

Quantum fluctuation theorem for heat exchange in the strong coupling regime

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We study quantum heat exchange in a multistate impurity coupled to two thermal reservoirs. Allowing for strong system-bath interactions, we show that a steady-state heat-exchange fluctuation theorem holds, though the dynamical processes nonlinearly involve the two reservoirs. We accomplish a closed expression for the cumulant generating function, and use it to obtain the heat current and its cumulants in a nonlinear thermal junction, the two-bath spin-boson model.

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Exact fluctuation relations for nonequilibrium classical systems have been recently discovered and exemplified, dealing with work and entropy fluctuations in various (open, closed, driven) systems.¹ In particular, the fluctuation theorem (FT) for entropy production quantifies the probability of negative entropy generation, measuring “second law violation.”^{2,3} Both transient and steady-state fluctuation theorems (SSFTs) have been derived, where the latter measures entropy production in nonequilibrium steady-state systems over a long interval. In the context of heat exchange between two equilibrium reservoirs $\nu = L, R$, the SSFT can be roughly stated as $\ln[P_t(+\omega)/P_t(-\omega)] = \Delta\beta\omega$.^{4,5} Here $P_t(\omega)$ denotes the probability distribution of the net heat transfer ω , from L to R , over the (long) interval t , with $\Delta\beta = T_R^{-1} - T_L^{-1}$ as the difference between the inverse temperatures of the reservoirs. A related quantity is the cumulant generating function (CGF), providing general relations between transport coefficients under the FT symmetry.^{6,7}

Extending the work and heat FT to the quantum domain has recently attracted significant attention.^{7,8} Specifically, a quantum exchange FT, for the transfer of energy between two reservoirs maintained at different temperatures, has been derived in Refs. 4, 9, and 10 using projective measurements, and in Refs. 11 and 12, based on the unraveling of the quantum master equation (QME). These derivations assume that the interaction between the two thermal baths is weak, and can be neglected with respect to overall energy changes. Using the Keldysh approach, an exact analysis was carried out in Ref. 13. However, it is valid only for harmonic systems. It is thus an open question as to whether a heat-exchange FT is obeyed by an anharmonic quantum system *strongly coupled* to multiple reservoirs.

Practically, understanding and controlling energy transport and heat dissipation in nanoscale junctions is crucial for making further progress in device miniaturization.¹⁴ Theoretical studies adopting simple models can reveal the role of different system parameters on the transport mechanisms.^{15–18} However, such treatments either assume weak coupling between the nanoscale object and the environment, an assumption that is not always justified, or are limited to very simple models.

It is our objective here to investigate quantum heat exchange in two-terminal impurity models: (i) To derive the SSFT for heat currents in open quantum systems, incorporating anharmonic interactions, allowing for strong system-bath interactions (“strong coupling”), and (ii) to obtain the CGF

and gain explicit expressions for the heat current and its second moment, useful for understanding heat current characteristics for anharmonic strongly coupled systems.

Our analysis begins with a general model for the impurity, reservoirs and the interaction form. Describing the dynamics at the level of the noninteracting-blip approximation (NIBA),¹⁹ a scheme accommodating strong system-bath interactions, we derive a QME for the system dynamics, under the Markovian limit. Unraveling these equations into trajectories with a particular amount of net energy dissipated, e.g., to the R reservoir, a heat-exchange SSFT is verified. We also obtain the CGF, independent of the particular physical realization. The scheme is exemplified on the two-terminal spin-boson model.

Model. Consider a quantum impurity (system) placed between two thermal reservoirs (baths). The energy structure of the impurity is not necessarily uniform, thus anharmonic systems, with finite spectrum and uneven energy spacings, are comprised. Further, system-bath interactions are potentially strong relative to the system energetics. We adopt the dressed-tunneling Hamiltonian

$$H = \sum_n \epsilon_n |n\rangle\langle n| + \sum_\nu H_\nu + \sum_{n>m} \frac{\Delta_{nm}}{2} (|n\rangle\langle m| e^{-i\Omega_{nm}} + |m\rangle\langle n| e^{i\Omega_{nm}}), \quad (1)$$

where $|n\rangle$ denotes the impurity quantum states, coupled through the tunneling elements Δ_{nm} , dressed by the baths operator $\Omega_{nm} = \Omega_{nmL} + \Omega_{nmR}$. The operators $\Omega_{nm\nu}$ depend on the coordinates of the $\nu = L, R$ bath and may represent, for example, a collection of displacements or momentum operators as in the standard small polaron model.¹⁹ Furthermore, different bath operators may couple to different transitions. The thermal reservoirs H_ν are assumed to be in a canonical state, maintained at a temperature $T_\nu = \beta_\nu^{-1}$. Besides that, we do not specify the reservoirs, and they may be composed of fermions, spins, photons, or phonons. The Hamiltonian (1) allows only for energy-transfer processes between the two baths, mediated by a system excitation. Transfer of particles is not considered in the present Rapid Communication.

Population dynamics. System dynamics is explored at the level of the NIBA scheme:^{20–22} Applying the Born approximation to the dressed Hamiltonian (1), equations of motion for the impurity reduced density matrix can be readily obtained.²³ This approximation is generally valid for $\Delta < \omega_c$, where ω_c

is a cutoff of the reservoirs modes, at high temperatures and in the strong coupling regime.¹⁹ Furthermore, we apply the secular approximation, assuming that energy spacings in the system are larger than bath-induced relaxation rates. This results in the decoupling of the diagonal and nondiagonal reduced density matrix equations.²³ Finally, we also execute the Markov approximation, assuming that the reservoirs' dynamics is fast relative to the system relaxation dynamics. For a two-state system coupled to a bosonic bath, these set of approximations lead to the celebrated Marcus expression, describing a donor-acceptor nonadiabatic electron transfer rate.²⁴ In the present model we acquire quantum kinetic equations for the population p_n ,

$$\dot{p}_n = -p_n \sum_{m \neq n} C_{nm}(\omega_{nm}) + \sum_{m \neq n} p_m C_{nm}(\omega_{mn}). \quad (2)$$

The nontrivial aspect of these equation is that the transition rate from state n to m , $C_{nm}(\omega_{nm})$, is a *convolution* of L -induced and R -induced processes¹⁶

$$\begin{aligned} C_{nm}(\omega_{nm}) &= \int_{-\infty}^{\infty} e^{i\omega_{nm}t} C_{nmL}(t) C_{nmR}(t) dt \\ &= \int_{-\infty}^{\infty} C_{nmL}(\omega_{nm} - \omega) C_{nmR}(\omega) d\omega, \end{aligned} \quad (3)$$

describing a joint L - R energy-transfer process. Here $\omega_{nm} = \epsilon_n - \epsilon_m$. The indices of C_{nm} are ordered such that $n > m$. The ν -bath correlation function is given by the thermal average

$$C_{nm\nu}(t) = \frac{\Delta_{nm}}{2} \langle e^{i\Omega_{nm\nu}(t)} e^{-i\Omega_{nm\nu}(0)} \rangle. \quad (4)$$

The operators are written in the interaction representation $\Omega_{nm\nu}(t) = e^{iH_\nu t} \Omega_{nm\nu} e^{-iH_\nu t}$. In the frequency domain we write $C_{nm\nu}(\omega) = \int_{-\infty}^{\infty} dt e^{i\omega t} C_{nm\nu}(t)$, which are the elements in (3). While these bath-specific rates satisfy a detailed balance relation

$$\frac{C_{nm\nu}(\omega)}{C_{nm\nu}(-\omega)} = e^{\omega\beta_\nu}, \quad (5)$$

an analogous condition *does not* hold for the combined rates $C_{nm}(\omega_{nm})$ ruling the dynamics in Eq. (2). This fact reflects rich-complex dynamics, as we discuss immediately. Since energy is dissipated or absorbed in such a complex L - R process, energy “counting” is a nontrivial task, as reflected in the resolved master equation (6).

The QME (2) encloses complex physical processes as Eq. (3) draws nontrivial transfer rates. For example, when the system decays, making a transition from state n to m , it disposes the energy ω_{nm} into both reservoirs cooperatively; an energy ω is dissipated into the R bath while the L bath gains (or contributes) the rest, $\omega_{nm} - \omega$. Similarly, excitation of the system occurs through an L - R compound process. We highlight the three nontrivial mechanisms involved here: (i) Nonresonance energy-transfer processes are allowed, where each reservoir donates (absorbs) an energy which does not overlap with the system's energy spacings. (ii) Anharmonic processes are allowed. For example, in the context of vibrational energy transfer, multiphonon processes are incorporated within the relaxation rates C_{nm} —see, e.g., Eq. (14). (iii) The transport process takes place, conjoining the reservoirs' dynamics in a nonadditive manner, as discussed above.

In contrast, the weak coupling limit^{11,12,16} admits only resonant transmission processes and single-phonon effects. Moreover, in the weak coupling limit the reservoirs additively act on the system.²⁵

Cumulant generating function. We define the function $P_t(n, \omega)$ as the probability distribution that within the time t a net energy ω has been dissipated into the R bath, with the system populating the n state at time t . For later use we also construct $P_t(\omega) = \sum_n P_t(n, \omega)$, the distribution of ω at t , irrespective of the system state. The time evolution of $P_t(n, \omega)$ obeys

$$\begin{aligned} \dot{P}_t(n, \omega) &= \sum_{m \neq n} \int_{-\infty}^{\infty} [P_t(m, \tilde{\omega}) C_{nmR}(\omega - \tilde{\omega}) \\ &\quad \times C_{nmL}(\tilde{\omega} - \omega - \omega_{nm}) d\tilde{\omega}] \\ &\quad - P_t(n, \omega) \sum_{m \neq n} \int_{-\infty}^{\infty} C_{nmR}(\tilde{\omega}) C_{nmL}(\omega_{nm} - \tilde{\omega}) d\tilde{\omega}. \end{aligned} \quad (6)$$

This can be justified by energy resolving the population dynamics in Eq. (2), then collecting the matching energy terms from the left- and the right-hand side of the equation. The first term here describes a process whereby the time t a net energy $\tilde{\omega}$ has been damped into R , whereas the system occupies the state m . At the moment t the system (assisted by the bath) transits from $m \rightarrow n$, further dissipating an energy $\omega - \tilde{\omega}$ into the R reservoir. Similarly, the second term collects all transitions which deplete $P_t(n, \omega)$. Next we introduce the counting field χ and Fourier transform the resolved probabilities $P_t(n, \chi) = \int_{-\infty}^{\infty} d\omega e^{i\omega\chi} P_t(n, \omega)$, yielding

$$\begin{aligned} \dot{P}_t(n, \chi) &= -P_t(n, \chi) \sum_{m \neq n} C_{nm}(\omega_{nm}) + \sum_{m > n} P_t(m, \chi) f_{nm}^+(\chi) \\ &\quad + \sum_{m < n} P_t(m, \chi) f_{nm}^-(\chi). \end{aligned} \quad (7)$$

For brevity, we introduce the short notation

$$f_{nm}^\pm(\chi) = \int_{-\infty}^{\infty} e^{i\omega\chi} C_{nmR}(\omega) C_{nmL}(\pm\omega_{nm} - \omega) d\omega. \quad (8)$$

These equations can be encapsulated in a matrix form $|\dot{\Psi}(\chi, t)\rangle = -\hat{\mu}(\chi)|\Psi(\chi, t)\rangle$, with Ψ a vector of the probabilities $P_t(n, \chi)$. We define the characteristic function $Z(\chi, t) = \langle I | \Psi(\chi, t) \rangle$, with $\langle I |$ as a left vector of unity, and the *cumulant generating function* $G(\chi) = \lim_{t \rightarrow \infty} \frac{1}{t} \ln Z(\chi, t)$, recovered as the negative of the smallest eigenvalue of the matrix $\hat{\mu}$.

Steady-state fluctuation theorem. We now prove that $G(\chi) = G(i\Delta\beta - \chi)$, implying that a SSFT for heat exchange holds. In order to derive this relation we analyze the symmetry properties of the matrix $\hat{\mu}$. For clarity, we write our proof using a three-state impurity. Its $\hat{\mu}$ matrix is given by

$$\hat{\mu}(\chi) = \begin{pmatrix} \mu_{1,1} & -f_{21}^+(\chi) & -f_{31}^+(\chi) \\ -f_{21}^-(\chi) & \mu_{2,2} & -f_{32}^+(\chi) \\ -f_{31}^-(\chi) & -f_{32}^-(\chi) & \mu_{3,3} \end{pmatrix}. \quad (9)$$

The diagonal terms $\mu_{i,i}$ constitute the decay rates from each level, and are independent of χ . The characteristic polynomial

$D_{\hat{\mu}(\chi)}(\lambda)$, with the roots λ , is given by

$$\begin{aligned} D_{\hat{\mu}(\chi)}(\lambda) = & f_{31}^+(\chi)[f_{21}^-(\chi)f_{32}^-(\chi) - (\lambda - \mu_{2,2})f_{31}^-(\chi)] \\ & - f_{21}^+(\chi)[f_{21}^-(\chi)(\lambda - \mu_{3,3}) - f_{32}^+(\chi)f_{31}^-(\chi)] \\ & + (\lambda - \mu_{1,1})[(\lambda - \mu_{2,2})(\lambda - \mu_{3,3}) \\ & - f_{32}^-(\chi)f_{32}^+(\chi)]. \end{aligned}$$

One can show that the following three properties hold here, and in higher dimensions as well: (i) $\hat{\mu}(\chi)$ is symmetric under the operation $f_{nm}^+(\chi) \rightarrow f_{nm}^-(\chi)$. Thus, the roots λ are also symmetric in this respect. (ii) Each element in the characteristic polynomial is cyclic, in the sense that a series of transitions must end at the initial state. For example, the product $f_{31}^+(\chi)f_{21}^-(\chi)f_{32}^-(\chi)$ describes a relaxation process from state 3 to 1, followed by an excitation from state 1 to 2, finishing with an excitation term $f_{32}^-(\chi)$, bringing the system back to state 3. (iii) The correlation function $f_{nm}^+(\chi)$ satisfies the identity

$$f_{nm}^+(i\Delta\beta - \chi) = e^{\beta L \omega_{nm}} f_{nm}^-(\chi), \quad (10)$$

gathered by manipulating Eq. (8) with (5). Under these three properties we prove that $D_{\hat{\mu}(\chi)}(\lambda) = D_{\hat{\mu}(i\Delta\beta - \chi)}(\lambda)$: The symmetric terms in the characteristic polynomial are mapped one onto the other as a result of the symmetry (10), whereas the *system-dependent* prefactors, i.e., the term $e^{\beta L \omega_{nm}}$ in Eq. (10), overall cancel, a result of the cyclic property (ii). We conclude that the eigenvalues of $\hat{\mu}$ satisfy a symmetry relation, and in particular $G(\chi) = G(i\Delta\beta - \chi)$. The probability distribution of ω is obtained as $P_t(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} d\chi Z(\chi, t) e^{-i\chi\omega}$. Since $Z(\chi, t) \sim e^{G(\chi)t}$ in the long time limit, a heat-exchange fluctuation relation is resolved

$$\lim_{t \rightarrow \infty} \frac{1}{t} \ln \frac{P_t(\omega)}{P_t(-\omega)} = \frac{\Delta\beta\omega}{t}. \quad (11)$$

The FT relation has been derived without specifying either the system energy structure and its interaction with the reservoirs, or the form of the reservoirs. It allows for strong coupling between the impurity and the baths, reflected in the compound transition rates. Moreover, an explicit expression for the CGF, $G(\chi)$, can now be written, bearing analytical expressions for the current cumulants, as we achieve below for the spin-boson model. In the right-hand side of (11) we identify the heat current $J \equiv \omega/t$, the total energy transferred over an interval t .

Spin-boson model. The equilibrium spin-boson (SB) model, referring to a spin immersed in an equilibrated boson reservoir, is an eminent model in chemistry and physics, useful for describing, e.g., solvent-assisted electron transfer reactions and the Kondo resonance.¹⁹ The nonequilibrium spin-boson model, where the spin is coupled to more than one thermal reservoir, has been suggested as a prototype model for exploring heat transfer through nanojunctions.^{16,18} We now analytically obtain the CGF, thus the current and its cumulants, for the nonequilibrium SB model at strong coupling

$$\begin{aligned} H = & \frac{\omega_0}{2}\sigma_z + \frac{\Delta}{2}\sigma_x + \sigma_z \sum_{\nu,j} \lambda_{j,\nu} (b_{j,\nu}^\dagger + b_{j,\nu}) \\ & + \sum_{\nu,j} \omega_j b_{j,\nu}^\dagger b_{j,\nu}. \end{aligned} \quad (12)$$

Here σ_x and σ_z are the Pauli matrices, ω_0 is the energy gap between the spin levels, and Δ is the tunneling energy. The two reservoirs include a collection of uncoupled harmonic oscillators, and $b_{j,\nu}^\dagger$ ($b_{j,\nu}$) is the bosonic creation (annihilation) operator of the mode j in the ν reservoir. The parameter $\lambda_{j,\nu}$ accounts for the system-bath interaction strength. The Hamiltonian is transformed to the displaced bath-oscillator basis using the small polaron transformation¹⁹ $H_S = U^\dagger H U$, $U = e^{i\sigma_z \Omega/2}$,

$$H_S = \frac{\omega_0}{2}\sigma_z + \frac{\Delta}{2}(\sigma_+ e^{i\Omega} + \sigma_- e^{-i\Omega}) + \sum_{\nu,j} \omega_j b_{j,\nu}^\dagger b_{j,\nu}, \quad (13)$$

where $\sigma_\pm = \frac{1}{2}(\sigma_x \pm i\sigma_y)$ are the auxiliary Pauli matrices, $\Omega = \sum_\nu \Omega_\nu$, and $\Omega_\nu = 2i \sum_j \frac{\lambda_{j,\nu}}{\omega_j} (b_{j,\nu}^\dagger - b_{j,\nu})$. Under the NIBA, the system population obeys a convolution-type master equation²⁰⁻²² ($\langle \sigma_z \rangle = p_1 - p_0$)

$$\begin{aligned} \dot{p}_1 = & -\frac{\Delta^2}{2} \int_0^t e^{-Q'(t-s)} \cos[\omega_0(t-s) - Q''(t-s)] p_1(s) ds \\ & + \frac{\Delta^2}{2} \int_0^t e^{-Q'(t-s)} \cos[\omega_0(t-s) + Q''(t-s)] p_0(s) ds, \end{aligned}$$

with conserved total occupation $p_0(t) + p_1(t) = 1$. The function $Q(t) = \sum_\nu Q_\nu(t)$, made of a real and imaginary components $Q_\nu(t) = Q'_\nu(t) + iQ''_\nu(t)$, is defined by

$$\begin{aligned} Q'_\nu(t) = & \int_0^\infty \frac{J_\nu(\omega)}{\pi\omega^2} [1 - \cos(\omega t)] [1 + 2n_\nu(\omega)] d\omega, \\ Q''_\nu(t) = & \int_0^\infty \frac{J_\nu(\omega)}{\pi\omega^2} \sin(\omega t) d\omega. \end{aligned} \quad (14)$$

Here $J_\nu(\omega) = 4\pi \sum_j \lambda_{j,\nu}^2 \delta(\omega - \omega_j)$ is the ν -bath spectral function, and $n_\nu(\omega)$ is the Bose-Einstein distribution.

It is of interest to carry out the analysis in the non-Markovian limit, allowing for a long decorrelation time for the baths. The assumption of no memory enforces a strict energy conservation condition for processes between the system and the environment. In contrast, in the non-Markovian regime there is no such energy-conservation statement, and thus it is not obvious that the FT symmetry relation (11) still holds.^{8,9,27}

In the Markovian case the QME for the population dynamics [Eqs. (2) and (3)] follows $\dot{p}_1 = -C(\omega_0)p_1 + C(-\omega_0)p_0$, with the rates $C(\omega_0) = \int_{-\infty}^{\infty} e^{i\omega_0 t} C_L(t) C_R(t) dt$; $C_\nu(t) = e^{-Q_\nu(t)}$. Since only a single correlation function

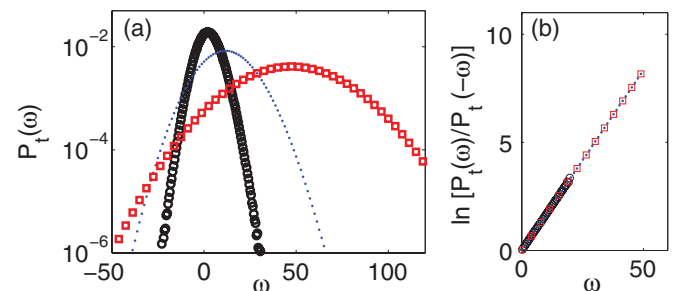


FIG. 1. (Color online) Nonequilibrium spin-boson model: (a) Plot of $P_t(\omega)$ at various times. (b) Demonstration of the validity of the SSFT. $T_L = 3$, $T_R = 2$, $E_r^v = 1$, $\omega_0 = 0.5$, $t = 20$ (\circ), $t = 100$ (dotted), and $t = 400$ (\square).

matters, the level indices were discarded. Following Eqs. (6)–(8), we identify the matrix $\hat{\mu}$ by

$$\hat{\mu}(\chi) = \begin{pmatrix} C(-\omega_0) & -f^+(\chi) \\ -f^-(\chi) & C(\omega_0) \end{pmatrix}, \quad (15)$$

with $f^\pm(\chi) = \int_{-\infty}^{\infty} e^{i\omega\chi} C_R(\omega) C_L(\pm\omega_0 - \omega) d\omega$. Its smallest eigenvalue is

$$G(\chi) = -\frac{1}{2}[C(\omega_0) + C(-\omega_0)] + \frac{1}{2}\sqrt{[C(\omega_0) - C(-\omega_0)]^2 + 4f^-(\chi)f^+(\chi)}. \quad (16)$$

The averaged heat current can be readily obtained,

$$\begin{aligned} \langle J \rangle &\equiv \frac{\langle \omega \rangle_t}{t} = \frac{dG(\chi)}{d(i\chi)} \Big|_{\chi=0} \\ &= \int_{-\infty}^{\infty} [C_R(\omega)C_L(\omega_0 - \omega)p_1 - C_R(-\omega)C_L(-\omega_0 + \omega)p_0] \omega d\omega. \end{aligned} \quad (17)$$

The population here is calculated in steady state, $p_0 = C(\omega_0)/[C(\omega_0) + C(-\omega_0)]$. This expression was heuristically suggested in Ref. 16, and here it is derived from the basic dynamics. Note that the details of the function $Q(t)$ are not utilized in this derivation. Furthermore, Eq. (16) provides the averaged current for non-Markovian systems as well.²⁶ The formal structure for the noise power is

given by

$$\begin{aligned} \langle S \rangle &= \frac{d^2 G(\chi)}{d(i\chi)^2} \Big|_{\chi=0} \\ &= -2[C(\omega_0) + C(-\omega_0)]^{-1} \\ &\quad \times \left[\int_{-\infty}^{\infty} \omega C_-(\omega) d\omega \int_{-\infty}^{\infty} \omega C_+(\omega) d\omega + \langle J \rangle^2 \right] \\ &\quad + \int_{-\infty}^{\infty} d\omega \omega^2 [C_+(\omega)p_1 + C_-(\omega)p_0], \end{aligned} \quad (18)$$

where we defined $C_\pm(\omega) = C_R(\pm\omega)C_L(\pm\omega_0 \mp \omega)$. We can also plot the distribution $P_t(\omega)$. Assuming high temperatures $T_v > \omega_0$ and strong coupling, Eq. (14) can be simplified, $Q'_v(t) = E_r^v T_v t^2$, $Q''_v(t) = E_r^v t$, with the reorganization energy defined as $E_r^v = \sum_j 4\lambda_{j,v}^2/\omega_j$.²⁴ Using this form, Fig. 1 displays the entropy production distribution and the validity of the SSFT (inset).

To conclude, a heat-exchange SSFT has been derived for quantum systems incorporating strong system-bath interactions and anharmonic effects. Our study provides closed expressions for the CGF, useful for deriving the distribution of heat fluctuations, the averaged current, and the thermal noise power. For the spin-boson model one can show that in the non-Markovian case the SSFT does not generally hold.²⁷ It is satisfied in the Markovian limit, when energy conservation is enforced. Future work will be devoted to generalizing our study to systems showing coherence effects.

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²⁵In the weak coupling limit we expand $e^{i\Omega} = e^{i\Omega_L} e^{i\Omega_R} \sim 1 + i\Omega_L + i\Omega_R$ in Eq. (1). Following the Born-Markov approximation with the system-bath coupling strength as the small parameter, one finds that the system relaxation rate is additive with respect to the two reservoirs (Ref. 16).

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