Nonequilibrium work distributions in quantum impurity system–bath mixing processes

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The fluctuation theorem, where the central quantity is the work distribution, is an important characterization of nonequilibrium thermodynamics. In this work, based on the dissipaton–equation–of–motion theory, we develop an exact method to evaluate the work distributions in quantum impurity system–bath mixing processes, in the presence of non-Markovian and strong couplings. Our results not only precisely reproduce the Jarzynski equality and Crooks relation, but also reveal rich information on large deviation. The numerical demonstrations are carried out with a spin–boson model system.

I. INTRODUCTION

The fluctuation theorem plays pivotal roles in investigating nonequilibrium thermodynamics [1–4]. The celebrated Jarzynski equality [4, 5] and Crooks relation [6, 7] are considered as two foundational components of the fluctuation theorem, which have been experimentally tested in several systems [8–12]. At the center of fluctuation theorem is the work distribution $p(w)$ during a nonequilibrium process [13–16]. Practically, the work distribution is equivalent to the characteristic function of work (CFW),

$$\varphi(\tau) = \int_{-\infty}^{\infty} dw e^{iw\tau} p(w),$$

the Fourier transform of work distribution. Generally, the CFW is ubiquitous in modern physical researches, such as Loschmidt echo [17, 18] and dynamical quantum phase transitions [19, 20]. Nevertheless, it is still a challenge to exactly evaluate the CFW for nonequilibrium processes, especially when the non-Markovian and non-perturbative effects are proaminent.

In this work, we aim at investigating the CFW and work distribution of system–bath mixing processes, which are under time–dependent mixing functions. To that end, we extends the original framework of the fluctuation theorem, which have been experimentally tested in several systems. At the center of fluctuation theorem is the work distribution $p(w)$ during a nonequilibrium process. Practically, the work distribution is equivalent to the characteristic function of work (CFW),

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with
\[ \tilde{H}(t) = U^\dagger(t, 0) H(t) U(t, 0). \] (5)

It can be shown that
\[ \varphi(\tau) = \text{Tr}[\Phi(t_f; \tau)]. \] (6)

See Appendix for details. Note that the methodology here is closely related to that in Ref. [24].

Turn to the equation of motion (EOM) for the work generating operator \( \Phi(t; \tau) \), abbreviated as \( \Phi(t) \) since \( \tau \) is a parameter throughout this paper. As detailed in Appendix, we obtain
\[ \dot{\Phi}(t) = -i[H^\times + h^\times + \Lambda_-(t) H^s_{\text{sh}} - \Lambda_+(t) H^s_{\text{sh}}]\Phi(t) \] (7)
with
\[ \Lambda_\pm(t) = \lambda(t) \pm \frac{\tau}{2}, \] (8)
whereas \( \hat{A}_\times = \hat{A}^\times - \hat{A}^\times \hat{A} \). The left–hand–side of Eq. (10), the hybridization free–energy, respectively. On the right–hand–side of Eq. (10), the hybridization free–energy and the hybridization work
\[ \lambda^=_{\text{hyb}}(t) = \eta(t) = \rho^0_\text{hyb}(t) \] (9)
Jarnyński equality claims [4]
\[ \varphi(i\beta) = \frac{Z_\text{T}}{Z_\text{b}} \] (10)
This is the equality between the hybridization work \( w \) and the hybridization free–energy \( A_{\text{hyb}} \), relating further to the ratio between \( Z_\text{T} = \text{Tr}(e^{-\beta H_T}) \) and \( Z_\text{b} = \text{Tr}(e^{-\beta H_0}) \). These are the partition function of fully hybridized and unhybridized system–bath composite, respectively. On the right–hand–side of Eq. (10), the hybridization free–energy, \( A_{\text{hyb}} \), is equilibrium thermodynamic quantities, which can be evaluated various methods, including \( \lambda\text{–DEOM}, \) imaginary–time DEOM and free–energy spectrum approaches [21, 22]. The left–hand–side of Eq. (10) is to be handled with the \( \lambda\text{–DEOM} \) developed in this work; see Sec.IV.

Crooks relation is about a pair of conjugate processes: the forward process controlled by \( \lambda(t) \) and the backward process controlled by \( \lambda(t_f - t) \). The backward process represents a system–bath separation, with \( \lambda(0) = 1 \) and \( \lambda(t_f) = 0 \). We denote the work distributions in the forward and backward processes as \( p(w) \) and \( \tilde{p}(-w) \), respectively.

Assuming the total system–and–bath composite is time–reversal invariant, the Crooks relation claims [6]
\[ p(w) = e^{\beta(w - A_{\text{hyb}})} \tilde{p}(-w). \] (11)
Equivalently, we can express Eq. (11) using the CFWs as
\[ \varphi(\tau) = e^{\beta A_{\text{hyb}}} \tilde{\varphi}(i\beta - \tau). \] (12)
Here, \( \tilde{\varphi} \) is the backward CFW [3]. Evidently, if we set \( \tau = i\beta \) in Eq. (12), it recovers Jarnyński equality Eq. (10).

### III. NONEQUILIBRIUM \( \lambda\text{–DEOM} \)

#### A. Prelude

In this section, we introduce the \( \lambda\text{–DEOM} \) formalism to evaluate the CFWs of the system–bath mixing processes. We set the interaction Hamiltonian to be
\[ H_{\text{sh}} = \hat{Q}_b \hat{F}_b. \] (13)

While the dissipative system mode \( \hat{Q}_b \) is an arbitrary dimensionless Hermitian operator, the hybridization mode \( \hat{F}_b \) is linear. It together with harmonic bath \( h_b \) constitute a Gaussian environment. For the Gaussian bath, the correlation function of hybrid mode, \( \langle \hat{F}_b(t)\hat{F}_b(0) \rangle_b \), completely characterizes the environmental influences. Here, \( \hat{F}_b(t) \equiv e^{ih_b t} \hat{F} e^{-ih_b t} \) and \( \langle (\cdot) \rangle_b \equiv \text{tr}_b[(\cdot)e^{-\beta h_b}]/\text{tr}_b(e^{-\beta h_b}) \). We can do exponential series expansion by adopting a certain the sum–over–poles scheme to expand the Fourier integrand here, followed by Cauchy’s contour integration. Together with the identity \( \langle \hat{F}_b^n(0)\hat{F}_b^n(t) \rangle_b = \langle \hat{F}_b^n(t)\hat{F}_b^n(0) \rangle_b^\text{\(n\)} \), we obtain that [25]
\[ \langle \hat{F}_b^n(t)\hat{F}_b^n(0) \rangle_b = \sum_{k=1}^K \eta_k e^{-\gamma_k t} \] (14)
\[ \langle \hat{F}_b^n(0)\hat{F}_b^n(t) \rangle_b = \sum_{k=1}^K \eta_k^* e^{-\gamma_k t}. \] (15)

Here, since the exponents \( \{\gamma_k\} \) in Eq. (14) must be either real or complex conjugate paired [25], we may set \( \gamma_k = \gamma_k^* \).

The \( \lambda\text{DEOM} \) theory adopts dissipatons as quasi–particles associated with the coupling bath influence [25–27]. It is a second–quantization version HEOM, which is also able to deal with the hybrid mode dynamics. To be concrete, DEOM decompose \( \hat{F} \) into many dissipaton operators
\[ \hat{F}_b = \sum_{k=1}^K \hat{F}_k \] (16)

To reproduce Eq. (14), we set
\[ \langle \hat{F}_k(t)\hat{F}_k'(0) \rangle_b = \delta_{kk'}\eta_k e^{-\gamma_k t}, \]
\[ \langle \hat{F}_k'(0)\hat{F}_k(t) \rangle_b = \delta_{kk'}\eta_k^* e^{-\gamma_k t}. \] (17)

Each forward–and–backward pair of dissipaton correlation functions are associated with a single–exponent \( \gamma_k \).

The conventional DEOM defines also the dynamical variables, the dissipatons–augmented–reduced density operators (DDOs), as [25–27]
\[ \rho^{(n)}_{\text{hyb}}(t) = \rho^{(n)}_{n_1 \cdots n_K}(t) = \text{tr}_b[(\hat{F}_K^{n_K} \cdots \hat{F}_1^{n_1}) \rho_T(t)]. \] (18)

Here, \( n = n_1 + \cdots + n_K \), with \( n_k \geq 0 \) for bosonic dissipatons. The product of dissipaton operators inside \( (\cdot) \) is
irreducible, satisfying \((\hat{f}_k, \hat{f}_k) = (\hat{f}_k, \hat{f}_k) = 0\) for bosonic dissipatons. Each \(n\)-particles DDO, \(\rho^{(n)}_n(t)\), is specified with an ordered set of indexes, \(n \equiv \{n_1 \cdots n_K\}\). Denote for later use also \(n_k^\pm\) that differ from \(n\) only at the specified \(\hat{f}_k\)-dissipaton participation number \(n_k\) by \(\pm 1\). The reduced system density operator is just \(\rho^{(0)}_0 = \rho^{(0)}_{0\cdots 0}\). We will extend the definition (17) from the density operator \(\rho(t)\) to the work generating operator \(\Phi(t)\) in the following.

**B. Dissipatons–augmented work generating operator and its EOM**

Similar to DDOs, we introduce the dissipatons–augmented work generating operators (DDOs),

\[
\Phi^{(n)}_n (t) \equiv \text{tr}_n \left[ (\hat{f}_{K}^{nK} \cdots \hat{f}_{1}^{n1})^\circ \Phi(t) \right],
\]

where \(\Phi^{(n)}_n (t) \equiv \Phi^{(n)}_{n_1 \cdots n_K} (t)\) specifies certain configuration of given \(n\)-dissipatons excitation. Initially, \(\Phi^{(n)}_n (0) = \delta_{n0} e^{-\beta H_S} / \text{tr}_n (e^{-\beta H_S})\). Evidently, \(\varphi(\tau) = \text{tr}_n [\Phi^{(0)}_n (t>\tau)]\) [cf. Eq. (6)].

To obtain the EOM that governs the time evolution of DDOs, we apply for \(\Phi^{(n)}_n (t)\) of Eq. (18) the equation Eq. (7). We evaluate, one-by-one, the specified four components in total composite Hamiltonian, for their contributions.

(i) The \(H^{(\times)}_S\)-contribution: Apparently,

\[
\text{tr}_n \left[ (\hat{f}_{K}^{nK} \cdots \hat{f}_{1}^{n1})^\circ H^{(\times)}_S \Phi(t) \right] = H^{(\times)}_S \Phi^{(n)}_n (t).
\]

This is the coherent dynamics contribution.

(ii) The \(h^{(\times)}_S\)-contribution: Each dissipaton is subject a sort of “diffusive” motion in bare–bath, satisfying

\[
\text{tr}_n \left[ (\hat{f}_k / \partial t) \Phi(t) \right] = -\gamma_k \text{tr}_n [\hat{f}_k \Phi(t)].
\]

Together with \(i (\hat{f}_k / \partial t) \Phi(t) = [\hat{f}_k, \hat{h}_k]\), we obtain

\[
\text{tr}_n \left[ (\hat{f}_{K}^{nK} \cdots \hat{f}_{1}^{n1})^\circ \hat{h}^\circ_k \Phi(t) \right] = -i \gamma_k \Phi^{(n)}_n (t),
\]

with \(\gamma_n \equiv \sum_k n_k \gamma_k\). This is the “diffusive” dynamics contribution.

(iii) The \(H^{(\circ)}_S\)-contribution: By applying Eq. (13), we obtain readily the following expressions,

\[
\text{tr}_n \left[ (\hat{f}_{K}^{nK} \cdots \hat{f}_{1}^{n1})^\circ H^{(\circ)}_S \Phi(t) \right]
= \text{tr}_n \left[ (\hat{f}_{K}^{nK} \cdots \hat{f}_{1}^{n1})^\circ \hat{Q}^\circ_S \hat{F}^\circ_n \Phi(t) \right]
= \hat{Q}^\circ_S \sum_k \text{tr}_n \left[ (\hat{f}_{K}^{nK} \cdots \hat{f}_{1}^{n1})^\circ \hat{f}_k^\circ \Phi(t) \right]
= \hat{Q}^\circ_S \sum_k \Phi^{(n+1)}_n (t) + n_k \eta_k \Phi^{(n-1)}_n (t).
\]

In the last step, we have used the forward generalized Wick’s theorem:

\[
\text{tr}_n \left[ (\hat{f}_{K}^{nK} \cdots \hat{f}_{1}^{n1})^\circ \Phi(t) \right] = \Phi^{(n+1)}_n + n_k \eta_k \Phi^{(n-1)}_n.
\]

(iv) The \(H^{(\circ)}_S\)-contribution: Similarly, we obtain

\[
\text{tr}_n \left[ (\hat{f}_{K}^{nK} \cdots \hat{f}_{1}^{n1})^\circ H^{(\circ)}_S \Phi(t) \right]
= \hat{Q}^\circ_S \sum_k \left[ \Phi^{(n+1)}_n (t) + n_k \eta_k \Phi^{(n-1)}_n (t) \right]
\]

by using the backward generalized Wick’s theorem

\[
\text{tr}_n \left[ (\hat{f}_{K}^{nK} \cdots \hat{f}_{1}^{n1})^\circ \Phi(t) \right] = \Phi^{(n+1)}_n + n_k \eta_k \Phi^{(n-1)}_n.
\]

The above (i)-(iv) lead to the EOM of DWOs in the neq-\(\lambda\)-DEOM formalism the expression

\[
\phi^{(n)}_n (t) = -i (H^{(\times)}_S - i \gamma_n) \phi^{(n)}_n (t) - i \sum_k \mathcal{A}(t) \phi^{(n+1)}_n (t)
- i \sum_k \mathcal{C}(t) n_k \phi^{(n-1)}_n (t)
\]

where

\[
\mathcal{A}(t) = \lambda_- (t) \hat{Q}^+_S - \lambda_+ (t) \hat{Q}^-_S,
\]

\[
\mathcal{C}(t) = \eta_k \lambda_- (t) \hat{Q}^+_S - \eta_k \lambda_+ (t) \hat{Q}^-_S,
\]

with \(\lambda_\pm (t)\) being given in Eq. (8) that depends also on the parameter \(\tau\).

**IV. NUMERICAL DEMONSTRATIONS**

For numerical demonstrations, we consider a spin-boson model, in which system Hamiltonian and dissipative mode are

\[
\hat{H}_S = \varepsilon \hat{\sigma}_z + \Delta \hat{\sigma}_x \quad \text{and} \quad \hat{Q}_S = \hat{\sigma}_z,
\]

respectively. Here, \(\{\hat{\sigma}_1\}\) are the Pauli matrices, \(\varepsilon\) is the energy bias parameter and \(\Delta\) the interstate coupling. Adopt for the bath spectral density the Drude model,

\[
J(\omega) = \frac{\eta \gamma \omega}{\omega^2 + \gamma^2},
\]

where \(\eta\) and \(\gamma\) are the system-bath coupling strength and bath cut-off frequency, respectively. In all the simulations below, we set \(\varepsilon = 0.5\Delta, \gamma = 4\Delta\) and \(\eta = 0.5\Delta\). We set the forward time–dependent mixing function as

\[
\lambda(t) = \frac{1 - e^{-\alpha t}}{1 - e^{-\alpha t}},
\]

with \(\alpha \geq 0\). Correspondingly, the backward time–dependent mixing function reads

\[
\bar{\lambda}(t) = \lambda(t_f - t) = \frac{e^{\alpha t} - e^{\alpha t}}{e^{\alpha t} - 1}.
\]

In Fig. 1, we evaluate the left–hand–side and right–hand–side of Eq. (10), the Jarzynski equality, respectively. On the right–hand–side of Eq. (10), the hybridization free–energy, \(A_{\text{hyb}}\), is computed via the equilibrium
FIG. 1. Validation of the Jarzynski equality: $\langle e^{-\beta w} \rangle$ versus $e^{-\beta A_{\text{hyb}}}$ with different temperatures. We set $\varepsilon = 0.5\Delta$, $\gamma = 4\Delta$ and $\eta = 0.5\Delta$ in the spectral density (29) and $\alpha = 0.01$ and $t_j = 50$ in the forward and backward protocols Eqs. (30) and (31).

FIG. 2. $\varphi(\tau)$ versus $\varphi(i\beta - \tau)$. We choose $\beta = 0.5\Delta^{-1}$. Other parameters are the same with that in Fig. 1.

Fig. 3. Work distributions $p(\omega)$ and $\bar{p}(-\omega)$ coincide at $w = A_{\text{hyb}}$. Parameters are the same with that in Fig. 2.

FIG. 3. Work distributions $p(\omega)$ and $\bar{p}(\omega)$ coincide at $w = A_{\text{hyb}}$. Parameters are the same with that in Fig. 2.

The numerical validation of the Crook relation. In Fig. 2, the CFWs of both mixing process with $\lambda(t)$ [cf. Eq. (30)] and separation process with $\bar{\lambda}(t)$ [cf. Eq. (31)] are exhibited. Intentionally, we compare the two sides of Eq. (12), with both the real and imaginary parts. Fig. 3 depicts the work distributions at high and low temperature, where $p(\omega)$ and $\bar{p}(\omega)$ coincide at $w = A_{\text{hyb}}$ [cf. Eq. (11)]. The difference is much more evident when temperature goes lower, while other parameters remain intact. The above results accurately reproduce the fluctuation theorems.

Turn to the hybridization work, which according to the Second Law, satisfies

$$\langle w \rangle \geq A_{\text{hyb}}.$$ \hfill (32)

The irreversible work is given by

$$w_{\text{irr}} \equiv \langle w \rangle - A_{\text{hyb}} = \langle w \rangle - \beta^{-1} \ln(e^{-\beta \omega}).$$ \hfill (33)
It can be approximated as [28]

\[ w_{\text{irr}} = \langle w \rangle - \beta^{-1} \sum_{n=1}^{\infty} \kappa_n \frac{(-\beta)^n}{n!} \approx \frac{\beta}{2} \kappa_2 = w'_{\text{irr}} \tag{34} \]

where \( \kappa_n \) is the \( n \)th-order cumulant of the work distribution. Specifically, \( \kappa_1 = \langle w \rangle \) and \( \kappa_2 = \langle w^2 \rangle - \langle w \rangle^2 \). The error of \( w'_{\text{irr}} \) originates from the non-Gaussianity of \( p(w) \). In Fig. 4, we compare the approximate result with the exact one, which is obtained directly from the definition (33). As shown in the figure, the differences between \( w_{\text{irr}} \) and \( w'_{\text{irr}} \) become smaller as temperature decreases, which implies there are more similarities between the two level system and harmonic oscillators. The similar phenomenon is also observed in the dynamical properties of spin–boson model [29]. The obtained work distribution reveal rich information on other large deviation properties beyond the second–order cumulant.

V. CONCLUDING REMARKS

To conclude, we establish the neq–\( \lambda \)-DEOM formalism to study the work distributions in isothermal systems–bath mixing processes under a time–dependent mixing function. This formalism extends the original framework of \( \lambda \)-DEOM nonequilibrium scenarios. Using neq–\( \lambda \)-DEOM, we precisely reproduce the Jarzynski equality and Crooks relation, two foundational components of the fluctuation theorem. Moreover, the rich information contained in the distribution will help investigate the large deviation properties. The methods proposed in this work are rather general and can readily be extended to the study of other nonequilibrium thermodynamic quantities, including time–dependent entropy production and correlation functions of transport current fluctuations.

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Appendix A: Derivation of Eqs. (6) and (7)

To derive the relation given in Eq. (6), we first rewrite Eq. (2) as

\[ p(w) = \frac{1}{2\pi} \int_{-\infty}^{\infty} d\tau e^{-i(w-E_{N+n})\tau} P_{N,n}(t_f,0)P_n(0). \tag{A1} \]

By further noting

\[ P_{N,n}(t_f,0) = \langle N|U(t_f,0)|n\rangle\langle n|U^\dagger(t_f,0)|N\rangle, \tag{A2} \]

we obtain

\[ p(w) = \frac{1}{2\pi} \int_{-\infty}^{\infty} d\tau e^{-i\mu\tau} \varphi(\tau), \tag{A3} \]

with \( \varphi(\tau) = \text{Tr}[\Phi(\tau,t_f)] \) where \( \Phi(\tau,t_f) = e^{iH\tau/2}U(t_f,0)e^{-iH\tau/2}\rho^\text{eq}_{0}(T)e^{-iH\tau/2}U^\dagger(t_f,0)e^{iH\tau/2} \) is the the work generating operator. Equation (A3) is seen as the inverse Fourier transform with respect to Eq. (1). According to Eq. (5), we can then rewrite the work generating operator as

\[ \Phi(\tau,t_f) = U(t_f,0)e^{iH(t_f)\tau/2}e^{-iH(0)\tau/2}\rho^\text{eq}_{0}(T)e^{-iH(0)\tau/2} \]

\[ \times e^{iH(t_f)\tau/2}U^\dagger(t_f,0) \]

\[ = U(t_f,0)V_+(\tau,t_f)\rho^\text{eq}_{0}(T)V_-(\tau,t_f)U^\dagger(t_f,0). \tag{A4} \]

Here, \( V_+(t;\tau) = \text{exp}_{\text{+}}\{i[H(\tau) - H(0)/\tau]\} \) and it is equivalent to that in Eq. (4) due to the existence of time–ordering operators together with the fact that \( dH(t)/dt = \dot{H}(t)/\dot{\tau} \) as inferred from Eq. (5). This concludes the derivation of Eq. (6). As noted by the erratum of Ref. [2], there is a caveat in the derivation due to the equal–time non–commutativity between \( \hat{H}(t) \) and \( \dot{H}(t) \), even inside the time–ordering operators. This problem can be fixed by pre-assuming a certain type of order, e.g., \( T_+\{\hat{A}(t)\hat{B}(t)\} = [\hat{A}(t)\hat{B}(t) + \hat{B}(t)\hat{A}(t)])/2, \forall \hat{A}(t) \) and \( \hat{B}(t) \), between equal–time operators in the definition of time–ordering. This supplementary assumption makes \( \dot{H}(t) \) and \( \hat{H}(t) \) interchangeable inside the time–ordering operator, and will not affect the derivations elsewhere.

Now turn to the derivation of Eq. (7). According to the definition in Eq. (3), we can obtain

\[ \dot{\Phi}(t) = -i \left[ \hat{\hat{H}}^\times(t) - \tau \frac{\dot{\hat{H}}}{2} \right] \Phi(t). \tag{A5} \]

Here, \( \hat{\hat{H}}^\times \equiv \hat{A}^\times + \hat{A}^\times \) and \( \dot{\hat{H}}^\times(\tau) = \partial\hat{H}^\times(\tau)/\partial\tau \). While the derivation of \( -i\hat{H}^\times(\tau) \) term is rather direct, the derivation of \( i(\tau/2)\dot{\hat{H}}^\times(\tau) \) is as follows:

\[ U(t,0)V_+(t)\rho^\text{eq}_{0}(T)V_-(t)U^\dagger(t,0) \]

\[ = U(t,0)\left[ \frac{i\tau}{2} \frac{\partial\hat{H}(t)}{\partial t} \right] V_+(t)\rho^\text{eq}_{0}(T)V_-(t)U^\dagger(t,0) \]

\[ = i\frac{\tau}{2} \frac{\partial\hat{H}(t)}{\partial t} U(t,0)V_+(t)\rho^\text{eq}_{0}(T)V_-(t)U^\dagger(t,0) \]

\[ = i\frac{\tau}{2} \frac{\partial\hat{H}(t)}{\partial t} \Phi(\tau). \tag{A6} \]

In the first step, we use the property of time–ordering operator and the definition (4), while in the second step we used the relation \( \partial\hat{H}(t)/\partial t = U^\dagger(t,0)[\partial\hat{H}(t)/\partial\tau]U(t,0) \).

The \( U(t,0)V_+(t)\rho^\text{eq}_{0}(T)V_-(t)U^\dagger(t,0) \) contribution is similar. Substitute the Hamiltonian \( (??) \) into Eq. (A5), and we readily obtain Eq. (7).
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