir reciprocity relations to the nonlinear response coefficients.

## I. INTRODUCTION

Quantum systems can be driven out of equilibrium by time-dependent perturbations, by interaction with reservoirs at different chemical potentials or temperatures, or by combining both. In the latter cases, the quantum system is open and currents of energy and particles are flowing across the system. Such processes take place in mesoscopic electronic conductors as well as in chemical reactions. These nonequilibrium processes can be characterized by the relations linking their currents to the differences of chemical potentials. These relations may be linear in the case of Ohm's law, but are typically nonlinear, which defines the nonlinear response coefficients.

Alternatively, the full counting statistics of the particles transferred between the reservoirs can be considered. This statistics aims to characterize the transfers of particles in terms of the functions generating all the statistical moments of the fluctuating numbers of particles. The knowledge of this generating function gives access not only to the conductance and the noise power but also to higher-order moments and thus to the properties of nonlinear response. The full counting statistics has attracted considerable theoretical interest and is also envisaged in experimental measurements [1–3]. After the pioneering work of Ref. [4], several methods have been developed in order to obtain the full counting statistics in mesoscopic conductors. One of them is based on Keldysh Green's function formalism, in which an expression for the generating function has been obtained within a semiclassical approximation [5–9]. The full counting statistics can also be obtained on the basis of quantum Markovian master equations describing the fluctuations of the currents [10], as well as in terms of stochastic path integrals [11]. The generating function obtained in the approaches using the semiclassical approximation or the Markovian master equation has been shown to obey a symmetry relation as the consequence of time reversibility [12]. In nonequilibrium statistical mechanics, this relation is known as the fluctuation theorem which has been established for several classes of systems. These latter are either time-independent deterministic [13–15] or stochastic systems sustaining nonequilibrium steady states [16–23], or time-dependent Hamiltonian or stochastic systems, in which case the fluctuation theorem is closely related to Jarzynski nonequilibrium work theorem [24–27]. Similar symmetry relations have been considered for continuous-time random walks [28]. Quantum versions of the fluctuation theorem and Jarzynski nonequilibrium work theorem have also been obtained [29–47]. Moreover, a further relationship has recently been proved for time-dependent quantum Hamiltonian systems [48], allowing the derivation of Green-Kubo formulas and Onsager-Casimir reciprocity relations for the linear

response coefficients [49–52].

An open question is to bridge the gap separating the time-dependent situations from the nonequilibrium steady states which are expected to be reached in the long-time limit. The problem is to deal with nonequilibrium steady states without relying on the semiclassical or Markovian approximations, or on the neglect of the energy or particle content of the subsystem coupling the reservoirs.

In the present paper, our purpose is to prove the fluctuation theorem for the currents in open systems obeying Hamiltonian quantum dynamics and sustaining nonequilibrium steady states in the long-time limit. We start by considering a time-dependent quantum system in contact with energy and particle reservoirs at different temperatures and chemical potentials. The amounts of energy and particles which are exchanged between the initial and final times are determined by quantum measurements. This framework is similar to the one considered by Kurchan to obtain a fluctuation theorem for quantum systems [29]. Here, this framework is extended by taking the initial states as grand-canonical instead of canonical equilibrium states, which allows us to deal with transfers of particles between the reservoirs. In this way, we obtain an exact relationship which is the consequence of microreversibility for the probability of a certain exchange of energy and particles between the reservoirs during the time-dependent external drive. An equivalent symmetry relation is obtained for the generating function of all the fluctuating variables. However, these symmetry relations are expressed in terms of the temperatures and chemical potentials of the reservoirs. The problem is that we need a symmetry relation in terms of the *differences* of temperatures and chemical potentials, which define the thermodynamic forces (also called the affinities) driving the currents across the system. The importance of this point has recently been discussed in the review [42].

The central contribution of the present paper is the proof that, in the long-time limit, the aforementioned generating function only depends on the *differences* between the parameters of the reservoirs. This proof is carried out by obtaining lower and upper bounds on the generating function in terms of a new generating function which only depends on the *differences* of parameters and further functions which are bounded in the long-time limit. Combining this fundamental result with the previously established symmetry relation of the generating function, the fluctuation theorem is proved for nonequilibrium steady states in open quantum systems. Thanks to this quantum fluctuation theorem, the Onsager-Casimir reciprocity relations and their generalizations to the nonlinear response coefficients can be inferred [21, 53].

The plan of the paper is the following. The protocols for the forward and reversed drives of the open system are introduced in Sec. II. The symmetry relations for the probability and the generating function are proved in Sec. III. In Sec. IV, we obtain the quantum fluctuation theorem for the currents in the steady state reached in the long-time limit. In Sec. V, the consequences of the fluctuation theorem on the linear and nonlinear response coefficients are deduced. The conclusions are drawn in Sec. VI.

## II.   OPEN QUANTUM SYSTEM AND TIME-DEPENDENT PROTOCOLS

### A.   The total Hamiltonian

We consider a total quantum system composed of a subsystem in contact with several reservoirs of energy and particles. Initially, the reservoirs are decoupled from each other. During a time interval $\mathcal{T}$, the reservoirs are put in contact with each other through the subsystem by some time-dependent interaction which has the effect of changing the energy and the particle numbers in each reservoir. The total Hamiltonian of the system is thus given by

$$H(t; B) = \mathcal{H}_{\mathrm{s}} + \sum_{j=1}^{r} \mathcal{H}_j + \mathcal{V}(t) \qquad \text{for} \quad 0 < t < \mathcal{T} \tag{1}$$

where $\mathcal{H}_{\mathrm{s}}$ denotes the Hamiltonian of the isolated subsystem, $\mathcal{H}_j$ the Hamiltonian of the $j^{\mathrm{th}}$ isolated reservoir before the interaction is switched on, and $\mathcal{V}(t)$ the time-dependent interaction to which the total system is submitted during the time interval $0 \leq t \leq \mathcal{T}$. The interaction is supposed to vanish before the initial time $t = 0$ so that $\mathcal{V}(t) = 0$ for $t < 0$. Beyond the final time $t = \mathcal{T}$, the subsystems are decoupled into the Hamiltonians $\tilde{\mathcal{H}}_{\mathrm{s}}$ and $\tilde{\mathcal{H}}_j$ whereupon the total Hamiltonian becomes

$$H(t; B) = \tilde{\mathcal{H}}_{\mathrm{s}} + \sum_{j=1}^{r} \tilde{\mathcal{H}}_j \qquad \text{for} \quad \mathcal{T} \leq t . \tag{2}$$

Furthermore, we suppose that the whole system is placed in a magnetic field $B$.

The observables of the total system include not only the Hamiltonian operators but also the numbers of particles of species $\alpha = 1, 2, ..., c$ inside the subsystem $\mathcal{N}_{\mathrm{s}\alpha}$ and the reservoirs $\mathcal{N}_{j\alpha}$ with $j = 1, 2, ..., r$. The total number of

particles of species $\alpha$ is thus given by

$$N_\alpha = \mathcal{N}_{\mathrm{s}\alpha} + \sum_{j=1}^{r} \mathcal{N}_{j\alpha} \,. \tag{3}$$

We suppose that the total Hamiltonian operator has the symmetry

$$\Theta H(t; B)\Theta = H(t; -B) \tag{4}$$

under the time-reversal operator $\Theta$. This latter is an antilinear operator such that $\Theta^2 = I$ and which has the effect of changing the sign of all odd parameters such as magnetic fields. Equation (4) expresses the microreversibility in an external magnetic field. The numbers of particles are symmetric under time reversal:

$$\Theta \mathcal{N}_{j\alpha} \Theta = \mathcal{N}_{j\alpha} \,, \tag{5}$$

for $j = \mathrm{s}, 1, 2, ..., r$.

Since the numbers of particles of species $\alpha$ are conserved within each isolated subsystem before and after their coupling, we have that

$$[\mathcal{H}_j, \mathcal{N}_{j'\alpha}] = 0 \qquad \text{and} \qquad \left[\tilde{\mathcal{H}}_j, \mathcal{N}_{j'\alpha}\right] = 0 \,, \tag{6}$$

for all $j, j' = \mathrm{s}, 1, 2, ..., r$ and $\alpha = 1, 2, ..., c$.

For our purposes, we are going to introduce a temperature and a chemical potential associated with each reservoir. Such quantities can be introduced as characterizing the statistical distribution of initial conditions and, as such, can be applied not only to the reservoirs but also to the subsystem. However, in a nonequilibrium system with currents flowing between reservoirs, the thermodynamic forces or affinities are determined by the differences of temperature and chemical potentials between the reservoirs, in which case the initial temperature and chemical potentials of the subsystem are not relevant. In this regard, we can simplify the formulation of the problem by regrouping the subsystem with one of the reservoirs, for instance the first one, and redefine the Hamiltonian and particle-number operators as follows:

$$
\begin{array}{llll}
H_1 = \mathcal{H}_{\mathrm{s}} + \mathcal{H}_1 \,, & \tilde{H}_1 = \tilde{\mathcal{H}}_{\mathrm{s}} + \tilde{\mathcal{H}}_1 \,, & N_{1\alpha} = \mathcal{N}_{\mathrm{s}\alpha} + \mathcal{N}_{1\alpha} \,, & \text{for} \quad j = 1\,; \\
H_j = \mathcal{H}_j \,, & \tilde{H}_j = \tilde{\mathcal{H}}_j \,, & N_{j\alpha} = \mathcal{N}_{j\alpha} \,, & \text{for} \quad j = 2, ..., r\,; \quad \text{and} \quad (7) \\
V(t) = \mathcal{V}(t) \,. & & &
\end{array}
$$

In this case, the total Hamiltonian given by Eqs. (1) and (2) can be rewritten as

$$H(t; B) = \begin{cases} \sum_{j=1}^{r} H_j & \text{for} \quad t \leq 0 \,, \\ \sum_{j=1}^{r} H_j + V(t) & \text{for} \quad 0 < t < \mathcal{T} \,, \\ \sum_{j=1}^{r} \tilde{H}_j & \text{for} \quad \mathcal{T} \leq t \,, \end{cases} \tag{8}$$

and the total number of particles of species $\alpha = 1, 2, ..., c$ as

$$N_\alpha = \sum_{j=1}^{r} N_{j\alpha} \,. \tag{9}$$

An alternative formulation would be to consider that the subsystem Hamiltonian is included in the interaction potential, in which case $H_j = \mathcal{H}_j$ and $V(t) = \mathcal{H}_{\mathrm{s}} + \mathcal{V}(t)$ in Eq. (8), while $N_{j\alpha} = \mathcal{N}_{j\alpha}$ in Eq. (9).

We notice that, in the further case where the subsystem is considered on equal footing with the reservoirs, the sums should be extended to $j = \mathrm{s}, 1, 2, ..., r$ in Eqs. (8) and (9).

In the following, we define protocols with two quantum measurements before and after a unitary time evolution (see Ref. [42] for a review).

### B. The forward protocol

The forward time evolution is defined as

$$i\hbar \frac{\partial}{\partial t} U_{\mathrm{F}}(t; B) = H(t; B) U_{\mathrm{F}}(t; B) \,, \tag{10}$$

with the initial condition $U_{\mathrm{F}}(0; B) = I$. In the Heisenberg representation, the observables evolve according to

$$A_{\mathrm{F}}(t) = U_{\mathrm{F}}^{\dagger}(t; B) \, A \, U_{\mathrm{F}}(t; B) \,, \tag{11}$$

which also concerns the time-dependent Hamiltonian

$$H_{\mathrm{F}}(t) = U_{\mathrm{F}}^{\dagger}(t; B) H(t; B) U_{\mathrm{F}}(t; B) \,. \tag{12}$$

The average of an observable is thus obtained from

$$\langle A_{\mathrm{F}}(t) \rangle = \mathrm{tr} \rho(0; B) A_{\mathrm{F}}(t) \,. \tag{13}$$

We note that the dependence on the magnetic field is implicit in these expressions.

The initial state of the system is taken as the following grand-canonical equilibrium state of the decoupled subsystems at the different inverse temperatures $\beta_j = 1/(k_{\mathrm{B}} T_j)$ and chemical potentials $\mu_{j\alpha}$:

$$\rho(0; B) = \prod_j \frac{\mathrm{e}^{-\beta_j (H_j - \sum_\alpha \mu_{j\alpha} N_{j\alpha})}}{\Xi_j(B)} = \prod_j \mathrm{e}^{-\beta_j \left[ H_j - \sum_\alpha \mu_{j\alpha} N_{j\alpha} - \Phi_j(B) \right]} \,, \tag{14}$$

where $\Phi_j(B) = -k_{\mathrm{B}} T_j \ln \Xi_j(B)$ denotes the thermodynamic grand-potential of the $j^{\mathrm{th}}$ subsystem in the initial equilibrium state.

An *initial quantum measurement* is performed which prepares the system in the eigenstate $|\Psi_k\rangle$ of the subsystem operators of energy and particle numbers:

$$t \leq 0 : \qquad H_j |\Psi_k\rangle = \epsilon_{jk} |\Psi_k\rangle \,, \tag{15}$$
$$N_{j\alpha} |\Psi_k\rangle = \nu_{j\alpha k} |\Psi_k\rangle \,. \tag{16}$$

After the time interval $0 < t < \mathcal{T}$, a *final quantum measurement* is performed in which the system is observed in the eigenstate $|\tilde{\Psi}_l\rangle$ of the subsystem operators of energy and particle numbers:

$$\mathcal{T} \leq t : \qquad \tilde{H}_j |\tilde{\Psi}_l\rangle = \tilde{\epsilon}_{jl} |\tilde{\Psi}_l\rangle \,, \tag{17}$$
$$N_{j\alpha} |\tilde{\Psi}_l\rangle = \tilde{\nu}_{j\alpha l} |\tilde{\Psi}_l\rangle \,. \tag{18}$$

We notice that semi-infinite time intervals are available to perform the initial and final quantum measurements of well-defined eigenvalues. Accordingly, this scheme based on two quantum measurements provides a way to measure the energies and the numbers of particles exchanged between the reservoirs during the time interval $0 < t < \mathcal{T}$ of their mutual interaction. Indeed, the energy in the $j^{\mathrm{th}}$ subsystem is observed to change by the amount

$$\Delta \epsilon_j = \tilde{\epsilon}_{jl} - \epsilon_{jk} \,, \tag{19}$$

while the number of particles of species $\alpha$ in the $j^{\mathrm{th}}$ subsystem changes by

$$\Delta \nu_{j\alpha} = \tilde{\nu}_{j\alpha l} - \nu_{j\alpha k} \,, \tag{20}$$

during the forward protocol.

### C. The reversed protocol

The evolution operator of the reversed process is defined as

$$i\hbar \frac{\partial}{\partial t} U_{\mathrm{R}}(t; B) = H(\mathcal{T} - t; B) U_{\mathrm{R}}(t; B) \,, \tag{21}$$

with the initial condition $U_{\mathrm{R}}(0; B) = I$, and is related to the one of the forward process by the following

**Lemma:** *The forward and reversed time evolution operators at the final time $\mathcal{T}$ are related to each other by*

$$U_{\mathrm{R}}(\mathcal{T}; -B) = \Theta U_{\mathrm{F}}^{\dagger}(\mathcal{T}; B) \Theta \,. \tag{22}$$

This lemma is proved by noting that the forward time evolution in the magnetic field $B$, followed by the operation of time reversal, by the reversed time evolution in the magnetic field $-B$, and finally by time reversal again is equal to the identical operator:

$$\Theta U_{\mathrm{R}}(\mathcal{T}; -B) \Theta U_{\mathrm{F}}(\mathcal{T}; B) = I \;, \tag{23}$$

from which we deduce Eq. (22).

The reversed protocol is supposed to start with the following grand-canonical equilibrium state of the final decoupled subsystems:

$$\rho(\mathcal{T}; -B) = \prod_j \frac{\mathrm{e}^{-\beta_j(\tilde{H}_j - \sum_\alpha \mu_{j\alpha} N_{j\alpha})}}{\tilde{\Xi}_j(-B)} = \prod_j \mathrm{e}^{-\beta_j\left[\tilde{H}_j - \sum_\alpha \mu_{j\alpha} N_{j\alpha} - \tilde{\Phi}_j(-B)\right]} \;, \tag{24}$$

at the same inverse temperatures $\beta_j = 1/(k_{\mathrm{B}} T_j)$ and chemical potentials $\mu_{j\alpha}$ as in the forward protocol and where $\tilde{\Phi}_j(-B) = -k_{\mathrm{B}} T_j \ln \tilde{\Xi}_j(-B)$ denotes the grand-canonical thermodynamic potential of the $j^{\mathrm{th}}$ subsystem in the final equilibrium state and reversed magnetic field.

Similarly to the forward protocol, initial and final quantum measurements are performed to determine the changes of energies and particle numbers in the subsystems.

## III. CONSEQUENCES OF MICROREVERSIBILITY

### A. The symmetry relation for the probability of the fluctuations

The probability distribution function to observe the energy (19) and particle transfers (20) during the forward protocol is defined as

$$p_{\mathrm{F}}(\Delta\epsilon_j, \Delta\nu_{j\alpha}; B) \equiv \sum_{kl} \prod_j \delta\left[\Delta\epsilon_j - (\tilde{\epsilon}_{jl} - \epsilon_{jk})\right] \prod_{j\alpha} \delta\left[\Delta\nu_{j\alpha} - (\tilde{\nu}_{j\alpha l} - \nu_{j\alpha k})\right]$$
$$\times |\langle\tilde{\Psi}_l(B)|U_{\mathrm{F}}(T; B)|\Psi_k(B)\rangle|^2 \, \langle\Psi_k(B)|\rho(0; B)|\Psi_k(B)\rangle \;. \tag{25}$$

We notice that this function is a probability density because the quantities $\delta(\cdot)$ are Dirac distributions for both the energy and the particle numbers.

Inserting the expression of the initial density matrix (14), using the Dirac delta distributions to replace the initial energies and numbers into the final ones, we find that

$$p_{\mathrm{F}}(\Delta\epsilon_j, \Delta\nu_{j\alpha}; B) = \sum_{kl} \prod_j \delta\left[\Delta\epsilon_j - (\tilde{\epsilon}_{jl} - \epsilon_{jk})\right] \prod_{j\alpha} \delta\left[\Delta\nu_{j\alpha} - (\tilde{\nu}_{j\alpha l} - \nu_{j\alpha k})\right]$$
$$\times |\langle\tilde{\Psi}_l(B)|U_{\mathrm{F}}(T; B)|\Psi_k(B)\rangle|^2 \, \mathrm{e}^{-\sum_j \beta_j\left[\epsilon_{jk} - \sum_\alpha \mu_{j\alpha} \nu_{j\alpha k} - \Phi_j(B)\right]}$$

$$= \mathrm{e}^{\sum_j \beta_j(\Delta\epsilon_j - \sum_\alpha \mu_{j\alpha} \Delta\nu_{j\alpha} - \Delta\Phi_j)}$$
$$\times \sum_{kl} \prod_j \delta\left[\Delta\epsilon_j - (\tilde{\epsilon}_{jl} - \epsilon_{jk})\right] \prod_{j\alpha} \delta\left[\Delta\nu_{j\alpha} - (\tilde{\nu}_{j\alpha l} - \nu_{j\alpha k})\right]$$
$$\times |\langle\tilde{\Psi}_l(B)|U_{\mathrm{F}}(T; B)|\Psi_k(B)\rangle|^2 \, \mathrm{e}^{-\sum_j \beta_j\left[\tilde{\epsilon}_{jl} - \sum_\alpha \mu_{j\alpha} \tilde{\nu}_{j\alpha l} - \tilde{\Phi}_j(-B)\right]} \;, \tag{26}$$

where we have introduced the difference of the thermodynamic grand-potential of the $j^{\mathrm{th}}$ subsystem as

$$\Delta\Phi_j \equiv \tilde{\Phi}_j(-B) - \Phi_j(B) \;. \tag{27}$$

According to the lemma (22), the probability of the transition $k \to l$ during the forward process is equal to the probability of the transition $l \to k$ in the reversed process and magnetic field:

$$|\langle\tilde{\Psi}_l(B)|U_{\mathrm{F}}(\mathcal{T}; B)|\Psi_k(B)\rangle|^2 = |\langle\tilde{\Psi}_l(B)|\Theta U_{\mathrm{R}}^\dagger(\mathcal{T}; -B)\Theta|\Psi_k(B)\rangle|^2$$
$$= |\langle\Psi_k(-B)|U_{\mathrm{R}}(\mathcal{T}; -B)|\tilde{\Psi}_l(-B)\rangle|^2 \;. \tag{28}$$

Substituting this identity in Eq. (26) and introducing the probability of negative changes in the energies and particle numbers during the reversed process as

$$p_R(-\Delta\epsilon_j, -\Delta\nu_{j\alpha}; -B) \equiv \sum_{kl} \prod_j \delta\left[-\Delta\epsilon_j - (\epsilon_{jk} - \tilde{\epsilon}_{jl})\right] \prod_{j\alpha} \delta\left[-\Delta\nu_{j\alpha} - (\nu_{j\alpha k} - \tilde{\nu}_{j\alpha l})\right]$$
$$\times |\langle \Psi_k(-B)|U_R(\mathcal{T}; -B)|\tilde{\Psi}_l(-B)\rangle|^2 \langle \tilde{\Psi}_l(-B)|\rho(\mathcal{T}; -B)|\tilde{\Psi}_l(-B)\rangle$$

$$(29)$$

with the final density matrix (24), we obtain the following symmetry relation:

$$p_F(\Delta\epsilon_j, \Delta\nu_{j\alpha}; B) = e^{\sum_j \beta_j(\Delta\epsilon_j - \sum_\alpha \mu_{j\alpha}\Delta\nu_{j\alpha} - \Delta\Phi_j)} p_R(-\Delta\epsilon_j, -\Delta\nu_{j\alpha}; -B) . \tag{30}$$

If this relation is restricted to the energy change in a single system, this fluctuating quantity is the work $W$ performed on the system and we recover the quantum version of Crooks' fluctuation theorem

$$p_F(W; B) = e^{\beta(W-\Delta F)} p_R(-W; -B) \tag{31}$$

with the corresponding difference of free energy $\Delta F = \tilde{F}(-B) - F(B)$ [25]. The relation (30) extends this result to the transfer of particles under the effect of the differences of chemical potentials driving the system out of equilibrium.

## B. The symmetry relation for the generating function

The generating functions of the statistical moments of the exchanges of energy and particles are defined by

$$G_{F,R}(\xi_j, \eta_{j\alpha}; B) \equiv \int \prod_{j\alpha} d\Delta\epsilon_j \, d\Delta\nu_{j\alpha} \, e^{-\sum_j \xi_j \Delta\epsilon_j - \sum_\alpha \eta_{j\alpha}\Delta\nu_{j\alpha}} \, p_{F,R}(\Delta\epsilon_j, \Delta\nu_{j\alpha}; B) \tag{32}$$

for the forward and reversed processes. The knowledge of these generating functions provides the full counting statistics of the process. We notice that the generating function of the forward protocol is alternatively defined as

$$G_F(\xi_j, \eta_{j\alpha}; B) = \left\langle e^{-\sum_j \xi_j \tilde{H}_{jF} - \sum_{j\alpha} \eta_{j\alpha} N_{j\alpha F}} e^{\sum_j \xi_j H_j + \sum_{j\alpha} \eta_{j\alpha} N_{j\alpha}} \right\rangle_F \tag{33}$$

with

$$\tilde{H}_{jF} = U_F^\dagger(\mathcal{T}; B)\tilde{H}_j U_F(\mathcal{T}; B) , \tag{34}$$
$$N_{j\alpha F} = U_F^\dagger(\mathcal{T}; B)N_{j\alpha} U_F(\mathcal{T}; B) , \tag{35}$$

and the generating function of the reversed protocol as

$$G_R(\xi_j, \eta_{j\alpha}; -B) = \left\langle e^{-\sum_j \xi_j H_{jR} - \sum_{j\alpha} \eta_{j\alpha} N_{j\alpha R}} e^{\sum_j \xi_j \tilde{H}_j + \sum_{j\alpha} \eta_{j\alpha} N_{j\alpha}} \right\rangle_R \tag{36}$$

with

$$H_{jR} = U_R^\dagger(\mathcal{T}; -B)H_j U_R(\mathcal{T}; -B) , \tag{37}$$
$$N_{j\alpha R} = U_R^\dagger(\mathcal{T}; -B)N_{j\alpha} U_R(\mathcal{T}; -B) . \tag{38}$$

Taking the Laplace transforms of the symmetry relation (30), we obtain an equivalent symmetry relation in terms of the generating functions:

$$G_F(\xi_j, \eta_{j\alpha}; B) = e^{-\sum_j \beta_j \Delta\Phi_j} G_R(\beta_j - \xi_j, -\beta_j \mu_{j\alpha} - \eta_{j\alpha}; -B) , \tag{39}$$

in terms of the temperatures and chemical potentials of the subsystems. As mentioned in the introduction, this symmetry relation has not yet the appropriate form because the thermodynamic forces or affinities do not appear.

## IV. QUANTUM FLUCTUATION THEOREM FOR THE CURRENTS

In this section, we prove that, in the long-time limit, the generating functions entering into the symmetry relation (39) only depend on the differences of the parameters $\xi_j$ and $\eta_{j\alpha}$, leading to the requested symmetry. In the long-time limit, a nonequilibrium steady state can be reached between the reservoirs if the coupling remains constant over the whole time interval except finite transients. In this respect, it is important to suppose that the temperatures and chemical potentials which have been introduced here above concern the reservoirs themselves. Accordingly, from now on, the subsystem can no longer be considered as a subsystem on equal footing with the reservoirs, and the subsystem Hamiltonian is supposed to be included in either one of the reservoir Hamiltonians or in the interaction potential as formulated in Eqs. (8) and (9) with the indices $j = 1, 2, ..., r$ referring to the reservoirs themselves.

### A. The theorem

We consider a situation where two large quantum systems interact through a bounded time-dependent perturbation described by $V(t)$. Then, the generator of time evolution of the whole system is given by

$$H = H_1 + H_2 + V(t) \,, \tag{40}$$

where the subsystem Hamiltonian $\mathcal{H}_s$ is included in either $H_1$, $H_2$, or $V(t)$ (imagine a quantum dot located between two electrodes). Hereafter, we assume that $V(0) = 0$, $V(t) = V(\mathcal{T} - t)$ and $V(t) = V_0$ for $t_0 \leq t \leq \mathcal{T} - t_0$, meaning that the interaction is switched on over a short time interval $t_0$, remains constant during the long lapse of time $\mathcal{T} - 2t_0$, and is finally switched off again over a short time interval $t_0$.

Let $N_{j\alpha}$ $(j = 1, 2)$ be the number of $\alpha$-particles in the $j^{\text{th}}$ large system and assume that $[N_{1\alpha} + N_{2\alpha}, H_1 + H_2 + V_0] = 0$.

Since the interaction is symmetric under time reversal $V(t) = V(\mathcal{T} - t)$, the evolution operator of the forward and reversed protocols are identical

$$U_{\text{F}}(t; B) = U_{\text{R}}(t; B) \equiv U(t; B) \tag{41}$$

and they are therefore solutions of one and the same equation:

$$i\frac{\partial}{\partial t}U(t; B) = [H_1 + H_2 + V(t)]\, U(t; B) \tag{42}$$

with the initial condition $U(0; B) = I$ and $\hbar = 1$. For the same reason, the initial and final reservoir Hamiltonians are the same, $H_j = \tilde{H}_j$ for all $j = 1, 2, ..., r$, so that the initial and final density matrices have the same definition

$$\rho(B) = \prod_{j=1}^{r} e^{-\beta_j \left[H_j - \sum_\alpha \mu_{j\alpha} N_{j\alpha} - \Phi_j(B)\right]} \,, \tag{43}$$

where $\Phi_j(B)$ is the thermodynamic grand-potential of the $j^{\text{th}}$ reservoir in magnetic field $B$. Accordingly, the forward and reversed generating functions also have the same definition

$$G(\xi_j, \eta_{j\alpha}; B) \equiv \left\langle e^{-\sum_j \xi_j H_{j\text{F}} - \sum_{j\alpha} \eta_{j\alpha} N_{j\alpha\text{F}}}\; e^{\sum_j \xi_j H_j + \sum_{j\alpha} \eta_{j\alpha} N_{j\alpha}} \right\rangle \tag{44}$$

with Eqs. (34) and (35) and where the average $\langle \cdot \rangle$ is carried out with respect to the density matrix (43).

According to Eq. (39), this generating function has the symmetry

$$G(\xi_j, \eta_{j\alpha}; B) = e^{-\sum_j \beta_j \Delta \Phi_j}\, G(\beta_j - \xi_j, -\beta_j \mu_{j\alpha} - \eta_{j\alpha}; -B) \,, \tag{45}$$

in terms of the temperatures and chemical potentials of the reservoirs.

Our purpose in this section is to prove the

**Proposition.** *Assume that the limit*

$$Q(\xi_j, \eta_{j\alpha}; B) \equiv -\lim_{\mathcal{T} \to \infty} \frac{1}{\mathcal{T}} \ln G(\xi_j, \eta_{j\alpha}; B) \tag{46}$$

*exists, it is a function only of $\xi_1 - \xi_2$ and $\eta_{1\alpha} - \eta_{2\alpha}$:*

$$Q(\xi_j, \eta_{j\alpha}; B) = \widetilde{Q}(\xi_1 - \xi_2, \eta_{1\alpha} - \eta_{2\alpha}; B) \,. \tag{47}$$

We would like to remark that, if the system had very long but finite recurrent times and much shorter relaxation times, the quantities $Q$ and $\tilde{Q}$ would exist provided $\mathcal{T}$ is sufficiently longer than the relaxation times but shorter than the recurrent times.

The interpretation of this proposition is that, because of the finiteness of the subsystem and the interaction $V_0$, the energy and particles lost by the left (respectively right) reservoir are transferred to the right (respectively left) reservoir within the overwhelming duration $t_0 \leq t \leq \mathcal{T} - t_0$ and, as a result, $Q$ becomes a function $\tilde{Q}$ depending only on the differences $\xi_1 - \xi_2$ and $\eta_{1\alpha} - \eta_{2\alpha}$. We remark that the explicit form of the generating function $\tilde{Q}(\xi_1 - \xi_2, \eta_{1\alpha} - \eta_{2\alpha}; B)$ is given by Eq. (92).

The above proposition implies that

$$
\begin{aligned}
\widetilde{Q}(\xi_1 - \xi_2, \eta_{1\alpha} - \eta_{2\alpha}; B) &= Q(\xi_j, \eta_{j\alpha}; B) && (48) \\
&= Q(\beta_j - \xi_j, -\beta_j \mu_{j\alpha} - \eta_{j\alpha}; -B) && (49) \\
&= \widetilde{Q}(\beta_1 - \beta_2 - \xi_1 + \xi_2, -\beta_1 \mu_{1\alpha} + \beta_2 \mu_{2\alpha} - \eta_{1\alpha} + \eta_{2\alpha}; -B) && (50) \\
&= \widetilde{Q}(A_0 - \xi_1 + \xi_2, A_\alpha - \eta_{1\alpha} + \eta_{2\alpha}; -B) , && (51)
\end{aligned}
$$

where we have introduced the affinities:

$$
\begin{aligned}
A_0 &\equiv \beta_1 - \beta_2 , && (52) \\
A_\alpha &\equiv \beta_2 \mu_{2\alpha} - \beta_1 \mu_{1\alpha} , && \text{for} \quad \alpha = 1, 2, ..., c, && (53)
\end{aligned}
$$

driving respectively the heat current and the $\alpha$-particle currents from reservoir 2 to reservoir 1. The result (51) is obtained by using the definition (47) at the line (48), the symmetry (45) and the independency of the quantities $\Delta\Phi_j$ on the time interval $\mathcal{T}$ at the line (49), again the definition (47) at the line (50), and finally the definitions of the affinities (52) and (53). Hence, we have the

**Fluctuation theorem.** *The generating function of the independent currents satisfies the symmetry*

$$
\widetilde{Q}(\xi, \eta_\alpha; B) = \widetilde{Q}(A_0 - \xi, A_\alpha - \eta_\alpha; -B) . \tag{54}
$$

In the particular case where the two systems have the same temperature, $\beta_1 = \beta_2$, the generating function has the symmetry:

$$
\widetilde{Q}(\xi, \eta_\alpha; B) = \widetilde{Q}(-\xi, A_\alpha - \eta_\alpha; -B) , \tag{55}
$$

and we recover the symmetry

$$
\widetilde{Q}(0, \eta_\alpha; B) = \widetilde{Q}(0, A_\alpha - \eta_\alpha; -B) \tag{56}
$$

of the generating function of the independent particle currents, which has already been proved elsewhere for stochastic processes [23].

We notice that the fluctuation theorem (54) which is here proved thanks to the proposition (46)-(47) reduces to the steady-state fluctuation theorem presented as Eq. (104) in the review [42] for vanishing magnetic field, $B = 0$. Accordingly, the proposition (46)-(47) also provides a rigorous proof of such steady-state fluctuation theorems.

## B. Setting

In order to demonstrate the above proposition, the time evolution is decomposed into different pieces corresponding to the short initial transient over $0 < t < t_0$, the long steady interaction over $t_0 < t < \mathcal{T} - t_0$, and the final short transient over $\mathcal{T} - t_0 < t < \mathcal{T}$. We introduce the lapse of time of the steady interaction

$$
\tau \equiv \mathcal{T} - 2t_0 . \tag{57}
$$

In addition to $U(t; B)$ defined by Eq. (10), we introduce $U_1(t; B)$ as the solution of

$$
i\frac{\partial}{\partial t} U_1(t; B) = [H_1 + H_2 + V(t_0 - t)] U_1(t; B) \qquad \text{with} \quad U_1(0; B) = I . \tag{58}
$$

It is then easy to show

$$U(\tau + 2t_0; B) = U_1(t_0; B)e^{-i\bar{H}\tau}U(t_0; B) \equiv U_f U_\tau U_i \ , \tag{59}$$

where $\bar{H} = H_1 + H_2 + V_0$, $U_f = U_1(t_0; B)$, $U_\tau = e^{-i\bar{H}\tau}$ and $U_i = U(t_0; B)$. We further note that

$$e^{iH_0(\tau+t_0)}U(\tau + 2t_0; B)e^{iH_0 t_0} = e^{iH_0\tau}\Gamma_f e^{-iH_0\tau}\Gamma_\tau e^{-iH_0 t_0}\Gamma_i e^{iH_0 t_0} \ , \tag{60}$$

where $H_0 = H_1 + H_2$, $\Gamma_f = e^{iH_0 t_0}U_f$, $\Gamma_\tau = e^{iH_0\tau}U_\tau$, and $\Gamma_i = e^{iH_0 t_0}U_i$.

Therefore, with the aid of $[H_0, H_j] = [H_0, N_{j\alpha}] = [H_0, \rho] = 0$, we have

$$\begin{aligned}
&G(\xi_j, \eta_{j\alpha}; B)\\
&= \langle U(\tau + 2t_0; B)^\dagger e^{-\sum_j \xi_j H_j - \sum_{j\alpha} \eta_{j\alpha} N_{j\alpha}} \, U(\tau + 2t_0; B) \, e^{\sum_j \xi_j H_j + \sum_{j\alpha} \eta_{j\alpha} N_{j\alpha}} \rangle\\
&= \langle U_i^\dagger U_\tau^\dagger U_f^\dagger e^{-\sum_j \xi_j H_j - \sum_{j\alpha} \eta_{j\alpha} N_{j\alpha}} \, U_f U_\tau U_i \, e^{\sum_j \xi_j H_j + \sum_{j\alpha} \eta_{j\alpha} N_{j\alpha}} \rangle\\
&= \langle e^{-iH_0 t_0} U_i^\dagger U_\tau^\dagger U_f^\dagger e^{-iH_0(\tau+t_0)} e^{-\sum_j \xi_j H_j - \sum_{j\alpha} \eta_{j\alpha} N_{j\alpha}} \, e^{iH_0(\tau+t_0)} U_f U_\tau U_i \, e^{\sum_j \xi_j H_j + \sum_{j\alpha} \eta_{j\alpha} N_{j\alpha}} e^{iH_0 t_0} \rangle\\
&= \langle \Gamma_i(-t_0)^\dagger \Gamma_\tau^\dagger \Gamma_f(\tau)^\dagger e^{-\sum_j \xi_j H_j - \sum_{j\alpha} \eta_{j\alpha} N_{j\alpha}} \, \Gamma_f(\tau) \Gamma_\tau \Gamma_i(-t_0) \, e^{\sum_j \xi_j H_j + \sum_{j\alpha} \eta_{j\alpha} N_{j\alpha}} \rangle \ ,
\end{aligned} \tag{61}$$

where $\Gamma_\lambda(\tau) = e^{iH_0\tau}\Gamma_\lambda e^{-iH_0\tau}$ ($\lambda = i$ or $f$).

For later purpose, we introduce

$$\sum_j \xi_j H_j + \sum_{j\alpha} \eta_{j\alpha} N_{j\alpha} = 2C + 2D \ , \tag{62}$$

$$2C = \frac{\xi_1 + \xi_2}{2} H_0 + \sum_\alpha \frac{\eta_{1\alpha} + \eta_{2\alpha}}{2} N_{0\alpha} \ , \tag{63}$$

$$2D = (\xi_1 - \xi_2)\Delta H_0 + \sum_\alpha (\eta_{1\alpha} - \eta_{2\alpha})\Delta N_{0\alpha} \ , \tag{64}$$

$$2A = \sum_j \beta_j \left( H_j - \sum_\alpha \mu_{j\alpha} N_{j\alpha} \right) \ , \tag{65}$$

where $H_0 = H_1 + H_2$, $N_{0\alpha} = N_{1\alpha} + N_{2\alpha}$, $\Delta H_0 = (H_1 - H_2)/2$, and $\Delta N_{0\alpha} = (N_{1\alpha} - N_{2\alpha})/2$. Since $[C, \rho] = [D, \rho] = 0$, we have

$$G(\xi_j, \eta_{j\alpha}; B) = \langle e^{C+D}\Gamma_i(-t_0)^\dagger \Gamma_\tau^\dagger \Gamma_f(\tau)^\dagger e^{-2C-2D} \, \Gamma_f(\tau)\Gamma_\tau\Gamma_i(-t_0) \, e^{C+D} \rangle \ . \tag{66}$$

This is our starting point. Note that $C$ and $D$ are Hermitian for real $\xi_j$ and $\eta_{j\alpha}$ and that $D$ is the function only of $\xi_1 - \xi_2$ and $\eta_{1\alpha} - \eta_{2\alpha}$.

### C. Some Inequalities

Here, for the sake of self-containedness, well-known equalities and inequalities [54] necessary for the following proof are summarized. For an operator $X$, the operator norm $\|X\|$ is defined by

$$\|X\| \equiv \sup_{|\varphi\rangle \neq 0} \sqrt{\frac{\langle\varphi|X^\dagger X|\varphi\rangle}{\langle\varphi|\varphi\rangle}} \tag{67}$$

and it satisfies:
**Equality 1:** For any unitary $U$, $\|U^\dagger X U\| = \|X\|$.

Indeed, we find

$$\|U^\dagger X U\|^2 = \sup_{|\varphi\rangle \neq 0} \frac{\langle\varphi|U^\dagger X^\dagger X U|\varphi\rangle}{\langle\varphi|\varphi\rangle} = \sup_{|\psi\rangle \neq 0} \frac{\langle\psi|X^\dagger X|\psi\rangle}{\langle\psi|UU^\dagger|\psi\rangle} = \sup_{|\psi\rangle \neq 0} \frac{\langle\psi|X^\dagger X|\psi\rangle}{\langle\psi|\psi\rangle} = \|X\|^2 \ , \tag{68}$$

where we have set $|\psi\rangle = U|\varphi\rangle$.
**Inequality 1:** $\langle X^\dagger Y^\dagger Y X\rangle \leq \|Y\|^2 \langle X^\dagger X\rangle$.

Let $\{\varphi_\sigma\}$ be a complete orthonormal basis of eigenvectors of $\rho$: $\rho|\varphi_\sigma\rangle = \rho_\sigma|\varphi_\sigma\rangle$. Then, because of $\langle\varphi|X^\dagger X|\varphi\rangle \le \|X\|^2\langle\varphi|\varphi\rangle$,

$$
\begin{aligned}
\langle X^\dagger Y^\dagger Y X\rangle &\equiv \sum_\sigma \rho_\sigma\langle\varphi_\sigma|X^\dagger Y^\dagger Y X|\varphi_\sigma\rangle \\
&\le \sum_\sigma \rho_\sigma\|Y\|^2\langle\varphi_\sigma|X^\dagger X|\varphi_\sigma\rangle \\
&= \|Y\|^2\sum_\sigma \rho_\sigma\langle\varphi_\sigma|X^\dagger X|\varphi_\sigma\rangle \\
&= \|Y\|^2\langle X^\dagger X\rangle \, .
\end{aligned}
\tag{69}
$$

**Inequality 2:** $\langle X^\dagger Y^\dagger Y X\rangle \le \|e^{-A}X^\dagger e^A\|^2\langle Y^\dagger Y\rangle$ where $2A = \sum_j \beta_j(H_j - \sum_\alpha \mu_{j\alpha}N_{j\alpha})$.

Thanks to the cyclicity of the trace, we have the Kubo-Martin-Schwinger (KMS) condition $\langle XY\rangle = \langle e^A Y e^{-A} e^{-A} X e^A\rangle$ for canonical averages $\langle XY\rangle = \frac{1}{\Xi}\mathrm{Tr}(e^{-2A}XY)$ with $\Xi = \mathrm{Tr}\, e^{-2A}$. The KMS condition and Inequality 1 imply

$$
\begin{aligned}
\langle X^\dagger Y^\dagger Y X\rangle &= \langle e^A Y X e^{-A} e^{-A} X^\dagger Y^\dagger e^A\rangle = \langle e^A Y e^{-A} e^A X e^{-A} e^{-A} X^\dagger e^A e^{-A} Y^\dagger e^A\rangle \\
&\le \|e^{-A}X^\dagger e^A\|^2\langle e^A Y e^{-A} e^{-A} Y^\dagger e^A\rangle = \|e^{-A}X^\dagger e^A\|^2\langle Y^\dagger Y\rangle \, .
\end{aligned}
\tag{70}
$$

## D. Proof

**Step 1:**
Let $X_1 = e^{-C-D}\Gamma_\tau\Gamma_i(-t_0)\,e^{C+D}$. Then Inequality 1 leads to

$$
\begin{aligned}
G(\xi_j,\eta_{j\alpha};B) &= \langle X_1^\dagger\left[e^{-C-D}\Gamma_f(\tau)e^{C+D}\right]^\dagger\left[e^{-C-D}\Gamma_f(\tau)\,e^{C+D}\right]X_1\rangle \\
&\le \|e^{-C-D}\Gamma_f(\tau)\,e^{C+D}\|^2\langle X_1^\dagger X_1\rangle \, .
\end{aligned}
\tag{71}
$$

Since $\Gamma_f(\tau)^\dagger\Gamma_f(\tau) = 1$, we have

$$
\begin{aligned}
\langle X_1^\dagger X_1\rangle &= \langle X_1^\dagger e^{C+D}e^{-C-D}e^{-C-D}e^{C+D}X_1\rangle \\
&= \langle X_1^\dagger e^{C+D}\Gamma_f(\tau)^\dagger\Gamma_f(\tau)e^{-C-D}e^{-C-D}\Gamma_f(\tau)^\dagger\Gamma_f(\tau)e^{C+D}X_1\rangle \\
&= \langle X_1^\dagger e^{C+D}\Gamma_f(\tau)^\dagger e^{-C-D}\left[e^{C+D}\Gamma_f(\tau)e^{-C-D}\right]\left[e^{-C-D}\Gamma_f(\tau)^\dagger e^{C+D}\right]e^{-C-D}\Gamma_f(\tau)e^{C+D}X_1\rangle \\
&= \langle X_1^\dagger e^{C+D}\Gamma_f(\tau)^\dagger e^{-C-D}Y_1^\dagger Y_1\,e^{-C-D}\Gamma_f(\tau)e^{C+D}X_1\rangle \\
&\le \|Y_1\|^2\langle X_1^\dagger e^{C+D}\Gamma_f(\tau)^\dagger e^{-2C-2D}\Gamma_f(\tau)e^{C+D}X_1\rangle \\
&\le \|e^{-C-D}\Gamma_f(\tau)^\dagger e^{C+D}\|^2\langle X_1^\dagger e^{C+D}\Gamma_f(\tau)^\dagger e^{-2C-2D}\Gamma_f(\tau)e^{C+D}X_1\rangle \\
&= \|e^{-C-D}\Gamma_f(\tau)^\dagger e^{C+D}\|^2 G(\xi_j,\eta_{j\alpha};B) \, ,
\end{aligned}
\tag{72}
$$

where $Y_1 = e^{-C-D}\Gamma_f(\tau)^\dagger e^{C+D}$ and Inequality 1 has been used.

Since $\Gamma_f(\tau) = e^{iH_0\tau}\Gamma_f e^{-iH_0\tau}$ and $[H_0,C] = [H_0,D] = 0$,

$$
\begin{aligned}
\|e^{-C-D}\Gamma_f(\tau)\,e^{C+D}\| &= \|e^{-C-D}e^{iH_0\tau}\Gamma_f e^{-iH_0\tau}\,e^{C+D}\| \\
&= \|e^{iH_0\tau}e^{-C-D}\Gamma_f e^{C+D}e^{-iH_0\tau}\| \\
&= \|e^{-C-D}\Gamma_f e^{C+D}\| \, ,
\end{aligned}
\tag{73}
$$

where we have used Equality 1 for the norm. Similarly, $\|e^{-C-D}\Gamma_f(\tau)^\dagger e^{C+D}\| = \|e^{-C-D}\Gamma_f^\dagger e^{C+D}\|$.

In short, in terms of

$$
G_1(\xi_j,\eta_{j\alpha};B) \equiv \langle X_1^\dagger\,X_1\rangle = \langle e^{C+D}\Gamma_i(-t_0)^\dagger\Gamma_\tau^\dagger e^{-2C-2D}\Gamma_\tau\Gamma_i(-t_0)\,e^{C+D}\rangle \, ,
\tag{74}
$$

we have

$$
\frac{G_1(\xi_j,\eta_{j\alpha};B)}{\|e^{-C-D}\Gamma_f^\dagger e^{C+D}\|^2} \le G(\xi_j,\eta_{j\alpha};B) \le \|e^{-C-D}\Gamma_f\,e^{C+D}\|^2 G_1(\xi_j,\eta_{j\alpha};B) \, .
\tag{75}
$$

**Step 2:**

In terms of $X_2 = \mathrm{e}^{-C-D}\Gamma_i(-t_0)\mathrm{e}^{C+D}$, one has from Inequality 2

$$
\begin{aligned}
G_1(\xi_j, \eta_{j\alpha}; B) &= \langle \mathrm{e}^{C+D}\Gamma_i(-t_0)^\dagger \Gamma_\tau^\dagger \mathrm{e}^{-2C-2D}\Gamma_\tau \Gamma_i(-t_0)\,\mathrm{e}^{C+D}\rangle \\
&= \langle \mathrm{e}^{C+D}\Gamma_i(-t_0)^\dagger \mathrm{e}^{-C-D}\mathrm{e}^{C+D}\Gamma_\tau^\dagger \mathrm{e}^{-2C-2D}\Gamma_\tau \mathrm{e}^{C+D}\mathrm{e}^{-C-D}\Gamma_i(-t_0)\,\mathrm{e}^{C+D}\rangle \\
&= \langle X_2^\dagger \left[\mathrm{e}^{-C-D}\Gamma_\tau \mathrm{e}^{C+D}\right]^\dagger \left[\mathrm{e}^{-C-D}\Gamma_\tau \mathrm{e}^{C+D}\right] X_2\rangle \\
&\leq \|\mathrm{e}^{-A}X_2^\dagger \mathrm{e}^A\|^2 \langle \left[\mathrm{e}^{-C-D}\Gamma_\tau \mathrm{e}^{C+D}\right]^\dagger \left[\mathrm{e}^{-C-D}\Gamma_\tau \mathrm{e}^{C+D}\right]\rangle \\
&\leq \|\mathrm{e}^{-A}\mathrm{e}^{C+D}\Gamma_i(-t_0)^\dagger \mathrm{e}^{-C-D}\mathrm{e}^A\|^2 \langle \mathrm{e}^{C+D}\Gamma_\tau^\dagger \mathrm{e}^{-2C-2D}\Gamma_\tau \mathrm{e}^{C+D}\rangle\,.
\end{aligned}
\tag{76}
$$

Conversely, in terms of $Y_2 = \mathrm{e}^{-C-D}\Gamma_i(-t_0)^\dagger \mathrm{e}^{C+D}$, Inequality 2 leads to

$$
\begin{aligned}
&\langle \mathrm{e}^{C+D}\Gamma_\tau^\dagger \mathrm{e}^{-2C-2D}\Gamma_\tau \mathrm{e}^{C+D}\rangle \\
&= \langle \mathrm{e}^{C+D}\Gamma_i(-t_0)\mathrm{e}^{-C-D}\mathrm{e}^{C+D}\Gamma_i(-t_0)^\dagger \Gamma_\tau^\dagger \mathrm{e}^{-2C-2D}\Gamma_\tau \Gamma_i(-t_0)\mathrm{e}^{C+D}\mathrm{e}^{-C-D}\Gamma_i(-t_0)^\dagger \mathrm{e}^{C+D}\rangle \\
&= \langle Y_2^\dagger \mathrm{e}^{C+D}\Gamma_i(-t_0)^\dagger \Gamma_\tau^\dagger \mathrm{e}^{-2C-2D}\Gamma_\tau \Gamma_i(-t_0)\mathrm{e}^{C+D}Y_2\rangle \\
&\leq \|\mathrm{e}^{-A}Y_2^\dagger \mathrm{e}^A\|^2 \langle \mathrm{e}^{C+D}\Gamma_i(-t_0)^\dagger \Gamma_\tau^\dagger \mathrm{e}^{-2C-2D}\Gamma_\tau \Gamma_i(-t_0)\,\mathrm{e}^{C+D}\rangle \\
&\leq \|\mathrm{e}^{-A}\mathrm{e}^{C+D}\Gamma_i(-t_0)\mathrm{e}^{-C-D}\mathrm{e}^A\|^2 \langle \mathrm{e}^{C+D}\Gamma_i(-t_0)^\dagger \Gamma_\tau^\dagger \mathrm{e}^{-2C-2D}\Gamma_\tau \Gamma_i(-t_0)\,\mathrm{e}^{C+D}\rangle\,.
\end{aligned}
\tag{77}
$$

In short, let $G_2(\xi_j, \eta_{j\alpha}; B) \equiv \langle \mathrm{e}^{C+D}\Gamma_\tau^\dagger \mathrm{e}^{-2C-2D}\Gamma_\tau \mathrm{e}^{C+D}\rangle$, then

$$
\frac{G_2(\xi_j, \eta_{j\alpha}; B)}{\|\mathrm{e}^{-A}\mathrm{e}^{C+D}\Gamma_i(-t_0)\mathrm{e}^{-C-D}\mathrm{e}^A\|^2} \leq G_1(\xi_j, \eta_{j\alpha}; B) \leq \|\mathrm{e}^{-A}\mathrm{e}^{C+D}\Gamma_i(-t_0)^\dagger \mathrm{e}^{-C-D}\mathrm{e}^A\|^2 G_2(\xi_j, \eta_{j\alpha}; B)\,.
\tag{78}
$$

**Step 3:**

We set

$$
2\bar{C} = \frac{\xi_1 + \xi_2}{2}\bar{H} + \sum_\alpha \frac{\eta_{1\alpha} + \eta_{2\alpha}}{2}\bar{N}_\alpha\,,
\tag{79}
$$

where $\bar{H} = H_1 + H_2 + V_0$ and $\bar{N}_\alpha = N_{1\alpha} + N_{2\alpha}$. Then, in terms of $\tilde{\Gamma}_\tau = U_\tau \mathrm{e}^{iH_0\tau}$, we have

$$
\begin{aligned}
G_2(\xi_j, \eta_{j\alpha}; B) &= \langle \mathrm{e}^{C+D}\Gamma_\tau^\dagger \mathrm{e}^{-2C-2D}\Gamma_\tau \mathrm{e}^{C+D}\rangle \\
&= \langle \mathrm{e}^{C+D}\mathrm{e}^{iH_0\tau}\tilde{\Gamma}_\tau^\dagger \mathrm{e}^{-iH_0\tau}\mathrm{e}^{-2C-2D}\mathrm{e}^{iH_0\tau}\tilde{\Gamma}_\tau \mathrm{e}^{-iH_0\tau}\mathrm{e}^{C+D}\rangle \\
&= \langle \mathrm{e}^{iH_0\tau}\mathrm{e}^D\mathrm{e}^C\tilde{\Gamma}_\tau^\dagger \mathrm{e}^{-\bar{C}}\mathrm{e}^{-D}\mathrm{e}^{-iH_0\tau}\left[\mathrm{e}^{iH_0\tau}\mathrm{e}^D\mathrm{e}^{\bar{C}}\mathrm{e}^{-C}\mathrm{e}^{-D}\mathrm{e}^{-iH_0\tau}\right] \\
&\quad\times \left[\mathrm{e}^{iH_0\tau}\mathrm{e}^{-D}\mathrm{e}^{-C}\mathrm{e}^{\bar{C}}\mathrm{e}^D\mathrm{e}^{-iH_0\tau}\right]\mathrm{e}^{iH_0\tau}\mathrm{e}^{-D}\mathrm{e}^{-\bar{C}}\tilde{\Gamma}_\tau \mathrm{e}^C\mathrm{e}^D\mathrm{e}^{-iH_0\tau}\rangle \\
&= \langle X_3^\dagger \left[\mathrm{e}^{iH_0\tau}\mathrm{e}^{-D}\mathrm{e}^{-C}\mathrm{e}^{\bar{C}}\mathrm{e}^D\mathrm{e}^{-iH_0\tau}\right]^\dagger \left[\mathrm{e}^{iH_0\tau}\mathrm{e}^{-D}\mathrm{e}^{-C}\mathrm{e}^{\bar{C}}\mathrm{e}^D\mathrm{e}^{-iH_0\tau}\right] X_3\rangle \\
&\leq \|\mathrm{e}^{iH_0\tau}\mathrm{e}^{-D}\mathrm{e}^{-C}\mathrm{e}^{\bar{C}}\mathrm{e}^D\mathrm{e}^{-iH_0\tau}\|^2 \langle X_3^\dagger X_3\rangle \\
&= \|\mathrm{e}^{-D}\mathrm{e}^{-C}\mathrm{e}^{\bar{C}}\mathrm{e}^D\|^2 \langle X_3^\dagger X_3\rangle\,,
\end{aligned}
\tag{80}
$$

where $X_3 = \mathrm{e}^{iH_0\tau}\mathrm{e}^{-D}\mathrm{e}^{-\bar{C}}\tilde{\Gamma}_\tau \mathrm{e}^C\mathrm{e}^D\mathrm{e}^{-iH_0\tau}$ and $[H_0, C] = [H_0, D] = 0$, Inequality 1 and Equality 1 have been used. Because of $\mathrm{e}^{-\bar{C}}\tilde{\Gamma}_\tau \mathrm{e}^C = \mathrm{e}^{-iH_0\tau}\Gamma_\tau \mathrm{e}^{-\bar{C}}\mathrm{e}^C\mathrm{e}^{iH_0\tau}$, one has $X_3 = \mathrm{e}^{-D}\Gamma_\tau \mathrm{e}^{-\bar{C}}\mathrm{e}^C\mathrm{e}^D$ and, thus,

$$
G_2(\xi_j, \eta_{j\alpha}; B) \leq \|\mathrm{e}^{-D}\mathrm{e}^{-C}\mathrm{e}^{\bar{C}}\mathrm{e}^D\|^2 \langle \mathrm{e}^D\mathrm{e}^C\mathrm{e}^{-\bar{C}}\Gamma_\tau^\dagger \mathrm{e}^{-2D}\Gamma_\tau \mathrm{e}^{-\bar{C}}\mathrm{e}^C\mathrm{e}^D\rangle\,.
\tag{81}
$$

Furthermore, Inequality 2 gives

$$
\begin{aligned}
\langle \mathrm{e}^D\mathrm{e}^C\mathrm{e}^{-\bar{C}}\Gamma_\tau^\dagger \mathrm{e}^{-2D}\Gamma_\tau \mathrm{e}^{-\bar{C}}\mathrm{e}^C\mathrm{e}^D\rangle &= \langle \left[\mathrm{e}^{-D}\mathrm{e}^{-\bar{C}}\mathrm{e}^C\mathrm{e}^D\right]^\dagger \mathrm{e}^D\Gamma_\tau^\dagger \mathrm{e}^{-2D}\Gamma_\tau \mathrm{e}^D\left[\mathrm{e}^{-D}\mathrm{e}^{-\bar{C}}\mathrm{e}^C\mathrm{e}^D\right]\rangle \\
&\leq \|\mathrm{e}^{-A}\left[\mathrm{e}^{-D}\mathrm{e}^{-\bar{C}}\mathrm{e}^C\mathrm{e}^D\right]^\dagger \mathrm{e}^A\|^2 \langle \mathrm{e}^D\Gamma_\tau^\dagger \mathrm{e}^{-2D}\Gamma_\tau \mathrm{e}^D\rangle\,.
\end{aligned}
\tag{82}
$$

Thus, $G_3(\xi_j, \eta_{j\alpha}; B) \equiv \langle \mathrm{e}^D\Gamma_\tau^\dagger \mathrm{e}^{-2D}\Gamma_\tau \mathrm{e}^D\rangle$ satisfies

$$
G_2(\xi_j, \eta_{j\alpha}; B) \leq \|\mathrm{e}^{-D}\mathrm{e}^{-C}\mathrm{e}^{\bar{C}}\mathrm{e}^D\|^2 \|\mathrm{e}^{-A}\left[\mathrm{e}^{-D}\mathrm{e}^{-\bar{C}}\mathrm{e}^C\mathrm{e}^D\right]^\dagger \mathrm{e}^A\|^2 G_3(\xi_j, \eta_{j\alpha}; B)\,.
\tag{83}
$$

Conversely, we have

$$
\begin{aligned}
G_3(\xi_j, \eta_{j\alpha}; B) &= \langle \left[ e^{-D} e^{-C} e^{\bar{C}} e^{D} \right]^{\dagger} e^{D} e^{C} e^{-\bar{C}} \Gamma_\tau^{\dagger} e^{-2D} \Gamma_\tau e^{-\bar{C}} e^{C} e^{D} \left[ e^{-D} e^{-C} e^{\bar{C}} e^{D} \right] \rangle \\
&\leq \| e^{-A} \left[ e^{-D} e^{-C} e^{\bar{C}} e^{D} \right]^{\dagger} e^{A} \|^2 \langle e^{D} e^{C} e^{-\bar{C}} \Gamma_\tau^{\dagger} e^{-2D} \Gamma_\tau e^{-\bar{C}} e^{C} e^{D} \rangle \\
&= \| e^{-A} \left[ e^{-D} e^{-C} e^{\bar{C}} e^{D} \right]^{\dagger} e^{A} \|^2 \langle X_3^{\dagger} X_3 \rangle \, ,
\end{aligned}
\tag{84}
$$

where we have used Inequality 2. Let $Y_3 = e^{iH_0\tau} e^{-D} e^{-\bar{C}} e^{C} e^{D} e^{-iH_0\tau}$, then Inequality 1 and Equality 1 lead to

$$
\begin{aligned}
\langle X_3^{\dagger} X_3 \rangle &= \langle X_3^{\dagger} \left[ e^{iH_0\tau} e^{-D} e^{-C} e^{\bar{C}} e^{D} e^{-iH_0\tau} \right]^{\dagger} Y_3^{\dagger} Y_3 \left[ e^{iH_0\tau} e^{-D} e^{-C} e^{\bar{C}} e^{D} e^{-iH_0\tau} \right] X_3 \rangle \\
&\leq \| Y_3 \|^2 \langle X_3^{\dagger} \left[ e^{iH_0\tau} e^{-D} e^{-C} e^{\bar{C}} e^{D} e^{-iH_0\tau} \right]^{\dagger} \left[ e^{iH_0\tau} e^{-D} e^{-C} e^{\bar{C}} e^{D} e^{-iH_0\tau} \right] X_3 \rangle \\
&= \| e^{iH_0\tau} e^{-D} e^{-\bar{C}} e^{C} e^{D} e^{-iH_0\tau} \|^2 G_2(\xi_j, \eta_{j\alpha}; B) \\
&= \| e^{-D} e^{-\bar{C}} e^{C} e^{D} \|^2 G_2(\xi_j, \eta_{j\alpha}; B) \, .
\end{aligned}
\tag{85}
$$

Thus,

$$
\frac{G_3(\xi_j, \eta_{j\alpha}; B)}{\| e^{-A} \left[ e^{-D} e^{-C} e^{\bar{C}} e^{D} \right]^{\dagger} e^{A} \|^2 \| e^{-D} e^{-\bar{C}} e^{C} e^{D} \|^2} \leq G_2(\xi_j, \eta_{j\alpha}; B) \, .
\tag{86}
$$

**Step 4:**
From Steps 1 to 3, in terms of

$$
L = \frac{1}{\| e^{-\bar{C}-D} \Gamma_f^{\dagger} e^{C+D} \|^2 \| e^{-A} e^{C+D} \Gamma_i(-t_0) e^{-C-D} e^{A} \|^2 \| e^{-A} \left[ e^{-D} e^{-C} e^{\bar{C}} e^{D} \right]^{\dagger} e^{A} \|^2 \| e^{-D} e^{-\bar{C}} e^{C} e^{D} \|^2} \, ,
\tag{87}
$$

$$
K = \| e^{-D} e^{-C} e^{\bar{C}} e^{D} \|^2 \| e^{-A} \left[ e^{-D} e^{-\bar{C}} e^{C} e^{D} \right]^{\dagger} e^{A} \|^2 \| e^{-A} e^{C+D} \Gamma_i(-t_0)^{\dagger} e^{-C-D} e^{A} \|^2 \| e^{-C-D} \Gamma_f \, e^{C+D} \|^2 \, ,
\tag{88}
$$

we have

$$
L \, G_3(\xi_j, \eta_{j\alpha}; B) \leq G(\xi_j, \eta_{j\alpha}; B) \leq K \, G_3(\xi_j, \eta_{j\alpha}; B) \, .
\tag{89}
$$

Note that the constants $L$ and $K$ are independent of $\tau$ and that $G_3(\xi_j, \eta_{j\alpha}; B)$ is a function only of $\xi_1 - \xi_2$ and $\eta_{1\alpha} - \eta_{2\alpha}$ since the operator $D$ depends only on them.

**Step 5:**
We have here to notice that all the norms appearing in Eqs. (87) and (88) are bounded by constants independent of the reservoir volumes $\Omega$ if the interaction operator $V(t)$ has a finite norm. For instance, the operator $\Gamma_i(-t_0) = e^{-iH_0 t_0} \mathrm{T} \exp \left[ -i \int_0^{t_0} e^{iH_0 s} V(s) e^{-iH_0 s} ds \right] e^{iH_0 t_0}$ defined with the time-ordered exponential 'T exp' is unitary and its norm is thus equal to unity [54]. Moreover, $e^{-C-D}$ is $O(e^{\mp\Omega})$ if $e^{C+D}$ is $O(e^{\pm\Omega})$ so that the product $e^{C+D} \Gamma_i(-t_0) e^{-C-D}$ is independent of $\Omega$ and has a finite norm in the large-system limit. By similar arguments, all the norms in Eqs. (87) and (88) are found to be independent of $\Omega$. Reservoirs of arbitrarily large size can thus be considered in parallel with arbitrarily long interaction time in order to achieve a steady state.

Accordingly, if the following limit exists

$$
Q(\xi_j, \eta_{j\alpha}; B) \equiv -\lim_{\mathcal{T} \to \infty} \frac{1}{\mathcal{T}} \ln G(\xi_j, \eta_{j\alpha}; B) \, ,
\tag{90}
$$

one has

$$
\begin{aligned}
Q(\xi_j, \eta_{j\alpha}; B) &= -\lim_{\mathcal{T} \to \infty} \frac{1}{\mathcal{T}} \ln G(\xi_j, \eta_{j\alpha}; B) + \lim_{\mathcal{T} \to \infty} \frac{1}{\mathcal{T}} \ln L \\
&\leq -\lim_{\mathcal{T} \to \infty} \frac{1}{\mathcal{T}} \ln G_3(\xi_j, \eta_{j\alpha}; B) \\
&\leq -\lim_{\mathcal{T} \to \infty} \frac{1}{\mathcal{T}} \ln G(\xi_j, \eta_{j\alpha}; B) + \lim_{\mathcal{T} \to \infty} \frac{1}{\mathcal{T}} \ln K = Q(\xi_j, \eta_{j\alpha}; B) \, .
\end{aligned}
\tag{91}
$$

In short, we have shown:

$$Q(\xi_j, \eta_{j\alpha}; B) = -\lim_{\mathcal{T} \to \infty} \frac{1}{\mathcal{T}} \ln G_3(\xi_j, \eta_{j\alpha}; B) = -\lim_{\mathcal{T} \to \infty} \frac{1}{\mathcal{T}} \ln \langle e^D \Gamma_\tau^\dagger e^{-D} e^{-D} \Gamma_\tau e^D \rangle . \tag{92}$$

The left-most term only contains $D$, which is a function only of $\xi_1 - \xi_2$ and $\eta_{1\alpha} - \eta_{2\alpha}$, or

$$Q(\xi_j, \eta_{j\alpha}; B) = \widetilde{Q}(\xi_1 - \xi_2, \eta_{1\alpha} - \eta_{2\alpha}; B) . \tag{93}$$

*Q.E.D.*

## E. Generalization

The previous results can be generalized to the case of $r > 2$ reservoirs. In this case, the proposition (47) is that the generating function is a function

$$Q(\xi_j, \eta_{j\alpha}; B) = \widetilde{Q}(\tilde{\xi}_j, \tilde{\eta}_{j\alpha}; B) , \tag{94}$$

depending only on the independent parameters:

$$\tilde{\xi}_j \equiv \xi_j - \frac{1}{r} \sum_{k=1}^r \xi_k , \tag{95}$$

$$\tilde{\eta}_{j\alpha} \equiv \eta_{j\alpha} - \frac{1}{r} \sum_{k=1}^r \eta_{k\alpha} , \tag{96}$$

with $j = 1, 2, ..., r - 1$. The proof is similar as in the case $r = 2$ with the operators:

$$2C = \frac{1}{r} \sum_{k=1}^r \left( \xi_k H_0 + \sum_\alpha \eta_{k\alpha} N_{0\alpha} \right) , \tag{97}$$

$$2D = \sum_{k=1}^r \left( \tilde{\xi}_k H_k + \sum_\alpha \tilde{\eta}_{k\alpha} N_{k\alpha} \right) , \tag{98}$$

replacing Eqs. (63)-(64), where $H_0 = \sum_{k=1}^r H_k$ and $N_{0\alpha} = \sum_{k=1}^r N_{k\alpha}$.

In the general case, the fluctuation theorem should read

$$\tilde{Q}(\tilde{\xi}_j, \tilde{\eta}_{j\alpha}; B) = \tilde{Q}(\tilde{A}_{j0} - \tilde{\xi}_j, \tilde{A}_{j\alpha} - \tilde{\eta}_{j\alpha}; -B) , \tag{99}$$

in terms of the independent affinities

$$\tilde{A}_{j0} \equiv \beta_j - \frac{1}{r} \sum_{k=1}^r \beta_k , \tag{100}$$

$$\tilde{A}_{j\alpha} \equiv -\beta_j \mu_{j\alpha} + \frac{1}{r} \sum_{k=1}^r \beta_k \mu_{k\alpha} , \qquad \text{for} \quad \alpha = 1, 2, ..., c, \tag{101}$$

with $j = 1, 2, ..., r - 1$.

## V. SYMMETRY RELATIONS FOR THE RESPONSE COEFFICIENTS

### A. Fluctuation theorem and response coefficients

If we gather the independent parameters and affinities in the case of $r = 2$ reservoirs as

$$\boldsymbol{\lambda} = \{\xi_1 - \xi_2, \eta_{1\alpha} - \eta_{2\alpha}\} , \tag{102}$$

$$\boldsymbol{A} = \{A_0, A_\alpha\} , \tag{103}$$

or in the general case of $r > 2$ reservoirs as

$$\boldsymbol{\lambda} = \{\tilde{\xi}_j, \tilde{\eta}_{j\alpha}\} \,, \tag{104}$$

$$\boldsymbol{A} = \{\tilde{A}_{j0}, \tilde{A}_{j\alpha}\} \,, \tag{105}$$

with $\alpha = 1, 2, ..., c$ and $j = 1, 2, ..., r - 1$, the fluctuation theorem (54) reads

$$\widetilde{Q}(\boldsymbol{\lambda}, \boldsymbol{A}; B) = \widetilde{Q}(\boldsymbol{A} - \boldsymbol{\lambda}, \boldsymbol{A}; -B) \,, \tag{106}$$

where we have explicitly written the dependence of the generating function on the affinities defining the nonequilibrium steady state.

The idea is to differentiate successively the fluctuation theorem with respect to both $\boldsymbol{\lambda}$ and $\boldsymbol{A}$ to obtain symmetry relations for the linear and nonlinear response coefficients as well as further coefficients characterizing the statistics of the current fluctuations [21].

On the one hand, the mean currents can be obtained from the generating function and, on the other hand, expanded in powers of the affinities:

$$J_\alpha(B) \equiv \frac{\partial \widetilde{Q}}{\partial \lambda_\alpha}(\boldsymbol{0}, \boldsymbol{A}; B) = \sum_\beta L_{\alpha,\beta}(B) A_\beta + \frac{1}{2} \sum_{\beta,\gamma} M_{\alpha,\beta\gamma}(B) A_\beta A_\gamma + \frac{1}{6} \sum_{\beta,\gamma,\delta} N_{\alpha,\beta\gamma\delta}(B) A_\beta A_\gamma A_\delta + \cdots \,, \tag{107}$$

which defines the response coefficients:

$$L_{\alpha,\beta}(B) \equiv \frac{\partial^2 \widetilde{Q}}{\partial \lambda_\alpha \partial A_\beta}(\boldsymbol{0}, \boldsymbol{0}; B) \,, \tag{108}$$

$$M_{\alpha,\beta\gamma}(B) \equiv \frac{\partial^3 \widetilde{Q}}{\partial \lambda_\alpha \partial A_\beta \partial A_\gamma}(\boldsymbol{0}, \boldsymbol{0}; B) \,, \tag{109}$$

$$N_{\alpha,\beta\gamma\delta}(B) \equiv \frac{\partial^4 \widetilde{Q}}{\partial \lambda_\alpha \partial A_\beta \partial A_\gamma \partial A_\delta}(\boldsymbol{0}, \boldsymbol{0}; B) \,, \tag{110}$$

$$\ldots$$

around the state of thermodynamic equilibrium.

We notice that, if we set $\boldsymbol{\lambda} = \boldsymbol{0}$ in the fluctuation theorem (54), we obtain the identities

$$\widetilde{Q}(\boldsymbol{0}, \boldsymbol{A}; B) = 0 \,, \tag{111}$$

$$\widetilde{Q}(\boldsymbol{A}, \boldsymbol{A}; -B) = 0 \,. \tag{112}$$

The former is a condition of normalization and the latter a condition of global detailed balancing which is a consequence of the fluctuation theorem (54) but may be assumed for itself as a weaker property than the fluctuation theorem [55]. On the other hand, the generating function of the cumulants of the fluctuating currents at equilibrium satisfies

$$\widetilde{Q}(\boldsymbol{\lambda}, \boldsymbol{0}; B) = \widetilde{Q}(-\boldsymbol{\lambda}, \boldsymbol{0}; -B) \,, \tag{113}$$

obtained from the fluctuation theorem (54) at the equilibrium $\boldsymbol{A} = \boldsymbol{0}$.

We start by differentiating the fluctuation theorem with respect to the generating parameters $\{\lambda_\alpha\}$ and also the affinities $\{A_\alpha\}$ to get

$$\frac{\partial \widetilde{Q}}{\partial \lambda_\alpha}(\boldsymbol{\lambda}, \boldsymbol{A}; B) = -\frac{\partial \widetilde{Q}}{\partial \lambda_\alpha}(\boldsymbol{A} - \boldsymbol{\lambda}, \boldsymbol{A}; -B) \,, \tag{114}$$

$$\frac{\partial \widetilde{Q}}{\partial A_\alpha}(\boldsymbol{\lambda}, \boldsymbol{A}; B) = \frac{\partial \widetilde{Q}}{\partial \lambda_\alpha}(\boldsymbol{A} - \boldsymbol{\lambda}, \boldsymbol{A}; -B) + \frac{\partial \widetilde{Q}}{\partial A_\alpha}(\boldsymbol{A} - \boldsymbol{\lambda}, \boldsymbol{A}; -B) \,. \tag{115}$$

We set $\boldsymbol{\lambda} = \boldsymbol{0}$ in Eq. (115), use the conditions (111)-(112), and set $\boldsymbol{A} = \boldsymbol{0}$ to get

$$\frac{\partial \widetilde{Q}}{\partial \lambda_\alpha}(\boldsymbol{0}, \boldsymbol{0}; B) = 0 \,, \tag{116}$$

$$\frac{\partial \widetilde{Q}}{\partial A_\alpha}(\boldsymbol{0}, \boldsymbol{0}; B) = 0 \,, \tag{117}$$

from Eqs. (114)-(115), which shows in particular that the mean currents vanish at equilibrium.

## B. Onsager-Casimir reciprocity relations and Green-Kubo formulas

Now, we differentiate Eq. (114) with respect to $\lambda_\beta$ to obtain

$$\frac{\partial^2 \widetilde{Q}}{\partial \lambda_\alpha \partial \lambda_\beta}(\boldsymbol{\lambda}, \boldsymbol{A}; B) = \frac{\partial^2 \widetilde{Q}}{\partial \lambda_\alpha \partial \lambda_\beta}(\boldsymbol{A} - \boldsymbol{\lambda}, \boldsymbol{A}; -B) . \tag{118}$$

Setting $\boldsymbol{\lambda} = \boldsymbol{A} = \boldsymbol{0}$, we find the identity

$$\frac{\partial^2 \widetilde{Q}}{\partial \lambda_\alpha \partial \lambda_\beta}(\boldsymbol{0}, \boldsymbol{0}; B) = \frac{\partial^2 \widetilde{Q}}{\partial \lambda_\alpha \partial \lambda_\beta}(\boldsymbol{0}, \boldsymbol{0}; -B) , \tag{119}$$

for the second-order cumulant of the current fluctuations at equilibrium.

If we differentiate Eq. (114) with respect to $A_\beta$, we get

$$\frac{\partial^2 \widetilde{Q}}{\partial \lambda_\alpha \partial A_\beta}(\boldsymbol{\lambda}, \boldsymbol{A}; B) = -\frac{\partial^2 \widetilde{Q}}{\partial \lambda_\alpha \partial \lambda_\beta}(\boldsymbol{A} - \boldsymbol{\lambda}, \boldsymbol{A}; -B) - \frac{\partial^2 \widetilde{Q}}{\partial \lambda_\alpha \partial A_\beta}(\boldsymbol{A} - \boldsymbol{\lambda}, \boldsymbol{A}; -B) , \tag{120}$$

which reduces to

$$L_{\alpha,\beta}(B) = -\frac{\partial^2 \widetilde{Q}}{\partial \lambda_\alpha \partial \lambda_\beta}(\boldsymbol{0}, \boldsymbol{0}; B) - L_{\alpha,\beta}(-B) , \tag{121}$$

for $\boldsymbol{\lambda} = \boldsymbol{A} = \boldsymbol{0}$.

The differentiation of Eq. (115) with respect to $A_\beta$ leads to

$$\frac{\partial^2 \widetilde{Q}}{\partial A_\alpha \partial A_\beta}(\boldsymbol{\lambda}, \boldsymbol{A}; B) = \frac{\partial^2 \widetilde{Q}}{\partial \lambda_\alpha \partial \lambda_\beta}(\boldsymbol{A} - \boldsymbol{\lambda}, \boldsymbol{A}; -B) + \frac{\partial^2 \widetilde{Q}}{\partial \lambda_\alpha \partial A_\beta}(\boldsymbol{A} - \boldsymbol{\lambda}, \boldsymbol{A}; -B)$$
$$+ \frac{\partial^2 \widetilde{Q}}{\partial A_\alpha \partial \lambda_\beta}(\boldsymbol{A} - \boldsymbol{\lambda}, \boldsymbol{A}; -B) + \frac{\partial^2 \widetilde{Q}}{\partial A_\alpha \partial A_\beta}(\boldsymbol{A} - \boldsymbol{\lambda}, \boldsymbol{A}; -B) . \tag{122}$$

Using Eqs. (111) and (112) in the limit $\boldsymbol{\lambda} = \boldsymbol{A} = \boldsymbol{0}$, we have

$$0 = \frac{\partial^2 \widetilde{Q}}{\partial \lambda_\alpha \partial \lambda_\beta}(\boldsymbol{0}, \boldsymbol{0}; -B) + L_{\alpha,\beta}(-B) + L_{\beta,\alpha}(-B) . \tag{123}$$

We recover the formulas of Green-Kubo type in the case $\alpha = \beta$ [57]:

$$L_{\alpha,\alpha}(B) = -\frac{1}{2}\frac{\partial^2 \widetilde{Q}}{\partial \lambda_\alpha^2}(\boldsymbol{0}, \boldsymbol{0}; B) . \tag{124}$$

Combining Eq. (123) with Eq. (121), we finally find the Onsager-Casimir reciprocity relations:

$$L_{\alpha,\beta}(B) = L_{\beta,\alpha}(-B) . \tag{125}$$

We notice that Eq. (121) leading to the Onsager-Casimir relation requires the link established by the fluctuation theorem (54) between the variables $\boldsymbol{\lambda}$ and $\boldsymbol{A}$ and does not result from Eqs. (111), (112), and (113) alone.

## C. Symmetry relations at 2nd order

We proceed in a similar way to obtain relations for second-order response coefficients. The differentiation of Eq. (118) with respect to $\lambda_\gamma$ gives

$$\frac{\partial^3 \widetilde{Q}}{\partial \lambda_\alpha \partial \lambda_\beta \partial \lambda_\gamma}(\boldsymbol{\lambda}, \boldsymbol{A}; B) = -\frac{\partial^3 \widetilde{Q}}{\partial \lambda_\alpha \partial \lambda_\beta \partial \lambda_\gamma}(\boldsymbol{A} - \boldsymbol{\lambda}, \boldsymbol{A}; -B) , \tag{126}$$

which reduces to

$$\frac{\partial^3 \widetilde{Q}}{\partial \lambda_\alpha \partial \lambda_\beta \partial \lambda_\gamma}(\boldsymbol{0}, \boldsymbol{0}; B) = -\frac{\partial^3 \widetilde{Q}}{\partial \lambda_\alpha \partial \lambda_\beta \partial \lambda_\gamma}(\boldsymbol{0}, \boldsymbol{0}; -B) , \tag{127}$$

for $\boldsymbol{\lambda} = \boldsymbol{A} = \boldsymbol{0}$.

On the other hand, the differentiation of Eq. (118) with respect to $A_\gamma$ gives

$$\frac{\partial^3 \widetilde{Q}}{\partial \lambda_\alpha \partial \lambda_\beta \partial A_\gamma}(\boldsymbol{\lambda}, \boldsymbol{A}; B) = \frac{\partial^3 \widetilde{Q}}{\partial \lambda_\alpha \partial \lambda_\beta \partial \lambda_\gamma}(\boldsymbol{A} - \boldsymbol{\lambda}, \boldsymbol{A}; -B) + \frac{\partial^3 \widetilde{Q}}{\partial \lambda_\alpha \partial \lambda_\beta \partial A_\gamma}(\boldsymbol{A} - \boldsymbol{\lambda}, \boldsymbol{A}; -B) \ . \tag{128}$$

Here, we introduce the coefficients

$$R_{\alpha\beta,\gamma}(B) \equiv -\frac{\partial^3 \widetilde{Q}}{\partial \lambda_\alpha \partial \lambda_\beta \partial A_\gamma}(\boldsymbol{0}, \boldsymbol{0}; B) \ , \tag{129}$$

which characterizes the nonequilibrium response of the second cumulants of the current fluctuations. Setting $\boldsymbol{\lambda} = \boldsymbol{A} = \boldsymbol{0}$ in Eq. (128) leads to the relation

$$R_{\alpha\beta,\gamma}(B) - R_{\alpha\beta,\gamma}(-B) = \frac{\partial^3 \widetilde{Q}}{\partial \lambda_\alpha \partial \lambda_\beta \partial \lambda_\gamma}(\boldsymbol{0}, \boldsymbol{0}; B) \ . \tag{130}$$

Now, if we differentiate Eq. (120) with respect to $A_\gamma$, we get

$$\begin{aligned}
\frac{\partial^3 \widetilde{Q}}{\partial \lambda_\alpha \partial A_\beta \partial A_\gamma}(\boldsymbol{\lambda}, \boldsymbol{A}; B) = & -\frac{\partial^3 \widetilde{Q}}{\partial \lambda_\alpha \partial \lambda_\beta \partial \lambda_\gamma}(\boldsymbol{A} - \boldsymbol{\lambda}, \boldsymbol{A}; -B) - \frac{\partial^3 \widetilde{Q}}{\partial \lambda_\alpha \partial \lambda_\beta \partial A_\gamma}(\boldsymbol{A} - \boldsymbol{\lambda}, \boldsymbol{A}; -B) \\
& -\frac{\partial^3 \widetilde{Q}}{\partial \lambda_\alpha \partial A_\beta \partial \lambda_\gamma}(\boldsymbol{A} - \boldsymbol{\lambda}, \boldsymbol{A}; -B) - \frac{\partial^3 \widetilde{Q}}{\partial \lambda_\alpha \partial A_\beta \partial A_\gamma}(\boldsymbol{A} - \boldsymbol{\lambda}, \boldsymbol{A}; -B) \ ,
\end{aligned} \tag{131}$$

whereupon we find for $\boldsymbol{\lambda} = \boldsymbol{A} = \boldsymbol{0}$ that

$$M_{\alpha,\beta\gamma}(B) + M_{\alpha,\beta\gamma}(-B) = R_{\alpha\beta,\gamma}(-B) + R_{\alpha\gamma,\beta}(-B) + \frac{\partial^3 \widetilde{Q}}{\partial \lambda_\alpha \partial \lambda_\beta \partial \lambda_\gamma}(\boldsymbol{0}, \boldsymbol{0}; B) \ , \tag{132}$$

involving the second-order response coefficient (109).

We end with the differentiation of Eq. (122) with respect to $A_\gamma$ to obtain

$$\begin{aligned}
\frac{\partial^3 \widetilde{Q}}{\partial A_\alpha \partial A_\beta \partial A_\gamma}(\boldsymbol{\lambda}, \boldsymbol{A}; B) = & \ \frac{\partial^3 \widetilde{Q}}{\partial \lambda_\alpha \partial \lambda_\beta \partial \lambda_\gamma}(\boldsymbol{A} - \boldsymbol{\lambda}, \boldsymbol{A}; -B) + \frac{\partial^3 \widetilde{Q}}{\partial \lambda_\alpha \partial \lambda_\beta \partial A_\gamma}(\boldsymbol{A} - \boldsymbol{\lambda}, \boldsymbol{A}; -B) \\
& + \frac{\partial^3 \widetilde{Q}}{\partial \lambda_\alpha \partial A_\beta \partial \lambda_\gamma}(\boldsymbol{A} - \boldsymbol{\lambda}, \boldsymbol{A}; -B) + \frac{\partial^3 \widetilde{Q}}{\partial \lambda_\alpha \partial A_\beta \partial A_\gamma}(\boldsymbol{A} - \boldsymbol{\lambda}, \boldsymbol{A}; -B) \\
& + \frac{\partial^3 \widetilde{Q}}{\partial A_\alpha \partial \lambda_\beta \partial \lambda_\gamma}(\boldsymbol{A} - \boldsymbol{\lambda}, \boldsymbol{A}; -B) + \frac{\partial^3 \widetilde{Q}}{\partial A_\alpha \partial \lambda_\beta \partial A_\gamma}(\boldsymbol{A} - \boldsymbol{\lambda}, \boldsymbol{A}; -B) \\
& + \frac{\partial^3 \widetilde{Q}}{\partial A_\alpha \partial A_\beta \partial \lambda_\gamma}(\boldsymbol{A} - \boldsymbol{\lambda}, \boldsymbol{A}; -B) + \frac{\partial^3 \widetilde{Q}}{\partial A_\alpha \partial A_\beta \partial A_\gamma}(\boldsymbol{A} - \boldsymbol{\lambda}, \boldsymbol{A}; -B) \ .
\end{aligned} \tag{133}$$

Taking $\boldsymbol{\lambda} = \boldsymbol{A} = \boldsymbol{0}$ therein, we deduce

$$M_{\alpha,\beta\gamma}(B) + M_{\beta,\gamma\alpha}(B) + M_{\gamma,\alpha\beta}(B) = R_{\alpha\beta,\gamma}(B) + R_{\beta\gamma,\alpha}(B) + R_{\gamma\alpha,\beta}(B) - \frac{\partial^3 \widetilde{Q}}{\partial \lambda_\alpha \partial \lambda_\beta \partial \lambda_\gamma}(\boldsymbol{0}, \boldsymbol{0}; B) \ . \tag{134}$$

We notice that this relation is the consequence of the weaker condition of global detailed balancing (112) alone and could hold even though the fluctuation theorem (54) does not as recently shown in Ref. [55] where the versions of Eq. (134), which are (anti)symmetrized with respect to the magnetic field, appear with the notations $M_{\alpha,\beta\gamma} = (k_\mathrm{B}T)^2 G^{(2)}_{\alpha,\beta\gamma}$, $R_{\alpha\beta,\gamma} = k_\mathrm{B}T S^{(1)}_{\alpha\beta,\gamma}$, and $\frac{\partial^3 \widetilde{Q}}{\partial \lambda_\alpha \partial \lambda_\beta \partial \lambda_\gamma}(\boldsymbol{0}, \boldsymbol{0}; B) = C^{(0)}_{\alpha\beta\gamma}$. We point out that, on the other hand, Eqs. (130) and (132) are consequences of microreversibility and the stronger fluctuation theorem, as it is the case for the Onsager-Casimir reciprocity relations.

Combining Eq. (130) with Eqs. (132) and (134) yields [57]

$$M_{\alpha,\beta\gamma}(B) + M_{\alpha,\beta\gamma}(-B) = R_{\alpha\beta,\gamma}(B) + R_{\alpha\gamma,\beta}(-B) \, , \tag{135}$$

$$M_{\alpha,\beta\gamma}(B) + M_{\beta,\gamma\alpha}(B) + M_{\gamma,\alpha\beta}(B) = R_{\alpha\beta,\gamma}(-B) + R_{\beta\gamma,\alpha}(B) + R_{\gamma\alpha,\beta}(B) \, , \tag{136}$$

but no further reduction can be deduced from the fluctuation theorem and, in particular, Eq. (130) does not vanish in general.

If the magnetic field vanishes $B = 0$, Eqs. (127), (132), and (134) reduce to the relations [57]

$$\frac{\partial^3 \widetilde{Q}}{\partial\lambda_\alpha \partial\lambda_\beta \partial\lambda_\gamma}(\mathbf{0},\mathbf{0};0) = 0 \, , \tag{137}$$

$$M_{\alpha,\beta\gamma}(0) = \frac{1}{2}\left[R_{\alpha\beta,\gamma}(0) + R_{\alpha\gamma,\beta}(0)\right] \, , \tag{138}$$

$$M_{\alpha,\beta\gamma}(0) + M_{\beta,\gamma\alpha}(0) + M_{\gamma,\alpha\beta}(0) = R_{\alpha\beta,\gamma}(0) + R_{\beta\gamma,\alpha}(0) + R_{\gamma\alpha,\beta}(0) \, . \tag{139}$$

where Eq. (138) was previously deduced as the consequence of the fluctuation theorem [22, 53].

## D.   Symmetry relations at 3rd order

Besides the third-order response coefficient (110), we introduce the coefficients

$$S_{\alpha\beta\gamma,\delta}(B) \equiv \frac{\partial^4 \widetilde{Q}}{\partial\lambda_\alpha \partial\lambda_\beta \partial\lambda_\gamma \partial A_\delta}(\mathbf{0},\mathbf{0};B) \tag{140}$$

and

$$T_{\alpha\beta,\gamma\delta}(B) \equiv -\frac{\partial^4 \widetilde{Q}}{\partial\lambda_\alpha \partial\lambda_\beta \partial A_\gamma \partial A_\delta}(\mathbf{0},\mathbf{0};B) \, , \tag{141}$$

characterizing the nonequilibrium responses of respectively the second and third cumulants of the current fluctuations.

We continue the deduction by further differentiating the relations of the previous subsection with respect to $\lambda_\delta$ or $A_\delta$ at $\boldsymbol{\lambda} = \boldsymbol{A} = \mathbf{0}$. We find successively from Eq. (126):

$$\frac{\partial^4 \widetilde{Q}}{\partial\lambda_\alpha \partial\lambda_\beta \partial\lambda_\gamma \partial\lambda_\delta}(\mathbf{0},\mathbf{0};B) = \frac{\partial^4 \widetilde{Q}}{\partial\lambda_\alpha \partial\lambda_\beta \partial\lambda_\gamma \partial\lambda_\delta}(\mathbf{0},\mathbf{0};-B) \tag{142}$$

and

$$S_{\alpha\beta\gamma,\delta}(B) + S_{\alpha\beta\gamma,\delta}(-B) = -\frac{\partial^4 \widetilde{Q}}{\partial\lambda_\alpha \partial\lambda_\beta \partial\lambda_\gamma \partial\lambda_\delta}(\mathbf{0},\mathbf{0};B) \, , \tag{143}$$

from Eq. (128):

$$T_{\alpha\beta,\gamma\delta}(B) - T_{\alpha\beta,\gamma\delta}(-B) = S_{\alpha\beta\gamma,\delta}(B) - S_{\alpha\beta\delta,\gamma}(-B) \, , \tag{144}$$

from Eq. (131):

$$\begin{aligned} N_{\alpha,\beta\gamma\delta}(B) + N_{\alpha,\beta\gamma\delta}(-B) &= T_{\alpha\beta,\gamma\delta}(-B) + T_{\alpha\gamma,\beta\delta}(-B) + T_{\alpha\delta,\beta\gamma}(-B) \\ &\quad - S_{\alpha\beta\gamma,\delta}(-B) - S_{\alpha\beta\delta,\gamma}(-B) - S_{\alpha\gamma\delta,\beta}(-B) \\ &\quad - \frac{\partial^4 \widetilde{Q}}{\partial\lambda_\alpha \partial\lambda_\beta \partial\lambda_\gamma \partial\lambda_\delta}(\mathbf{0},\mathbf{0};B) \, , \end{aligned} \tag{145}$$

and from Eq. (133):

$$\begin{aligned} & N_{\alpha,\beta\gamma\delta}(B) + N_{\beta,\gamma\delta\alpha}(B) + N_{\gamma,\delta\alpha\beta}(B) + N_{\delta,\alpha\beta\gamma}(B) \\ &= T_{\alpha\beta,\gamma\delta}(B) + T_{\alpha\gamma,\beta\delta}(B) + T_{\alpha\delta,\beta\gamma}(B) + T_{\beta\gamma,\alpha\delta}(B) + T_{\beta\delta,\alpha\gamma}(B) + T_{\gamma\delta,\alpha\beta}(B) \\ &\quad - S_{\alpha\beta\gamma,\delta}(B) - S_{\beta\gamma\delta,\alpha}(B) - S_{\gamma\delta\alpha,\beta}(B) - S_{\delta\alpha\beta,\gamma}(B) \\ &\quad - \frac{\partial^4 \widetilde{Q}}{\partial\lambda_\alpha \partial\lambda_\beta \partial\lambda_\gamma \partial\lambda_\delta}(\mathbf{0},\mathbf{0};B) \, . \end{aligned} \tag{146}$$

This last relation is the consequence of the weaker condition of global detailed balancing in the same way as Eq. (134).

In the case of a vanishing magnetic field $B = 0$, Eqs. (143) and (145) reduce respectively to

$$S_{\alpha\beta\gamma,\delta}(0) = -\frac{1}{2}\frac{\partial^4 \widetilde{Q}}{\partial\lambda_\alpha\partial\lambda_\beta\partial\lambda_\gamma\partial\lambda_\delta}(\mathbf{0},\mathbf{0};0) \tag{147}$$

and

$$N_{\alpha,\beta\gamma\delta}(0) = \frac{1}{2}\left[T_{\alpha\beta,\gamma\delta}(0) + T_{\alpha\gamma,\beta\delta}(0) + T_{\alpha\delta,\beta\gamma}(0) - S_{\alpha\beta\gamma,\delta}(0)\right] , \tag{148}$$

which has been obtained elsewhere as a consequence of the fluctuation theorem [53].

## VI.  CONCLUSIONS

In this paper, a fluctuation theorem for the currents has been proved for open quantum systems reaching a nonequilibrium steady state in the long-time limit [56]. In the considered protocol, the heat and particle currents are defined in terms of the exchanges of energy and particles between reservoirs, as measured at the initial and final times when the reservoirs are decoupled.

We start from a general symmetry relation for the generating function of the exchanges of energy and particles, which is the consequence of the microreversibility guaranteed by the measurement protocol. This symmetry relation is expressed in terms of the temperatures and chemical potentials of the reservoirs. However, the fluctuation theorem for the currents requires a symmetry with respect to the thermodynamic forces or affinities which are given in terms of the *differences* of temperatures and chemical potentials.

We show that this symmetry indeed holds by proving that, in the long-time limit, the generating function only depends on the *differences* between the parameters corresponding to the different reservoirs. A steady state is reached if the interaction established by the subsystem coupling the reservoirs together remain constant over a lapse of time which is sufficiently long with respect to the transient time intervals associated with the initial switch on of the interaction and its final switch off. Although the generating function introduced by time-dependent protocols depends on the absolute values of the temperatures and chemical potentials, suitable inequalities allow us to relate it to an equivalent function which depends on the *differences* of temperatures and chemical potentials. The ratio of the generating function to the equivalent function is bounded by constants which are independent of the lapse of time during which the interaction is constant and, moreover, of the volumes of the reservoirs. Therefore, the lapse of time of constant interaction can be taken arbitrarily long and the reservoirs arbitrarily large to reach a steady state. Accordingly, the generating function of the currents has the symmetry of the fluctuation theorem with respect to the affinities characterizing the steady state. A rigorous proof is thus established for such steady-state fluctuation theorems as considered in the review [42].

As a consequence, the Onsager-Casimir reciprocity relations can be obtained for the linear response coefficients from the fluctuation theorem. Furthermore, generalizations of the reciprocity relations to the nonlinear response coefficients can also be deduced.

Finally, we notice that, besides the scheme based on two quantum measurements that we have here considered, another scheme can be envisaged where the currents of energy or particles are continuously monitored by ideal probes which are weakly coupled to the system. We hope to report on this further problem in a future publication.

[1] W. D. Oliver, J. Kim, R. C. Liu, and Y. Yamamoto, Science **284**, 299 (1999).
[2] T. Fujisawa, T. Hayashi, R. Tomita, and Y. Hirayama, Science **312**, 1634 (2006).

[3] S. Gustavsson, R. Leturcq, B. Simovič, R. Schleser, T. Ihn, P. Studerus, K. Ensslin, D. C. Driscoll, and A. C. Gossard, Phys. Rev. Lett. **96**, 076605 (2006).
[4] L. S. Levitov and G. B. Lesovik, Pis'ma Zh. Eksp. Teor. Fiz. **58**, 225 (1993) [JETP Lett. **58**, 230 (1993)].
[5] Yu. V. Nazarov and D. A. Bagrets, Phys. Rev. Lett. **88**, 196801 (2002).
[6] M. Kindermann, *Electron Counting Statistics in Nanostructures* (Ph. D. Thesis, University of Leiden, 2003).
[7] Yu. V. Nazarov, Ann. Phys. (Leipzig) **8**, 507 (1999).
[8] D. A. Bagrets and Yu. V. Nazarov, Phys. Rev. B **67**, 085316 (2003).
[9] Yu. V. Nazarov, Ann. Phys. (Leipzig) **16**, 720 (2007).
[10] K. E. Nagaev, Phys. Rev. B **66**, 075334 (2002).
[11] A. N. Jordan, E. V. Sukhorukov, and S. Pilgram, J. Math. Phys. **45**, 4386 (2004).
[12] J. Tobiska and Yu. V. Nazarov, Phys. Rev. B **72**, 235328 (2005).
[13] D. J. Evans, E. G. D. Cohen, and G. P. Morriss, Phys. Rev. Lett. **71**, 2401 (1993).
[14] G. Gallavotti and E. G. D. Cohen, Phys. Rev. Lett. **74**, 2694 (1995).
[15] G. Gallavotti, Phys. Rev. Lett. **77**, 4334 (1996).
[16] J. Kurchan, J. Phys. A: Math. Gen. **31**, 3719 (1998).
[17] J. L. Lebowitz and H. Spohn, J. Stat. Phys. **95**, 333 (1999).
[18] C. Maes, J. Stat. Phys. **95**, 367 (1999).
[19] C. Maes and K. Netočný, J. Stat. Phys. **110**, 269 (2003).
[20] B. Cleuren, C. Van den Broeck, and R. Kawai, Phys. Rev. E **74**, 021117 (2006).
[21] D. Andrieux and P. Gaspard, J. Chem. Phys. **121**, 6167 (2004); Erratum **125** 219902 (2006).
[22] D. Andrieux and P. Gaspard, J. Stat. Mech.: Th. Exp. P01011 (2006).
[23] D. Andrieux and P. Gaspard, J. Stat. Phys. **127**, 107 (2007).
[24] C. Jarzynski, Phys. Rev. Lett. **78**, 2690 (1997).
[25] G. E. Crooks, Phys. Rev. E **60**, 2721 (1999).
[26] R. Kawai, J. M. R. Parrondo, and C. Van den Broeck, Phys. Rev. Lett. **98**, 080602 (2007).
[27] M. F. Gelin and D. S. Kosov, Phys. Rev. E **78**, 011116 (2008).
[28] M. Esposito and K. Lindenberg, Phys. Rev. E **77**, 051119 (2008).
[29] J. Kurchan, *A quantum fluctuation theorem*, cond-mat/0007360.
[30] H. Tasaki, *Jarzynski relations for quantum systems and some applications*, cond-mat/0009244.
[31] T. Monnai, Phys. Rev. E **72**, 027102 (2005).
[32] T. Monnai and S. Tasaki, *Quantum correction of fluctuation theorem*, cond-mat/0308337.
[33] S. Mukamel, Phys. Rev. Lett. **90**, 170604 (2003).
[34] C. Jarzynski and D. K. Wójcik, Phys. Rev. Lett. **92**, 230602 (2004).
[35] W. De Roeck and C. Maes, Phys. Rev. E **69**, 026115 (2004).
[36] P. Talkner, E. Lutz, and P. Hänggi, Phys. Rev. E **75**, 050102R (2007).
[37] P. Talkner and P. Hänggi, J. Phys. A **40**, F569 (2007).
[38] M. Esposito and S. Mukamel, Phys. Rev. E **73**, 046129 (2006).
[39] U. Harbola, M. Esposito, and S. Mukamel, Phys. Rev. B **76**, 085408 (2007).
[40] M. Esposito, U. Harbola, and S. Mukamel, Phys. Rev. E **76**, 031132 (2007).
[41] M. Esposito, U. Harbola, and S. Mukamel, Phys. Rev. B **75**, 155316 (2007).
[42] M. Esposito, U. Harbola, and S. Mukamel, Rev. Mod. Phys. **81**, 1665 (2009).
[43] B. Cleuren and C. Van den Broeck, Europhys. Lett. **79**, 30001 (2007).
[44] K. Saito and A. Dhar, Phys. Rev. Lett. **99**, 180601 (2007).
[45] K. Saito and Y. Utsumi, Phys. Rev. B **78**, 115429 (2008).
[46] G. E. Crooks, J. Stat. Mech.: Th. Exp. P10023 (2008).
[47] P. Talkner, M. Campisi, and P. Hänggi, J. Stat. Mech.: Th. Exp. P02025 (2009).
[48] D. Andrieux and P. Gaspard, Phys. Rev. Lett. **100**, 230404 (2008).
[49] M. S. Green, J. Chem. Phys. **20**, 1281 (1952); **22**, 398 (1954).
[50] R. Kubo, J. Phys. Soc. Jpn. **12**, 570 (1957).
[51] L. Onsager, Phys. Rev. **37**, 405 (1931).
[52] H. B. G. Casimir, Rev. Mod. Phys. **17**, 343 (1945).
[53] D. Andrieux and P. Gaspard, J. Stat. Mech.: Th. Exp. P02006 (2007).
[54] O. Bratteli and D. W. Robinson, *Operator Algebras and Quantum Statistical Mechanics*, vols. 1 & 2 (Springer, Berlin, 2002), Corol. 2.3.4, Prop. 5.4.1.
[55] H. Förster and M. Büttiker, Phys. Rev. Lett. **101**, 136805 (2008).
[56] We obtained the symmetry relation (39) in March 2006 and the relations of Sec. V in April 2006, both for systems in a magnetic field. We finally established the connection between both thanks to the proposition (47) in June 2008.
[57] Erratum, New J. Phys. **11** (2009) 109802.