

Entangled system-and-environment dynamics: Phase-space dissipaton theory

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ABSTRACT

Dissipaton-equation-of-motion (DEOM) theory [Y. J. Yan, J. Chem. Phys. **140**, 054105 (2014)] is an exact and nonperturbative many-particle method for open quantum systems. The existing dissipaton algebra also treats the dynamics of hybrid bath solvation coordinates. The dynamics of conjugate momentums remain to be addressed within the DEOM framework. In this work, we establish this missing ingredient, the dissipaton algebra on solvation momentums, with rigorous validations against necessary and sufficient criteria. The resulted phase-space DEOM theory will serve as a solid ground for further developments of various practical methods toward a broad range of applications. We illustrate this novel dissipaton algebra with the phase-space DEOM-evaluation on heat current fluctuation.

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Entangled system-and-environment dynamics play crucial roles whenever the non-Markovian and nonperturbative quantum nature of environments cannot be neglected. Traditionally, this problem was addressed with the “core-system” approach.^{1–6} This is to divide the overall environment into the “first-shell” and “secondary” parts. The core-system comprises both the primary system and the first-shell hybrid bath solvation modes. Various approximate theories such as quantum master equations had been applied to treat the reduced core-system dynamics under the influence of the secondary bath environments.^{1–6}

As exact methods are concerned, one often exploits the hierarchical-equations-of-motion (HEOM) formalism.^{7–12} This is the time-derivative equivalence to the Feynman–Vernon influenced functional path integral formalism,¹³ which is exact for arbitrary systems coupling with Gaussian environments. However, HEOM involves a vast number of dynamical variables that are just mathematical auxiliaries without physical meanings. In this sense, HEOM is mainly a reduced primary-system theory. Its exact treatment on the system-plus-solvation core dynamics is, in general, too expensive. On the other hand, the dissipaton-equation-of-motion (DEOM) theory,^{14–16} which recovers the HEOM formalism, is by far capable of treating the hybrid bath solvation coordinate

dynamics. However, the conjugate momentum dynamics are yet to be addressed within the DEOM framework.

The main objective of this work is to complete the DEOM theory as an exact and nonperturbative “core-system” phase-space method. To that end, we construct the dissipaton algebra on the conjugate solvation momentum. The resulted phase-space DEOM theory is rigorously validated with respect to necessary and sufficient criteria. It is worth noting that open quantum systems are beyond the total system-plus-bath composite Hamiltonian description. Additional information such as temperature T and the interacting bath statistics would be needed.^{17–19} The underlying irreversibility will eventually lead to the total system-plus-bath composite bulk matter of the Boltzmann distribution at a given temperature T . In fact, the total composite Hamiltonian constitutes a “closed system” in the thermodynamics nomenclature, such as a solution system in chemistry, which is in thermal contact with surroundings. The solute-and-solvent mixing free-energy change is dictated by the coupling between them.²⁰ The exact and nonperturbative phase-space DEOM theory to be developed in this work would serve as a solid foundation for the development of various practical simulation methods toward realistic molecular systems in condensed phases.

Without loss of generality, we focus explicitly on a single-dissipative-mode case, with the system-bath coupling in the form of $H_{SB} = \hat{Q}_S \hat{x}_B$. While the dissipative system mode \hat{Q}_S is arbitrary, the solvation coordinate \hat{x}_B is linear, which together with harmonic bath h_B constitutes Gaussian–Wick’s environment. The total composite Hamiltonian considered explicitly in this work reads

$$H_T = H_S + h_B + \hat{Q}_S \hat{x}_B. \quad (1)$$

Throughout the paper, we set $\hbar = 1$ and $\beta = 1/(k_B T)$, with k_B representing the Boltzmann constant and T the temperature. Let $\rho_T^{\text{st}}(H_T)$ be a *steady-state* density operator in the total system-plus-bath composite space, which defines the ensemble average, $\langle (\cdot) \rangle \equiv \text{Tr}[(\cdot)\rho_T^{\text{st}}(H_T)]$. Denote $\hat{A}(t) \equiv e^{iH_T t} \hat{A} e^{-iH_T t}$ for an arbitrary dynamical operator. Set the time variable $t \geq 0$, unless further specified.

Let \hat{x}_B and \hat{p}_B be the dimensionless solvation coordinate and momentum, respectively. The solvation bath frequency ω_B can be specified later in relation to Gaussian–Wick’s environment description [see Eq. (6)]. We have

$$\dot{\hat{x}}_B = i[H_T, \hat{x}_B] = i[h_B, \hat{x}_B] = \omega_B \hat{p}_B. \quad (2)$$

This leads to $\langle \hat{A}(t) \hat{x}_B(0) \rangle = -\langle \hat{A}(t) \dot{\hat{x}}_B(0) \rangle$ the expression

$$\langle \hat{A}(t) \hat{x}_B(0) \rangle = -\omega_B \langle \hat{A}(t) \hat{p}_B(0) \rangle. \quad (3)$$

This together with $[\hat{x}_B, \hat{p}_B] = i$ constitutes the necessary and sufficient requirements for the to-be-developed dissipaton algebra on the conjugate solvation momentum, in addition to the existing DEOM framework.^{14–16}

Let us begin with the common setup for constructing the DEOM/HEOM theory—the exponential series expansion on the interacting bath correlation function via

$$\langle \hat{x}_B^B(t) \hat{x}_B^B(0) \rangle_B = \frac{1}{\pi} \int_{-\infty}^{\infty} d\omega \frac{e^{-i\omega t} J_B(\omega)}{1 - e^{-\beta\omega}}. \quad (4)$$

This is the fluctuation–dissipation theorem,¹⁷ with both $\hat{x}_B^B(t) \equiv e^{ih_B t} \hat{x}_B e^{-ih_B t}$ and the *equilibrium* ensemble average, $\langle (\cdot) \rangle_B \equiv \text{tr}_B[(\cdot)e^{-\beta h_B}]/\text{tr}_B(e^{-\beta h_B})$, are defined in the uncorrelated bare-bath subspace. Note that $\hat{x}_B^B(t) \neq \hat{x}_B(t)$ and $\langle (\cdot) \rangle_B \neq \langle (\cdot) \rangle$ used in Eq. (3). The involving hybridization bath spectral density in Eq. (4), which satisfies $J_B(-\omega) = -J_B(\omega)$, is given by¹⁷

$$J_B(\omega) \equiv \frac{1}{2} \int_{-\infty}^{\infty} dt e^{i\omega t} \langle [\hat{x}_B^B(t), \hat{x}_B^B(0)] \rangle_B. \quad (5)$$

This also determines the solvation frequency with^{17,19}

$$\omega_B = \frac{1}{\pi} \int_{-\infty}^{\infty} d\omega \omega J_B(\omega). \quad (6)$$

The required exponential series expansion on Eq. (4) can be achieved by adopting a certain sum-over-poles scheme to expand the Fourier integrand there, followed by Cauchy’s contour integration.

Together with the identity $\langle \hat{x}_B^B(0) \hat{x}_B^B(t) \rangle_B = \langle \hat{x}_B^B(t) \hat{x}_B^B(0) \rangle_B^*$, we obtain¹⁵

$$\begin{aligned} \langle \hat{x}_B^B(t) \hat{x}_B^B(0) \rangle_B &= \sum_{k=1}^K \eta_k e^{-\gamma_k t}; \quad (t \geq 0), \\ \langle \hat{x}_B^B(0) \hat{x}_B^B(t) \rangle_B &= \sum_{k=1}^K \eta_k^* e^{-\gamma_k^* t}; \quad (\gamma_k^* \equiv \gamma_k^*). \end{aligned} \quad (7)$$

The second expression follows the fact that $\{\gamma_k\}$ must be either real or complex conjugate paired. The associated index $\bar{k} \in \{k = 1, \dots, K\}$ is defined via $\gamma_{\bar{k}} \equiv \gamma_k^*$.

Note that $\hat{x}_B^B(0) = \hat{x}_B(0)$ and $\dot{\hat{x}}_B^B(0) = \omega_B \hat{p}_B(0) = \omega_B \hat{p}_B = \dot{\hat{x}}_B$, as inferred from Eq. (2). Thus, from Eq. (4), we have

$$\begin{aligned} \langle \dot{\hat{x}}_B \hat{x}_B \rangle_B &= \frac{1}{\pi i} \int_{-\infty}^{\infty} d\omega \frac{\omega J_B(\omega)}{1 - e^{-\beta\omega}} \\ &= \frac{1}{2\pi i} \int_{-\infty}^{\infty} d\omega \omega J_B(\omega) \\ &= \frac{\omega_B}{2i}. \end{aligned} \quad (8)$$

While the second expression uses the property of $J_B(-\omega) = -J_B(\omega)$, the last one is from Eq. (6). Moreover, from the identity, $\langle \dot{\hat{x}}_B \hat{x}_B \rangle_B = -\langle \dot{\hat{x}}_B \hat{x}_B \rangle_B$, and Eq. (7), we obtain

$$\omega_B = -2i \sum_k \gamma_k \eta_k = 2i \sum_k \gamma_k \eta_{\bar{k}}^*. \quad (9)$$

We also have

$$\langle \dot{\hat{x}}_B^2 \rangle_B = \sum_k \eta_k = \sum_k \eta_{\bar{k}}^*. \quad (10)$$

Turn to the existing DEOM framework.^{14–16} First of all, dissipatons $\{\hat{f}_k\}$ are statistically independent quasi-particles and characterize Gaussian solvation environments. To reproduce Eq. (7), we set

$$\hat{x}_B = \sum_{k=1}^K \hat{f}_k, \quad (11)$$

$\hat{f}_k(t) \equiv e^{ih_B t} \hat{f}_k e^{-ih_B t}$, and

$$\begin{aligned} \langle \hat{f}_k(t) \hat{f}_{k'}(0) \rangle_B &= \langle \hat{f}_k \hat{f}_{k'} \rangle_B e^{-\gamma_k t} = \delta_{kk'} \eta_k e^{-\gamma_k t}, \\ \langle \hat{f}_{k'}(0) \hat{f}_k(t) \rangle_B &= \langle \hat{f}_{k'} \hat{f}_k \rangle_B e^{-\gamma_k^* t} = \delta_{kk'} \eta_{\bar{k}}^* e^{-\gamma_k^* t}, \end{aligned} \quad (12)$$

with $\langle \hat{A} \hat{B} \rangle^> \equiv \langle \hat{A}(0+) \hat{B}(0) \rangle$ and $\langle \hat{A} \hat{B} \rangle^< \equiv \langle \hat{A}(0) \hat{B}(0+) \rangle$. Each forward-and-backward pair of dissipaton correlation functions is associated with a single-exponent γ_k . The resultant generalized diffusion equation reads^{14,15}

$$\text{tr}_B \left[\left(\frac{\partial}{\partial t} \hat{f}_k \right)_B \rho_T(t) \right] = -\gamma_k \text{tr}_B [\hat{f}_k \rho_T(t)]. \quad (13)$$

Dynamical variables in DEOM are the dissipaton-augmented-reduced density operators (DDOs),^{14–16}

$$\rho_{n_1, \dots, n_K}^{(n)}(t) \equiv \rho_{n_1, \dots, n_K}^{(n)}(t) \equiv \text{tr}_B \left[\left(\hat{f}_K^{n_K} \dots \hat{f}_1^{n_1} \right) \rho_T(t) \right]. \quad (14)$$

Here, $n = n_1 + \dots + n_K$, with $n_k \geq 0$ for bosonic dissipators. The product of dissipator operators inside $(\dots)^\circ$ is *irreducible*, satisfying $(\hat{f}_k \hat{f}_j)^\circ = (\hat{f}_j \hat{f}_k)^\circ$ for bosonic dissipators. Each n -particle DDO, $\rho_n^{(n)}(t)$, is specified with an ordered set of indexes, $\mathbf{n} \equiv \{n_1 \dots n_K\}$. Also denoted for later use is \mathbf{n}_k^\pm that differs from \mathbf{n} only at the specified \hat{f}_k -dissipator participation number n_k by ± 1 . The reduced system density operator is just $\rho_0^{(0)} \equiv \rho_{0\dots 0}^{(0)}$.

In Eq. (14), $\rho_T(t)$ denotes the total composite density operator that satisfies

$$\dot{\rho}_T = -i[H_T, \rho_T] = -i[H_S + h_B + \hat{Q}_S \hat{x}_B, \rho_T]. \quad (15)$$

For presenting the related dissipator algebra, we adopt hereafter the following notations:

$$\begin{aligned} \rho_n^{(n)}(t; \hat{A}^\times) &\equiv \text{tr}_B[(\hat{f}_K^{n_K} \dots \hat{f}_1^{n_1})^\circ \hat{A}^\times \rho_T(t)], \\ \rho_n^{(n)}(t; \hat{A}^\lessgtr) &\equiv \text{tr}_B[(\hat{f}_K^{n_K} \dots \hat{f}_1^{n_1})^\circ \hat{A}^\lessgtr \rho_T(t)], \end{aligned} \quad (16)$$

where $\hat{A}^\times \equiv \hat{A}^> - \hat{A}^<$, with

$$\hat{A}^> \rho_T(t) \equiv \hat{A} \rho_T(t), \quad \hat{A}^< \rho_T(t) \equiv \rho_T(t) \hat{A}. \quad (17)$$

The generalized diffusion equation (13) is now used together with $(\frac{\partial}{\partial t} \hat{f}_k)_B = -i[\hat{f}_k, h_B]$ and results in¹⁴

$$\rho_n^{(n)}(t; h_B^\times) = -i \left(\sum_k n_k \gamma_k \right) \rho_n^{(n)}(t). \quad (18)$$

This is the dissipator algebra on the bath h_B -action.

The action of system-bath coupling is treated with generalized Wick's theorem,^{14,15}

$$\begin{aligned} \rho_n^{(n)}(t; \hat{f}_k^>) &= \rho_{n_k^+}^{(n+1)}(t) + \sum_{k'} n_{k'} \langle \hat{f}_k \hat{f}_{k'} \rangle_B^> \rho_{n_{k'}^-}^{(n-1)}(t), \\ \rho_n^{(n)}(t; \hat{f}_k^<) &= \rho_{n_k^-}^{(n+1)}(t) + \sum_{k'} n_{k'} \langle \hat{f}_k \hat{f}_{k'} \rangle_B^< \rho_{n_{k'}^+}^{(n-1)}(t). \end{aligned}$$

Here, $\langle \hat{f}_k \hat{f}_{k'} \rangle_B^> = \delta_{kk'} \eta_k$ and $\langle \hat{f}_k \hat{f}_{k'} \rangle_B^< = \delta_{kk'} \eta_k^*$ via Eq. (12). Together with Eq. (11), we have

$$\rho_n^{(n)}(t; \hat{x}_B^\lessgtr) = \sum_k \rho_n^{(n)}(t; \hat{f}_k^\lessgtr), \quad (19)$$

with

$$\begin{aligned} \rho_n^{(n)}(t; \hat{f}_k^>) &= \rho_{n_k^+}^{(n+1)}(t) + n_k \eta_k \rho_{n_k^-}^{(n-1)}(t), \\ \rho_n^{(n)}(t; \hat{f}_k^<) &= \rho_{n_k^-}^{(n+1)}(t) + n_k \eta_k^* \rho_{n_k^+}^{(n-1)}(t). \end{aligned} \quad (20)$$

By applying Eq. (15) for the total composite density operator $\rho_T(t)$ in Eq. (14), followed by using Eqs. (18)–(20), we obtain¹⁴

$$\begin{aligned} \dot{\rho}_n^{(n)} &= - \left(i H_S^\times + \sum_k n_k \gamma_k \right) \rho_n^{(n)} - i \sum_k \hat{Q}_S^\times \rho_{n_k^+}^{(n+1)} \\ &\quad - i \sum_k n_k (\eta_k \hat{Q}_S^> - \eta_k^* \hat{Q}_S^<) \rho_{n_k^-}^{(n-1)}. \end{aligned} \quad (21)$$

As this recovers the HEOM formalism,^{7–12} we would also have *de facto* validated the existing dissipator algebra on the solvation coordinate \hat{x}_B [Eqs. (11)–(20)].

We are now in the position to develop the dissipator algebra on the solvation momentum \hat{p}_B , in addition to the existing DEOM framework. To proceed, we set in analogy to Eq. (11) the decomposition,

$$\hat{p}_B = \sum_{k=1}^K \hat{\phi}_k, \quad (22)$$

and thus,

$$\rho_n^{(n)}(t; \hat{p}_B^\lessgtr) = \sum_k \rho_n^{(n)}(t; \hat{\phi}_k^\lessgtr). \quad (23)$$

The proposed new ingredients read

$$\begin{aligned} \rho_n^{(n)}(t; \hat{\phi}_k^>) &= - \frac{\gamma_k}{\omega_B} [\rho_{n_k^+}^{(n+1)}(t) - n_k \eta_k \rho_{n_k^-}^{(n-1)}(t)], \\ \rho_n^{(n)}(t; \hat{\phi}_k^<) &= - \frac{\gamma_k}{\omega_B} [\rho_{n_k^-}^{(n+1)}(t) - n_k \eta_k^* \rho_{n_k^+}^{(n-1)}(t)]. \end{aligned} \quad (24)$$

The proof below goes with their satisfying two basic requirements.

Consider the result on $[\hat{x}_B, \hat{p}_B] = i$. In the DEOM-space algebra, this necessary requirement amounts to

$$\rho_n^{(n)}(t; [\hat{x}_B, \hat{p}_B]^\lessgtr) = i \rho_n^{(n)}(t). \quad (25)$$

Proof. Equation (24), together with Eq. (20), leads to

$$\begin{aligned} \rho_n^{(n)}[t; (\hat{f}_k \hat{\phi}_k)^>] &= \rho_{n_k^+}^{(n+1)}(t; \hat{\phi}_k^>) + n_k \eta_k \rho_{n_k^-}^{(n-1)}(t; \hat{\phi}_k^>) \\ &= - \frac{\gamma_k}{\omega_B} [\rho_{n_k^+}^{(n+2)}(t) - 2 \binom{n_k}{2} \eta_k^2 \rho_{n_k^+}^{(n-2)}(t)] \\ &\quad + \frac{\gamma_k \eta_k}{\omega_B} \rho_n^{(n)}(t) \end{aligned} \quad (26a)$$

and

$$\begin{aligned} \rho_n^{(n)}[t; (\hat{\phi}_k \hat{f}_k)^>] &= - \frac{\gamma_k}{\omega_B} [\rho_{n_k^+}^{(n+1)}(t; \hat{f}_k^>) - n_k \eta_k \rho_{n_k^-}^{(n-1)}(t; \hat{f}_k^>)] \\ &= - \frac{\gamma_k}{\omega_B} [\rho_{n_k^+}^{(n+2)}(t) - 2 \binom{n_k}{2} \eta_k^2 \rho_{n_k^+}^{(n-2)}(t)] \\ &\quad - \frac{\gamma_k \eta_k}{\omega_B} \rho_n^{(n)}(t). \end{aligned} \quad (26b)$$

The $\rho_n^{(n)}[t; (\hat{f}_k \hat{\phi}_k)^<]$ and $\rho_n^{(n)}[t; (\hat{\phi}_k \hat{f}_k)^<]$ counterparts are similar to $\rho_n^{(n)}[t; (\hat{\phi}_k \hat{f}_k)^>]$ and $\rho_n^{(n)}[t; (\hat{f}_k \hat{\phi}_k)^>]$, respectively, but with η_k being replaced by η_k^* . Together with

$$\rho_n^{(n)}(t; [\hat{f}_k, \hat{\phi}_k]^\lessgtr) \equiv \rho_n^{(n)}[t; (\hat{f}_k \hat{\phi}_k)^\lessgtr] - \rho_n^{(n)}[t; (\hat{\phi}_k \hat{f}_k)^\lessgtr],$$

we obtain

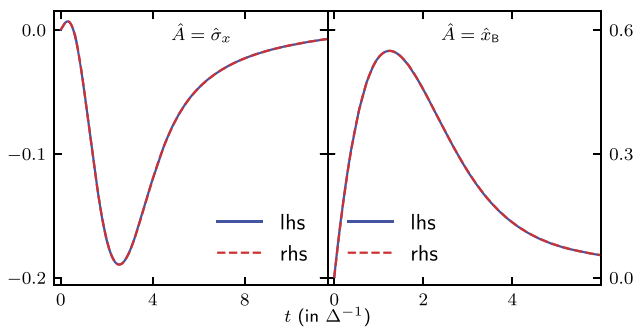


FIG. 1. Numerical validation of Eq. (24) via the equality between lhs and rhs of Eq. (3) exemplified with $\hat{A} = \hat{\sigma}_x$ (left panel) and \hat{x}_B (right panel) for $H_S = \frac{\Delta}{2} \hat{\sigma}_z + \frac{V}{2} \hat{\sigma}_x$ and $\hat{Q}_S = \Delta \hat{\sigma}_x$. Bath spectral density is $J_B(\omega) = (\omega_B \zeta_B \omega) / [(\omega_B^2 - \omega^2)^2 + \zeta_B^2 \omega^2]$. Parameters are $V = \omega_B = \zeta_B = k_B T = \Delta$. Plotted are only the real parts, whereas the imaginary parts are also equal (not shown here).

$$\begin{aligned} \rho_n^{(n)}(t; [\hat{f}_k, \hat{\phi}_{k'}]^>) &= 2\delta_{kk'} \frac{\gamma_k \eta_k}{\omega_B} \rho_n^{(n)}(t), \\ \rho_n^{(n)}(t; [\hat{f}_k, \hat{\phi}_{k'}]^<) &= -2\delta_{kk'} \frac{\gamma_k \eta_k^*}{\omega_B} \rho_n^{(n)}(t). \end{aligned} \quad (27)$$

Consequently,

$$\begin{aligned} \rho_n^{(n)}(t; [\hat{x}_B, \hat{p}_B]^>) &= \frac{2}{\omega_B} \left(\sum_k \gamma_k \eta_k \right) \rho_n^{(n)}(t), \\ \rho_n^{(n)}(t; [\hat{x}_B, \hat{p}_B]^<) &= -\frac{2}{\omega_B} \left(\sum_k \gamma_k \eta_k^* \right) \rho_n^{(n)}(t). \end{aligned} \quad (28)$$

Together with the expression of ω_B of Eq. (9), we obtain Eq. (25). It is worth noting that Eq. (27) would imply that $[\hat{f}_k, \hat{\phi}_{k'}]^> = 2\delta_{kk'} \gamma_k \eta_k / \omega_B$ and $[\hat{f}_k, \hat{\phi}_{k'}]^< = 2\delta_{kk'} \gamma_k \eta_k^* / \omega_B$. The information on $[\hat{f}_k, \hat{\phi}_k]$ is undetermined. However, the necessary requirement is concerned only with $\sum_k [\hat{f}_k, \hat{\phi}_k] = [\hat{x}_B, \hat{p}_B] = i$. Its DEOM-space equivalence [Eq. (25)] has just been proved to be satisfied by the new ingredients of dissipaton algebra in Eq. (24).

The sufficient requirement is concerned with Eq. (3), since it engages an arbitrary dynamical operator \hat{A} . We exploit Eq. (24) to evaluate $\langle \hat{A}(t) \hat{p}_B(0) \rangle$ in the right-hand side (rhs) of Eq. (3). In parallel, we evaluate the left-hand side (lhs) of Eq. (3), $\langle \hat{A}(t) \hat{x}_B(0) \rangle$, with the well-established dissipaton algebra on solvation coordinate \hat{x}_B . The agreement between these two DEOM evaluations is rigorously proved in the [supplementary material](#), on the basis of quantum mechanics linear-space constructions. We thus have analytically validated Eq. (24). In Fig. 1, we present the numerical demonstrations on the required consistency with two representing types of \hat{A} , the system-type vs hybrid bath-type.

To conclude this paper, we illustrate the novel phase-space dissipaton algebra with the heat current fluctuation. To this end, we adopt the heat current operator \hat{J} , the convention^{21,22} in analogy to that of electron transport,

$$\hat{J} \equiv -\frac{d\hat{h}_B}{dt} = -i[H_{SB}, \hat{h}_B] = \hat{Q}_S \omega_B \hat{p}_B. \quad (29)$$

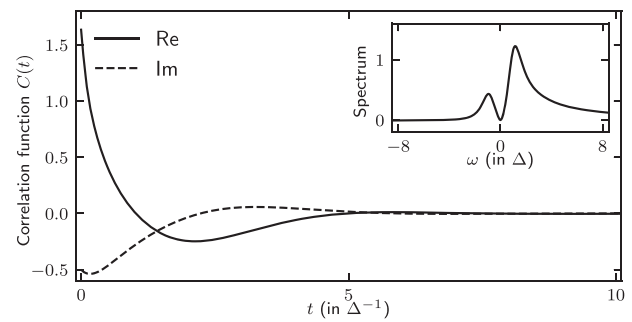


FIG. 2. Correlation function $C(t)$ [Eq. (30)] together with its spectrum for the same system of Fig. 1.

It is noted that there are other conventions of heat current adopted in various contexts.^{22–27} Nevertheless, for the main purpose of the present work, we adopt Eq. (29) to “visualize” the dissipaton momentum and the resulted phase-space DEOM-based evaluations. Figure 2 depicts the heat current correlation,

$$C(t) \equiv \langle \delta \hat{J}(t) \delta \hat{J}(0) \rangle, \quad (30)$$

with $\delta \hat{J} \equiv \hat{J} - \langle \hat{J} \rangle$, where the average current $\langle \hat{J} \rangle = 0$ at the equilibrium scenario considered here. The inset reports the zero-current fluctuation spectrum. The phase-space DEOM-based quantum mechanics evaluation is detailed in the [supplementary material](#).

In summary, we complete the phase-space DEOM theory by adding the dissipaton algebra for the hybrid bath solvation momentum. The new ingredients, Eqs. (22) and (23), are shown to satisfy the requirements of both necessary and sufficient criteria. The exemplified quantum heat current fluctuation, Eq. (30) with Eq. (29), is a new class of properties which would not be accessible without the present development. The resulted phase-space DEOM is a universal and versatile tool for accurate evaluations on system-plus-hybrid bath dynamics. The extension to a non-equilibrium scenario involving multiple bath reservoirs and multiple dissipative modes would be straightforward. It would also be anticipated that the phase-space DEOM theory will serve as a solid ground for the development of various practical simulation methods toward realistic molecular systems in condensed phases.

See the [supplementary material](#) for the DEOM-space quantum mechanics and an analytical proof of dissipaton momentum algebra satisfying Eq. (3).

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REFERENCES

- A. A. Golosov, R. A. Friesner, and P. Pechukas, *J. Chem. Phys.* **112**, 2095 (2000).
- M. Thoss, H. B. Wang, and W. H. Miller, *J. Chem. Phys.* **115**, 2991 (2001).
- A. Garg, J. N. Onuchic, and V. Ambegaokar, *J. Chem. Phys.* **83**, 4491 (1985).
- L. D. Zusman, *Chem. Phys.* **49**, 295 (1980).

- ⁵L. D. Zusman, *Chem. Phys.* **80**, 29 (1983).
- ⁶A. O. Caldeira and A. J. Leggett, *Physica A* **121**, 587 (1983).
- ⁷Y. Tanimura and R. Kubo, *J. Phys. Soc. Jpn.* **58**, 101 (1989).
- ⁸Y. Tanimura, *Phys. Rev. A* **41**, 6676 (1990).
- ⁹Y. Tanimura, *J. Phys. Soc. Jpn.* **75**, 082001 (2006).
- ¹⁰Y. A. Yan, F. Yang, Y. Liu, and J. S. Shao, *Chem. Phys. Lett.* **395**, 216 (2004).
- ¹¹R. X. Xu, P. Cui, X. Q. Li, Y. Mo, and Y. J. Yan, *J. Chem. Phys.* **122**, 041103 (2005).
- ¹²R. X. Xu and Y. J. Yan, *Phys. Rev. E* **75**, 031107 (2007).
- ¹³R. P. Feynman and F. L. Vernon, Jr., *Ann. Phys.* **24**, 118 (1963).
- ¹⁴Y. J. Yan, *J. Chem. Phys.* **140**, 054105 (2014).
- ¹⁵Y. J. Yan, J. S. Jin, R. X. Xu, and X. Zheng, *Front. Phys.* **11**, 110306 (2016).
- ¹⁶H. D. Zhang, R. X. Xu, X. Zheng, and Y. J. Yan, *Mol. Phys.* **116**, 780 (2018), Special Issue, "Molecular Physics in China."
- ¹⁷U. Weiss, *Quantum Dissipative Systems*, 3rd ed. Series in Modern Condensed Matter Physics, Vol. 13 (World Scientific, Singapore, 2008).
- ¹⁸H. Kleinert, *Path Integrals in Quantum Mechanics, Statistics, Polymer Physics, and Financial Markets*, 5th ed. (World Scientific, Singapore, 2009).
- ¹⁹Y. J. Yan and R. X. Xu, *Annu. Rev. Phys. Chem.* **56**, 187 (2005).
- ²⁰J. G. Kirkwood, *J. Chem. Phys.* **3**, 300 (1935).
- ²¹D. H. He, J. Thingna, and J. S. Cao, *Phys. Rev. B* **97**, 195437 (2018).
- ²²L. Song and Q. Shi, *Phys. Rev. B* **95**, 064308 (2017).
- ²³M. Esposito, M. A. Ochoa, and M. Galperin, *Phys. Rev. B* **92**, 235440 (2015).
- ²⁴R. Schmidt, M. F. Carusela, J. P. Pekola, S. Suomela, and J. Ankerhold, *Phys. Rev. B* **91**, 224303 (2015).
- ²⁵T. Motz, J. Ankerhold, and J. T. Stockburger, *New J. Phys.* **19**, 053013 (2017).
- ²⁶T. Motz, M. Wiedmann, J. T. Stockburger, and J. Ankerhold, *New J. Phys.* **20**, 113020 (2018).
- ²⁷M. Wiedmann, J. T. Stockburger, and J. Ankerhold, "Out-of-equilibrium operation of a quantum heat engine: The cost of thermal coupling control" [arXiv:1903.11368](https://arxiv.org/abs/1903.11368) (2019).