Quantum Fokker-Planck theory in a non-Gaussian-Markovian medium

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We develop a generalized quantum Fokker-Planck theory in a non-Gaussian-Markovian model bath. The semiclassical bath adopted in this work is charactered by three parameters. One denotes the strength of system-bath coupling and the other two are chosen to interpolate smoothly the solvation dynamics between the long- and short-time regimes. The fluctuation-dissipation relation in this model bath is analyzed in detail. Based on this model bath, we derive two sets of coupled Fokker-Planck equations. These two equation sets are equivalent in the second order of system-bath coupling but different in the higher orders. The corresponding reduced Liouville equation in one set of the Fokker-Planck formulation is characterized by a memory relaxation kernel, while that in the other is by a local-time relaxation tensor. Each resulting set of Fokker-Planck equations involves only the reduced density operator and a series of well-characterized Hilbert-space relaxation operators. The present theory is valid for arbitrary time-dependent Hamiltonians and is applicable to the study of quantum coherence and relaxation in various dynamic systems. [S1050-2947(98)05210-X]

I. INTRODUCTION

Molecular dynamics in dissipative media is of the center interest in quantum statistical mechanics. Relaxation processes occur in almost all fields of science, including NMR [1–5], quantum optics [6–8], optical spectroscopies [9–11], quantum transport [12–16], chemical reactions [16–20], and biological electron transfer [21,22]. The concept of relaxation is physically related to a reduced description on an open system in contact with its surroundings. In general, the surroundings consist of a practically infinite number of degrees of freedom and act as a whole identity, referred as the thermal bath, on the open system. Only the system of primary interest is considered microscopically. The bath is incorporated via its effect on the open system in a statistical manner.

The object of study in quantum statistical dynamics is the reduced density matrix for the system, denoted as $\rho(t) = \mathrm{tr}_B \rho_T(t)$, i.e., the trace of the total density matrix over all bath degrees of freedom. The equation of motion for the reduced density matrix $\rho(t)$, i.e., the reduced Liouville equation, can be formally derived via the Zwanzig-Mori projection operator approach [12–15,23–26]. There are two prescriptions of the reduced Liouville equation. One is characterized by the memory relaxation kernel $\gamma(t-\tau)$ and reads

$$\dot{\rho}(t) = -\frac{i}{\hbar}[H,\rho(t)] - \int_0^t d\tau\, \gamma(t-\tau)\rho(\tau). \quad (1.1)$$

As concerns the temporal sequence of the involving actions in $\gamma(t-\tau)\rho(\tau)$, Eq. (1.1) is also said to be in the chronological ordering prescription (COP). An alternative prescription of the reduced Liouville equation is characterized by the local-time kernel $\mathcal{R}(t)$ and reads

$$\dot{\rho}(t) = -\frac{i}{\hbar}[H,\rho(t)] - \mathcal{R}(t)\rho(t). \quad (1.2)$$

Equation (1.2) is also said to be in a partial ordering prescription (POP) according to the temporal sequence of the involving actions in $\mathcal{R}(t)\rho(t)$. The relaxation kernels γ and $\mathcal{R}$ are super-operators that act on the reduced density matrix. In principle, both γ and $\mathcal{R}$ can be formulated exactly in terms of the system-bath interaction. In this sense, the reduced Liouville equations in the COP [Eq. (1.1)] and POP [Eq. (1.2)] forms are equivalent. However, exact Liouville equations can only be numerically implemented in very few systems, such as a harmonic oscillator linearly coupled to a harmonic bath. In most cases, certain approximation schemes should be employed. One of the standard approximations is the weak-coupling limit in which the system-bath interaction is considered only up to second order. The contribution of higher-order system-bath interactions is only partially included in a certain resummation framework. In this case, Eqs. (1.1) and (1.2) would represent two approximation schemes and thus are no longer equivalent.

One of the main obstacles in the direct use of the reduced Liouville equation (1.1) or (1.2) is the tensor property of the relaxation kernel γ or $\mathcal{R}$. In a finite N basis set representation, the reduced density matrix $\rho=\{\rho_{mn}\}$ is described by its N^2 elements, while the relaxation kernel $\gamma=\{\gamma_{mn,m'n'}\}$ or $\mathcal{R}=\mathcal{R}_{mn,m'n'}$, is described by $N^2 \times N^2$ elements. In a continuum representation, such as a phase-space $\mathbf{pq}$ representation for a system of d degrees of freedom, $\rho(\mathbf{pq})$ is a function of two-dimensional variables, while $\gamma(\mathbf{pq},\mathbf{p'q'})$ or $\mathcal{R}(\mathbf{pq},\mathbf{p'q'})$ depends on four-dimensional variables.

There are two major theoretical approaches, namely, the Bloch-Redfield formulation and the Fokker-Planck equation, to the study of quantum relaxation dynamics. In the Bloch-Redfield approach the reduced Liouville equation is represented explicitly in the basis set of eigenstates of the time-independent system Hamiltonian H. The Redfield theory establishes the relationship among various relaxation tensor elements. The commonly used Redfield theory involves also the Markovian (white-noise) approximation in which $\gamma(t-\tau) = \mathcal{R}\delta(t-\tau)$ and $\mathcal{R}(t)$ is replaced by $\mathcal{R}(\infty)$. In this case, the reduced Liouville equations in the COP [Eq. (1.1)] and

POP [Eq. (1.2)] forms are identical, leading to a time-independent relaxation kernel $\mathcal{R}=\mathcal{R}(t\rightarrow\infty)$. The generalized Redfield theory beyond the Markovian limit will be considered elsewhere for both the COP and POP forms of the reduced Liouville equation.

In this paper we shall adopt the Fokker-Planck (FP) equations-of-motion approach to the reduced density matrix. That is to develop a set of coupled operator equations of motion for the study of quantum relaxation dynamics. The FP formulation constitutes an important theoretical framework for the study of dissipative processes. The FP equation was originally devised as a classical theory of Brownian motion [27,28]. A quantum FP theory was developed about 20 years ago by Dekker [29–31] via a canonical quantization procedure with complex variables. Currently, there are two theoretical approaches to the development of quantum FP equations in various systems. One approach is based on Feynman and Vernon's path integral influence functional method [32,33]. In this approach one considers explicitly a quantum system that linearly couples to a harmonic bath [33–39]. Using this method, Caldeira and Leggett [34] derived a quantum FP equation in the Markovian limit. Tanimura and co-workers [35–39] extended Caldeira and Leggett's result to the Gaussian-Markovian bath in which the time correlation function assumes an exponential form. In this case, a set of N-coupled quantum FP equations, instead of a single FP equation in the Markovian limit, is obtained [35–39]. An alternative approach to FP equations is to start with the stochastic description of a weak system-bath interaction [40–42]. This is the approach used in a recent work by Cao [41], who deduced a set of two coupled FP equations for the quantum relaxation in a Gaussian-Markovian bath. Note that for the same system, Tanimura and co-workers found in a set of $N\geqslant 2$ equations of motion [35–39]. The above plausible discrepancy originated from the different resummation approximation schemes used by these two groups. Tanimura and co-workers' formulation was based on a kind of second-order POP reduced Liouville equation, while Cao's pair of equations was based on the second-order COP scheme. In the Markovian limit, both formulations [35,41] recover the result of Caldeira and Leggett [34].

In this paper we shall develop a generalized quantum FP theory in a *non-Gaussian-Markovian* medium. We shall adopt a model bath that allows a smoothly interpolation of relaxation dynamics between the long- and short-time regimes. To be flexible for various representations, our theory will be developed thoroughly in the operator level. For the applicability of theory to time-resolved experiments with pulsed external fields, the system Hamiltonian $H(t)$ will be treated as a time-dependent operator. The remainder of this paper will be organized as follows. In Sec. II we summarize the background knowledge of the reduced density matrix. This includes the stochastic description of the system-bath interaction, a detailed derivation of the reduced Liouville equations in both the COP and POP forms, and the introduction of generalized Langevin forces. In Sec. III we propose a non-Gaussian-Markovian bath model that will be employed in this paper. The main contribution of this work is in Sec. IV, in which a generalized FP theory for the non-Gaussian-Markovian bath is developed for the reduced density matrix in both the COP and POP forms. The key step in the deriva-

tion is to construct for each of the COP and POP schemes a hierarchical series of bath induced relaxation operators $\{K_n(t),\ n=0,\ldots,N\}$. In Sec. V we discuss several topics related to the quantum FP theory. We first consider the FP equations in the Gaussian-Markovian and Markovian (white-noise) relaxation media as the limiting cases of the present theory. We further discuss the possible physical implication of the hierarchical set of relaxation operators $\{K_n(t),\ n=0,\ldots,N\}$, together with the truncation number N in relation to the non-Gaussian-Markovian bath. As the form of bath model is crucial to the generalized FP theory, we also present a detailed analysis of the semiclassical fluctuation-dissipation relation that is implied in the model. Finally, we summarize our results in Sec. VI.

II. REDUCED LIOUVILLE EQUATIONS AND GENERALIZED LANGEVIN FORCES

A. Stochastic description of the system-bath interaction

We shall in this section outline some formal results of the reduced Liouville equation that will serve as the starting point to the generalized FP theory to be developed in this work. Without losing generality, we adopt in this paper a stochastic description for the system-bath interaction [43–46]. Formally, it is equivalent to treating the total Hamiltonian that governs the time evolution of $\rho_T(t)$ as a time-dependent operator with the partitioning

$$H_T(t)=H(t)+H'(t). \tag{2.1}$$

Here $H(t)$ is the deterministic Hamiltonian that governs the coherent motion of the reduced system density matrix, while $H'(t)$ is a stationary stochastic dynamic variable for the system-bath interaction that governs the relaxation. We have

$$\langle H'(t)\rangle=0, \tag{2.2a}$$

$$\langle H'(t)H'(\tau)\rangle=\langle H'(t-\tau)H'(0)\rangle. \tag{2.2b}$$

In Eq. (2.2) and hereafter, the angular brackets denote the ensemble average over the initially stationary bath density matrix $\rho_B(0)$. Its formal definition can be expressed for an arbitrary operator $\hat{O}$ in the joint system-bath space as

$$\langle\hat{O}\rangle\equiv\mathrm{tr}_B[\hat{O}\rho_B(0)]. \tag{2.3}$$

Here tr_B denotes the trace over all bath degrees of freedom. Note that $\langle\hat{O}\rangle$ may remain as an operator in the system dynamic space. The deterministic Hamiltonian contains also the static mean field of the system-bath interaction so that $\langle H'(t)\rangle=0$ [Eq. (2.2a)]. Note that the deterministic Hamiltonian $H(t)$ may also depend on time via, for example, the external pulsed fields in the study of nonlinear spectroscopies in condensed phases. However, the time dependence of the stochastic Hamiltonian $H'(t)$ arises from the Brownian motion of practically infinite number of bath degrees of freedom.

B. Reduced Liouville equations in two prescriptions

We shall be interested in the time evolution of the reduced density matrix of an open system, defined as

$$\rho(t) \equiv \mathrm{tr}_B[\rho_T(t)]. \tag{2.4}$$

Here ρ_T is the total density matrix for both the system and the bath. The formally exact Liouville equation for reduced density matrix ρ can in principle be obtained via the Zwanzig-Mori projection operator techniques [12–15,23–26]. However, in any practical application, two approximations are commonly invoked. The first one is the initial factorization ansatz. It assumes that the total density matrix $\rho_T(0)$ at the initial time $t=0$ can be factorized as the product of the system and bath contributions, that is,

$$\rho_T(0) = \rho(0)\rho_B(0). \tag{2.5}$$

The second approximation is the weak system-bath interaction limit in which the second-order perturbation theory is applicable. However, there are a variety of partial resummation schemes to approximately account for the higher-order system-bath interaction. In the following, we shall present two partial resummation schemes that lead to two different prescriptions of the reduced Liouville equation.

Let us start with the formally exact Liouville equation for the total density matrix

$$\dot{\rho}_T(t) = -i\mathcal{L}(t)\rho_T(t) - i\mathcal{L}'(t)\rho_T(t). \tag{2.6}$$

The Liouvillians $\mathcal{L}$ and $\mathcal{L}'$ are the commutators of their corresponding Hamiltonians and are defined via an arbitrary operator $\hat{O}$ as

$$\mathcal{L}(t)\hat{O} \equiv \hbar^{-1}[H(t),\hat{O}], \tag{2.7a}$$

$$\mathcal{L}'(t)\hat{O} \equiv \hbar^{-1}[H'(t),\hat{O}]. \tag{2.7b}$$

For further theoretical development, we shall also introduce the Liouville-space Green's function $\mathcal{G}(t,\tau)$ for the deterministic Liouvillian $\mathcal{L}$. It satisfies the Liouville equation

$$\partial\mathcal{G}(t,\tau)/\partial t \equiv -i\mathcal{L}(t)\mathcal{G}(t,\tau). \tag{2.8}$$

The Liouville-space Green's function can also be defined in terms of the Hilbert-space Green's function $G(t,\tau)$ via the relation for an arbitrary operator $\hat{O}$,

$$\mathcal{G}(t,\tau)\hat{O} \equiv G(t,\tau)\hat{O}G^\dagger(t,\tau). \tag{2.9}$$

Here G satisfies the Schrödinger equation

$$\frac{\partial G(t,\tau)}{\partial t} \equiv -\frac{i}{\hbar}H(t)G(t,\tau). \tag{2.10}$$

The formal solution to the total density matrix $\rho_T(t)$ in Eq. (2.6) can be obtained via the interaction picture

$$\rho_T(t) \equiv \mathcal{G}(t,0)\rho_T^I(t), \tag{2.11a}$$

$$\mathcal{L}_I'(t) = \mathcal{G}^\dagger(t,0)\mathcal{L}'(t)\mathcal{G}(t,0). \tag{2.11b}$$

Equation (2.6) can thus be recast as

$$\dot{\rho}_T^I(t) = -i\mathcal{L}_I'(t)\rho_T^I(t). \tag{2.12}$$

The formal solution to the above equation is given by

$$\begin{aligned}
\rho_T^I(t) &= \rho_T(0) - i\int_0^t d\tau\, \mathcal{L}_I'(\tau)\rho_T^I(\tau) \\
&= \rho_T(0) - i\int_0^t d\tau\, \mathcal{L}_I'(\tau)\rho_T(0) \\
&\quad - \int_0^t d\tau \int_0^\tau d\tau'\, \mathcal{L}_I'(\tau)\mathcal{L}_I'(\tau')\rho_t^I(\tau') \\
&\equiv \exp_+\left[-i\int_0^t d\tau\mathcal{L}_I'(\tau)\right]\rho_T(0). \tag{2.13}
\end{aligned}$$

In deriving Eq. (2.13) we have made use of the relation of $\rho_T^I(0) = \rho_T(0)$ as implied in Eq. (2.11a).

We shall now turn to the reduced density matrix in the interaction picture,

$$\rho_I(t) \equiv \mathcal{G}^\dagger(t,0)\rho(t) = \mathrm{tr}_B[\rho_T^I(t)]. \tag{2.14}$$

Note that from Eq. (2.2a) we have

$$\langle\mathcal{L}_I'(t)\rangle = 0. \tag{2.15}$$

By using Eqs. (2.5), (2.14) and (2.15) we can obtain from the second and the third identities of Eq. (2.13), respectively, the two equivalent equations

$$\rho_I(t) = \rho(t_0) - \int_{t_0}^t d\tau \int_{t_0}^\tau d\tau' \mathrm{tr}_B[\mathcal{L}_I'(\tau)\mathcal{L}_I'(\tau')\rho_T^I(\tau')] \tag{2.16}$$

and

$$\rho_I(t) = \left\langle\exp_+\left[-i\int_{t_0}^t d\tau\mathcal{L}_I'(\tau)\right]\right\rangle\rho(t_0). \tag{2.17}$$

To continue, we shall employ two different approximation schemes to Eqs. (2.16) and (2.17), respectively. One scheme is to invoke a factorization approximation to the integrand in Eq. (2.16), that is,

$$\mathrm{tr}_B\{\mathcal{L}_I'(\tau)\mathcal{L}_I'(\tau')\rho_T^I(\tau')\} \approx \langle\mathcal{L}_I'(\tau)\mathcal{L}_I'(\tau')\rangle\rho_I(\tau'). \tag{2.18}$$

By substituting Eq. (2.18) into Eq. (2.16) followed by taking the time derivative we obtain

$$\dot{\rho}_I(t) = -\int_0^t d\tau\langle\mathcal{L}_I'(t)\mathcal{L}_I'(\tau)\rangle\rho_I(\tau). \tag{2.19}$$

The key quantity in this equation is $\mathcal{L}_I'(t)\mathcal{L}_I'(\tau)\rho_I(\tau)$, in which the reduced density matrix $\rho(\tau)$ and the subsequent Liouville-space actions $\mathcal{L}'(\tau)$ and $\mathcal{L}'(t)$ with $t \geq \tau$ are chronologically ordered. Equation (2.19) is therefore said to be in the chronological ordering prescription. The final reduced Liouville equation for the system density matrix can then be obtained by substituting Eqs. (2.11b) and (2.14) into Eq. (2.19). We have

$$\dot{\rho}^{\mathrm{COP}}(t) = -i\mathcal{L}(t)\rho^{\mathrm{COP}}(t) - 0\int_{t_0}^t d\tau\gamma(t,\tau)\rho^{\mathrm{COP}}(\tau), \tag{2.20a}$$

$$\gamma(t,\tau)=\langle \mathcal{L}'(t)\mathcal{G}(t,\tau)\mathcal{L}'(\tau)\rangle. \qquad (2.20b)$$

Here the superscript ''COP'' denotes the reduced Liouville equation in the chronological ordering prescription.

An alternative scheme of approximation is to invoke a second-order cummulant expansion of the time-ordered exponential function in Eq. (2.17), that is,

$$\left\langle \exp_+\left[-i\int_0^t d\tau \mathcal{L}_I'(\tau)\right]\right\rangle \approx \exp_+\left[-\int_0^t d\tau \mathcal{R}_I(\tau)\right], \qquad (2.21)$$

with

$$\mathcal{R}_I(t)=\int_0^t d\tau \langle \mathcal{L}_I'(t)\mathcal{L}_I'(\tau)\rangle. \qquad (2.22)$$

By substituting Eq. (2.21) into Eq. (2.17) followed by taking the time derivative we have

$$\dot\rho_I(t)=-\mathcal{R}_I(t)\rho_I(t). \qquad (2.23)$$

In contrast to Eq. (2.19) or (2.20), the temporal sequence in $\mathcal{R}_I(t)\rho_I(t)$ [cf. Eq. (2.22)] is only partially ordered. Equation (2.23) is therefore said to be in a partial ordering prescription. Equation (2.23) together with Eqs. (2.11b) and (2.14) leads to

$$\dot\rho^{POP}(t)=-i\mathcal{L}(t)\rho^{POP}(t)-\mathcal{R}(t)\rho^{POP}(t), \qquad (2.24a)$$

$$\mathcal{R}(t)\equiv\int_0^t d\tau \langle \mathcal{L}'(t)\mathcal{G}(t,\tau)\mathcal{L}'(\tau)\mathcal{G}^\dagger(t,\tau)\rangle. \qquad (2.24b)$$

Here the superscript ''POP'' denotes the reduced Liouville equation in the partial ordering prescription.

The COP Liouville equation [Eq. (2.20)] and the POP Liouville equation [Eq. (2.24)] involve the approximants of Eqs. (2.18) and (2.21), respectively. These two approximants are the same up to second order but different at higher orders in the system-bath interaction. There is no *a priori* criterion to which prescription is superior to other.

C. Generalized Langevin forces

In order to derive the generalized FP equations, we shall present the reduced Liouville equation in both the COP [Eq. (2.20)] and POP [Eq. (2.24)] forms in terms of the generalized Langevin force-force correlation functions. To do that, we shall decompose the system-bath interaction in terms of the generalized system coordinates and the generalized Langevin force

$$H'(t)=-\sum_a F_a(t)Q_a. \qquad (2.25)$$

The generalized coordinate Q_a is a Hermitian operator on the reduced system space, while the Langevin force $F_a(t)$ is a stationary stochastic Hermitian operator on the bath space. Equation (2.2a) implies that $\langle F_a(t)\rangle=0$. Let us denote the force-force correlation function as

$$C_{ab}(t-\tau)\equiv\langle F_a(t)F_b(\tau)\rangle\equiv\mathrm{tr}_B[F_a(t)F_b(\tau)\rho_B(0)]. \qquad (2.26)$$

The detailed balance or the quantum fluctuation-dissipation relation in term of the correlation function reads [47]

$$C_{ab}^*(t)=C_{ab}(t-i\beta). \qquad (2.27)$$

Here the asterisk denotes the complex conjugate and $\beta=\hbar/k_BT$, with k_B being the Boltzmann constant and T the temperature. Equation (2.27) is equivalent to the following relation in the frequency-domain [47]:

$$\hat C_{ba}(-\omega)=e^{-\beta\omega}\hat C_{ab}(\omega). \qquad (2.28)$$

In this equation $\hat C_{ab}(\omega)$ is the spectrum of the cross-correlation function and is defined as

$$\hat C_{ab}(\omega)=2\,\mathrm{Re}\int_0^\infty dt e^{i\omega t}C_{ab}(t). \qquad (2.29)$$

By using Eqs. (2.25) and (2.26), we can now recast the COP Liouville equation [Eq. (2.20)] as (cf. the Appendix)

$$\dot\rho^{COP}(t)=-(i/\hbar)[H(t),\rho^{COP}(t)]$$
$$-\hbar^{-2}\sum_a \{[Q_a,\tilde Q_a^{COP}(t)]+\mathrm{H.c.}\}, \qquad (2.30a)$$

$$\tilde Q_a^{COP}(t)=\sum_b \int_0^t d\tau C_{ab}(t-\tau)$$
$$\times G(t,\tau)Q_b\rho^{COP}(\tau)G^\dagger(t,\tau). \qquad (2.30b)$$

Similarly, we can recast the POP Liouville equation [Eq. (2.24)] as

$$\dot\rho^{POP}(t)=-(i/\hbar)[H(t),\rho^{POP}(t)]$$
$$-\hbar^{-2}\sum_a \{[Q_a,\tilde Q_a(t)\rho^{POP}(t)]+\mathrm{H.c.}\}, \qquad (2.31a)$$

$$\tilde Q_a(t)=\sum_b \int_0^t d\tau C_{ab}(t-\tau)G(t,\tau)Q_bG^\dagger(t,\tau). \qquad (2.31b)$$

The key quantities in Eqs. (2.30) and (2.31) are $\tilde Q_a^{COP}(t)$ and $\tilde Q_a(t)$, respectively. These two quantities are non-Hermitian operators in Hilbert space. Like their corresponding Liouville-space counterparts $\gamma(t,\tau)$ [Eq. (2.20b)] and $\mathcal{R}(t)$ [Eq. (2.24b)], these two Hilbert-space operators govern the relaxation dynamics in the two approximation schemes. We may therefore refer to $\tilde Q_a^{COP}(t)$ and $\tilde Q_a(t)$ as the Hilbert-space relaxation operators. Note that $\tilde Q_a^{COP}(t)$ at time t depends on $\rho^{COP}(\tau)$ in all $\tau\leqslant t$, while $\tilde Q_a(t)$ does not couple with the reduced density matrix at all.

Equations (2.30) and (2.31) will serve as the starting formulations for deriving the generalized FP equations in the above-mentioned two approximation schemes. Note in the FP approach, the relaxation dynamics are investigated via a

set of coupled equations of motion. It is in contrast with the Bloch-Redfield approach, which focuses on the relation among various relaxation tensor elements in the time-independent H-eigenstate representation. The Redfield theory in terms of the generalized Langevin force [Eq. (2.25)] has been developed by Friesner and co-workers [48–50] in the Markovian limit in which the COP and POP schemes lead to a same expression. The extension of Friesner and co-workers' approach to the generalized Redfield theory beyond the Markovian limit can be easily formulated based on Eqs. (2.30) and (2.31).

III. NON-GAUSSIAN-MARKOVIAN BATH MODEL

It is obvious that the generalized FP equations can only be developed for certain forms of bath correlation function. We shall in this section propose a non-Gaussian-Markovian model bath on which the generalized FP equations can be obtained (cf. Sec. IV). To simplify the notation, we shall consider explicitly a single generalized Langevin force $F(t)$ acting on a generalized system coordinate Q. We can therefore omit all the subindices arising from the multitude modes of system-bath interaction.

The non-Gaussian-Markovian model bath adopted in this work is described by

$$C(t) \equiv \langle F(t)F(0) \rangle = \Gamma^2 \exp[-g(t)], \quad (3.1a)$$

$$g(t) = (\Delta t_c)^2(t/t_c - 1 + e^{-t/t_c}) + i\lambda t_c(1 - e^{-t/t_c}), \quad (3.1b)$$

with

$$\lambda = \beta \Delta^2/2. \quad (3.1c)$$

Here $\beta = \hbar/k_B T$. Equation (3.1) implies that $g(0) = 0$ and $g(\infty) = \infty$, or $C(0) = \Gamma^2$ and $C(\infty) = 0$. Therefore, $\exp[-g(t)] = C(t)/C(0)$ is the normalized correlation function. Equation (3.1c) is the semiclassical fluctuation-dissipation relation. The detailed analysis that will be carried out in Sec. V D leads to the following condition for the validity of present model bath [cf. Eq. (3.2)]:

$$t \gg t_c \quad \text{or} \quad k_B T/\hbar \gg (\Delta^2/t_c)^{1/3}. \quad (3.2)$$

To simplify the notation for later theoretical development, we shall also denote

$$\zeta \equiv \Delta^2 t_c - i\lambda = \Delta^2(t_c - i\beta/2). \quad (3.3)$$

The bath model of Eq. (3.1) has been widely used in the electronic spectroscopies in condensed phases. It demonstrates a smooth interplay between the homogeneous (Lorentzian) and the inhomogeneous (Gaussian) spectral line broadenings [42–46,51]. In this model, the time scale parameter t_c controls the nature of the bath correlation function. For $t \gg t_c$, $g(t \gg t_c) \rightarrow (\Delta^2 t_c)t + i\lambda t_c$ and the bath correlation function assume the exponential form

$$C(t \gg t_c) \propto \exp(-Dt). \quad (3.4)$$

This is the Gaussian-Markovian limit with the damping constant $D = \Delta^2 t_c$. For $t \ll t_c$, we have $g(t \ll t_c) \rightarrow \Delta^2 t^2/2$, which corresponds to

$$C(t \ll t_c) \propto \exp(-\Delta^2 t^2/2). \quad (3.5)$$

Equations (3.4) and (3.5) describe properly the asymptotic behaviors of the bath correlation function in both the long- and short-time regimes.

To conclude this section, let us simplify the reduced equations of motion in both the COP [Eq. (2.30)] and POP [Eq. (2.31)] forms with the notation of single system-bath coupling mode [Eq. (3.1)]. They are given, respectively, by

$$\dot{\rho}^{COP}(t) = -(i/\hbar)[H(t), \rho^{COP}(t)]$$
$$-(\Gamma/\hbar)^2\{[Q, K^{COP}(t)] + \text{H.c.}\}, \quad (3.6a)$$

$$K^{COP}(t) = \int_0^t d\tau e^{-g(t-\tau)} G(t,\tau) Q \rho^{COP}(\tau) G^\dagger(t,\tau) \quad (3.6b)$$

and

$$\dot{\rho}^{POP}(t) = -(i/\hbar)[H(t), \rho^{POP}(t)]$$
$$-(\Gamma/\hbar)^2\{[Q, K(t)\rho^{POP}(t)] + \text{H.c.}\}, \quad (3.7a)$$

$$K(t) = \int_0^t d\tau e^{-g(t-\tau)} G(t,\tau) Q G^\dagger(t,\tau). \quad (3.7b)$$

Note that the Hilbert-space relaxation operator $K^{COP}(t)$ depends on the reduced density matrix, while $K(t)$ does not. As shown in Eqs. (3.6a) and (3.7a), these two relaxation operators involve in their respective Liouville equations in the different manners.

In the following section we shall start with Eqs. (3.6) and (3.7) to derive both the COP and POP generalized FP equations for the model bath proposed in Eq. (3.1). The theoretical development will involve two steps. The first step is to establish a hierarchy of an infinite number of coupled equations of motion. This is done by introducing a series of auxiliary bath induced operators for each of the COP and the POP forms of relaxation dynamics. The second step is to invoke an approximation that allows us to truncate the infinity hierarchy to a finite number. Thus the reduced density matrix in either the COP or POP form may be evaluated via a closed set of generalized FP equations.

IV. GENERALIZED FOKKER-PLANCK EQUATIONS FOR THE NON-GAUSSIAN-MARKOVIAN BATH

A. Equations of motion in the COP form

To obtain coupled equations of motion for solving ρ^{COP} [Eq. (3.6a)], we may introduce the set of auxiliary bath induced operators $(n = 0,1,...)$

$$K_n^{COP}(t) = \int_0^t d\tau J_n(t-\tau) G(t,\tau) Q \rho^{COP}(\tau) G^\dagger(t,\tau), \quad (4.1)$$

with $K_0^{COP} = K^{COP}$ [cf. Eq. (3.6b)] and

$$J_n(t) = e^{-nt/t_c} e^{-g(t)}. \quad (4.2)$$

For the non-Gaussian-Markovian bath proposed in Eq. (3.1) we have

$$\dot{J}_n(t) = -(n/t_c + \Delta^2 t_c) J_n(t) + \zeta J_{n+1}(t). \qquad (4.3)$$

Here ζ is given by Eq. (3.3). By using Eqs. (4.1)–(4.3) we can easily obtain the equation of motion for $K_n^{\mathrm{COP}}(t)$ [cf. Eq. (4.7b)], which is found to depend not only on $\rho^{\mathrm{COP}}(t)$ and itself, but also on $K_{n+1}^{\mathrm{COP}}(t)$. This hierarchy leads to an infinite series of coupled equations of motion for the reduced density matrix $\rho^{\mathrm{COP}}(t)$ and $K_n^{\mathrm{COP}}(t)$, $n = 0,1,\dots$.

To complete the theory, we shall be able to truncate the infinite series to a finite number of N. The truncation scheme for an arbitrary finite $t_c \neq 0$ is constructed as follows. For an given finite $t_c \neq 0$, there is always a sufficiently large $N+1$ such that the decaying factor $J_{N+1}(t-\tau)$ [Eq. (4.2)] can be considered as a rapidly varying function. It means that $J_{N+1}(t-\tau)$ behaves like a $\delta(t-\tau)$ function in comparison with the remaining components in the integrand of Eq. (4.1). We can therefore terminate the infinity series of equations of motion by the approximants

$$K_{N+1}^{\mathrm{COP}}(t) \approx \theta_{N+1} Q \rho^{\mathrm{COP}}(t). \qquad (4.4)$$

Here θ_{N+1} is a complex number defined as

$$\theta_n = \int_0^\infty d\tau J_n(\tau). \qquad (4.5)$$

By using the explicit form of function $J_n(\tau)$ [Eq. (4.2) with Eqs. (3.1) and (3.3)] we have (for $t_c \neq 0$)

$$1 + \zeta \theta_{N+1} = (N/t_c + \Delta^2 t_c) \theta_N. \qquad (4.6)$$

The final closed set of COP FP equations for $\{\rho^{\mathrm{COP}}(t), K_n^{\mathrm{COP}}(t), n = 0,1,\dots,N\}$ for $t_c \neq 0$ can now be obtained from Eqs. (3.6a) and (4.1)–(4.6) as

$$\dot{\rho}^{\mathrm{COP}}(t) = -(i/\hbar)[H(t),\rho^{\mathrm{COP}}(t)] - (\Gamma/\hbar)^2 \{[Q, K_0^{\mathrm{COP}}(t)] + \mathrm{H.c.}\}, \qquad (4.7a)$$

$$\dot{K}_n^{\mathrm{COP}}(t) = Q\rho^{\mathrm{COP}}(t) - (n/t_c + \Delta^2 t_c) K_n^{\mathrm{COP}}(t) - (i/\hbar)[H(t), K_n^{\mathrm{COP}}(t)] + \zeta K_{n+1}^{\mathrm{COP}}(t), \qquad (4.7b)$$

$$\dot{K}_N^{\mathrm{COP}}(t) = (N/t_c + \Delta^2 t_c)[\theta_N Q\rho^{\mathrm{COP}}(t) - K_N^{\mathrm{COP}}(t)] - (i/\hbar)[H(t), K_N^{\mathrm{COP}}(t)]. \qquad (4.7c)$$

Here N is the index of the terminal equation. Equation (4.7) therefore consists of a closed set of $(N+2)$-coupled FP equations for the COP reduced density matrix and the $N+1$ bath induced Hilbert-space relaxation operators. The initial conditions for solving these equations are given by $\rho^{\mathrm{COP}}(0)$ and $K_n^{\mathrm{COP}}(0) = 0$, $n = 0,1,\dots,N$ [cf. Eq. (4.1)]. The effect of the non-Gaussian-Markovian bath [Eq. (3.1)] is incorporated via the parameters Γ^2, Δ^2, t_c, and $\zeta = \Delta^2[t_c - i\hbar/2k_B T]$. The truncation number N is chosen according to the relative bath time scale $t_c \neq 0$ with respect to the system dynamics. We shall demonstrate in Sec. V that in the

limit of $t_c = 0$, i.e., the Gaussian-Markovian bath, the above hierarchy will lead to the truncation at the $N = 0$ level.

B. Equations of motion in the POP form

Similarly, we can construct a closed set of FP equations to evaluate the POP reduced density matrix. This is done by introducing the series of auxiliary bath induced operators [cf. Eq. (4.1)]

$$K_n(t) = \int_0^t d\tau J_n(t-\tau) G(t,\tau) Q G^\dagger(t,\tau), \qquad (4.8)$$

together with the N-truncation approximation [cf. Eq. (4.4)]

$$K_{N+1}(t) \approx \theta_{N+1} Q. \qquad (4.9)$$

Note that $K(t) = K_0(t)$ [cf. Eqs. (3.7b) and (4.8)]. By using Eqs. (4.8) and (4.9) together with Eqs. (3.7), (4.3), and (4.6) we can obtain for $t_c \neq 0$ the closed set of POP FP equations

$$\dot{\rho}^{\mathrm{POP}}(t) = -(i/\hbar)[H(t),\rho^{\mathrm{POP}}(t)]$$
$$- (\Gamma/\hbar)^2 \{[Q, K_0(t)\rho^{\mathrm{POP}}(t)] + \mathrm{H.c.}\}, \qquad (4.10a)$$

$$\dot{K}_n(t) = Q - (n/t_c + \Delta^2 t_c) K_n(t) - (i/\hbar)[H(t), K_n(t)] + \zeta K_{n+1}(t), \qquad (4.10b)$$

$$\dot{K}_N(t) = (N/t_c + \Delta^2 t_c)[\theta_N Q - K_N(t)] - (i/\hbar)[H(t), K_N(t)]. \qquad (4.10c)$$

The initial conditions for solving these equations are given by $\rho^{\mathrm{POP}}(0)$ and $K_n(0) = 0$, $n = 0,1,\dots,N$ [cf. Eq. (4.8)]. As in the COP form, the effect of non-Gaussian-Markovian bath [Eq. (3.1)] is incorporated in the POP FP equations via the parameters Γ^2, Δ^2, t_c, and $\zeta = \Delta^2[t_c - i\hbar/2k_B T]$.

Note that the bath induced operator $K_n(t)$ does not couple with the reduced density matrix $\rho^{\mathrm{POP}}(t)$ and $K_m(t)$ with $m < n$. As a result, the $N+2$ equations of motion in Eq. (4.10) are not really coupled. The solutions to $\rho^{\mathrm{POP}}(t)$ and $K_0(t),\dots,K_N(t)$ may thus be carried out *one by one* sequentially in the reversed order, that is, start with the integration of the equation of motion for K_N, then for K_{N-1} with the resulting K_N from the previous step, and so on down to the equation of motion for ρ^{POP}. In contrast, the solutions to $\rho^{\mathrm{COP}}(t)$ and $K_n^{\mathrm{COP}}(t)$, with $n = 0,\dots,N$, require a simultaneous integration of $(N+2)$-coupled equations of motion in Eq. (4.7).

In order to have a close comparison between the POP FP formulation [Eq. (4.10)] and its COP counterpart [Eq. (4.7)], we may define

$$K_n^{\mathrm{POP}}(t) \equiv K_n(t)\rho^{\mathrm{POP}}(t). \qquad (4.11)$$

Equation (4.10) can now be recast as

$$\dot{\rho}^{\text{POP}}(t) = -(i/\hbar)[H(t), \rho^{\text{POP}}(t)]$$

$$\times (\Gamma/\hbar)^2 \{[Q, K_0^{\text{POP}}(t)] + \text{H.c.}\}, \quad (4.12a)$$

$$\dot{K}_n^{\text{POP}}(t) = Q\rho^{\text{POP}}(t) - (i/\hbar)[H(t), K_n^{\text{POP}}(t)] - (n/t_c$$

$$+ \Delta^2 t_c) K_n^{\text{POP}}(t) + \zeta K_{n+1}^{\text{POP}}(t) + \xi_n^{\text{POP}}(t). \quad (4.12b)$$

Here $\xi_n^{\text{POP}}(t)$, defined as

$$\xi_n^{\text{POP}}(t) = -(\Gamma/\hbar)^2 K_n(t) \{[Q, K_0^{\text{POP}}(t)] + \text{H.c.}\}, \quad (4.13)$$

is the extra term in the POP formulation [Eq. (4.12b)] compared to its COP counterpart [Eq. (4.7b)]. We have not been able to incorporate the $\xi_n^{\text{POP}}(t)$ operator into a closed set of coupled equations of motion.

In the following section we shall show that the truncation scheme [cf. Eq. (4.4) or (4.9)] proposed in this section becomes exact in the limiting cases of the Gaussian-Markovian bath and the Markovian white-noise bath. For the Gaussian-Markovian limit in which $t_c = 0$, the truncation can be carried out at the $N = 0$ level. In this case, a pair of FP equations for $\{\rho^{\text{COP}}(t), K^{\text{COP}}(t) = K_0^{\text{COP}}(t)\}$ in the COP form or for $\{\rho^{\text{POP}}(t), K(t) = K_0(t)\}$ in the POP form will be obtained. In the Markovian white-noise limit, the COP and POP forms become identical. In this case the truncation can be carried out at the $\rho(t)$ level, leading to the well established FP equation originally derived by Caldeira and Leggett [34]. Included in the following section are also the possible physical origin of the bath induced relaxation operators $\{K_n^{\text{COP}}, n = 0, \ldots, N\}$ or $\{K_n, n = 0, \ldots, N\}$ and the detailed analysis of the fluctuation-dissipation relation in the semiclassical Gaussian-Markovian model bath [Eq. (3.1)].

V. DISCUSSION AND COMMENTS

A. Fokker-Planck equation pairs in the Gaussian-Markovian limit

1. Truncation at the $N = 0$ level

As we mentioned in Sec. III, the Gaussian-Markovian bath is a limiting case of the present model [Eq. (3.1)]. In this limit, $t_c \to 0$ and

$$e^{-t/t_c} \to t_c \delta(t), \quad (5.1)$$

while [cf. Eq. (3.1c)]

$$\Delta^2 t_c = D, \quad \lambda t_c = D\beta/2 \quad (5.2)$$

remain finite. Thus the truncations made in Eqs. (4.4) and (4.9) become exact at the $N = 0$ level, leading, respectively to the two identities

$$\zeta K_1^{\text{COP}}(t) = \lim_{t_c \to 0} (\zeta \theta_1) Q \rho^{\text{COP}}(t) \quad (5.3)$$

and

$$\zeta K_1(t) = \lim_{t_c \to 0} (\zeta \theta_1) Q. \quad (5.4)$$

Here

$$\lim_{t_c \to 0} (\zeta \theta_1) \equiv \lim_{t_c \to 0} \left[\zeta \int_0^t d\tau J_1(\tau) \right]$$

$$= \lim_{t_c \to 0} \left[\zeta \int_0^t d\tau e^{-\tau/t_c} e^{-g(\tau)} \right]$$

$$= \lim_{t_c \to 0} (\zeta t_c) = -iD\beta/2. \quad (5.5)$$

In deriving the last identity of Eq. (5.5), we made use of the relations of Eqs. (3.3) and (5.2).

2. Generalized Fokker-Planck equations in the COP

Let us start with the COP FP equations in a Gaussian-Markovian bath. By substituting Eqs. (5.3) and (5.5) into Eq. (4.7b) with $n = 0$, we obtain the pair of coupled equations of motion [i.e., closed at the $K^{\text{COP}} = K_0^{\text{COP}}$ level together with Eq. (4.7a)]

$$\dot{\rho}^{\text{COP}}(t) = -(i/\hbar)[H(t), \rho^{\text{COP}}(t)]$$

$$-(\Gamma/\hbar)^2 \{[Q, K^{\text{COP}}(t)] + \text{H.c.}\}, \quad (5.6a)$$

$$\dot{K}^{\text{COP}}(t) = (1 - iD\beta/2) Q \rho^{\text{COP}}(t)$$

$$-(i/\hbar)[H(t), K^{\text{COP}}(t)] - DK^{\text{COP}}(t). \quad (5.6b)$$

The above equations can be further simplified by introducing $R^{\text{COP}}(t) = -(i/\hbar)[K^{\text{COP}}(t) - \text{H.c.}]$. We can thus recast Eq. (5.6) as

$$\dot{\rho}^{\text{COP}}(t) = -\frac{i}{\hbar}[H(t), \rho^{\text{COP}}(t)] - \frac{i}{\hbar} \Gamma^2 [Q, R^{\text{COP}}(t)], \quad (5.7a)$$

$$\dot{R}^{\text{COP}}(t) = -\frac{i}{\hbar}[Q, \rho^{\text{COP}}(t)] - \frac{D}{2k_B T}[Q, \rho^{\text{COP}}(t)]_+$$

$$-\frac{i}{\hbar}[H(t), R^{\text{COP}}(t)] - DR^{\text{COP}}(t). \quad (5.7b)$$

Here $[A, B]_+ = AB + BA$. Equation (5.6) or (5.7) is the same as that obtained by Cao recently [41]. However, the present derivation avoids the singularity problem that appears at $t = 0$ in the Gaussian-Markovian limit [41]. Equation (5.7) constitutes the final pair of coupled FP equations for evaluating the COP reduced density matrix in a Gaussian-Markovian bath. The initial conditions are given by $\rho^{\text{COP}}(0)$ and $R^{\text{COP}}(0) = 0$. The effect of the Gaussian-Markovian bath is incorporated via the system-bath coupling strength Γ, the decay constant D, and the temperature T.

3. Generalized Fokker-Planck equations in the POP

We shall now consider the POP FP equations in a Gaussian-Markovian bath. By substituting Eqs. (5.4) and (5.5) into Eq. (4.10b) with $n = 0$, we obtain the pair of equations of motion [i.e., closed at the $K = K_0$ level together with Eq. (4.10a)]

$$\dot{\rho}^{\text{POP}}(t) = -(i/\hbar)[H(t),\rho^{\text{POP}}(t)]$$
$$-(\Gamma/\hbar)^2\{[Q,K(t)\rho^{\text{POP}}(t)]+\text{H.c.}\}, \quad (5.8a)$$

$$\dot{K}(t) = (1-iD\beta/2)Q - (i/\hbar)[H(t),K(t)] - DK(t).$$
$$(5.8b)$$

The initial conditions are given by $\rho^{\text{POP}}(0)$ and $K(0)=0$. As in the COP form [cf. Eq. (5.7)], the effect of the Markovian bath is incorporated in the POP FP equations via the coupling strength Γ, the exponential damping constant D, and the bath temperature T. Unlike its COP counterpart [Eq. (5.6b)], the equation of motion for $K(t)$ [Eq. (5.8b)] does not couple with $\rho^{\text{POP}}(t)$. As a result, Eq. (5.8) can be integrated one by one, first for $K(t)$ [Eq. (5.8b)] and then for $\rho^{\text{POP}}(t)$ [Eq. (5.8a)] with the resulting $K(t)$ from the previous step.

To conclude this subsection, we shall mention that Tanimura and Wolynes [36] have proposed a different hierarchical approach to construct a set of coupled quantum FP equations for a Gaussian-Markovian bath. Instead of a pair FP equations obtained in the present work, their hierarchical equation set converges at about $N\sim50$, for a Gaussian-Markovian bath ($t_c=0$). Obviously, Tanimura and Wolynes' FP equations were based on a POP scheme with a different partial resummation for the contribution from the higher-order system-bath interaction. A comparison of their result to the present formulation will be carried out elsewhere.

B. Fokker-Planck equation in the Markovian limit

The Markovian white-noise limit can be achieved from the Gaussian-Markovian bath by setting $D\rightarrow\infty$ and $\Gamma^2/D = \eta k_B T$. The semiclassical fluctuation-dissipation relation leads to the following form of the bath correlation function in the Markovian limit [41]:

$$C(t) \rightarrow \eta k_B T\delta(t) + \frac{i\hbar\eta}{2}\dot{\delta}(t). \quad (5.9)$$

It can be shown that the COP and the POP forms of the reduced density matrix become identical in the Markovian limit. To that end, let us first consider $K(t)=K_0(t)$ [cf. Eq. (4.8)]. In the Markovian limit we have

$$\Gamma^2 K(t) \equiv \int_0^t d\tau C(t-\tau)G(t,\tau)QG^\dagger(t,\tau)$$

$$\rightarrow \eta k_B TQ - \frac{\eta}{2}[H,Q] \quad (5.10)$$

or

$$\Gamma^2 K^{\text{POP}}(t) \equiv \Gamma^2 K(t)\rho^{\text{POP}}(t)$$

$$\rightarrow \left\{\eta k_B TQ - \frac{\eta}{2}[H,Q]\right\}\rho^{\text{POP}}(t). \quad (5.11)$$

On the other hand, we have

$$\Gamma^2 K^{\text{COP}}(t) = \int_0^t d\tau C(t-\tau)G(t,\tau)Q\rho^{\text{COP}}(\tau)G^\dagger(t,\tau)$$

$$\rightarrow \int_0^\infty d\tau\left[\eta k_B T\delta(t-\tau) + \frac{i\hbar\eta}{2}\dot{\delta}(t-\tau)\right]$$

$$\times G(t,\tau)Q\rho^{\text{COP}}(\tau)G^\dagger(t,\tau)$$

$$= \eta k_B TQ\rho^{\text{COP}}(t) + \frac{i\hbar\eta}{2}\left\{\frac{i}{\hbar}[H,Q\rho^{\text{COP}}(t)]\right.$$

$$\left.- Q\dot{\rho}^{\text{COP}}(t)\right\}$$

$$\approx \eta k_B TQ\rho^{\text{COP}}(t) - \frac{\eta}{2}\{[H,Q\rho^{\text{COP}}(t)]$$

$$- Q[H,\rho^{\text{COP}}(t)]\}$$

$$= \left\{\eta k_B TQ - \frac{\eta}{2}[H,Q]\right\}\rho^{\text{COP}}(t). \quad (5.12)$$

In deriving the penultimate identity of Eq. (5.12) we used the approximation $i\hbar\dot{\rho}^{\text{COP}}(t)\approx[H,\rho^{\text{COP}}(t)]$. Using this approximation in deriving Eq. (5.12) is appropriate for the Markovian bath that is weakly coupled with the system. Comparing Eq. (5.12) with Eq. (5.11), we conclude that the reduced density operators in the COP and POP forms are identical in the Markovian limit. This is consistent with the physical picture of Markovian limit in which the effect of the higher-order system-bath interaction is integrated to zero. We can thus eliminate the superscripts and denote $\rho^{\text{COP}}=\rho^{\text{POP}}=\rho$.

The final FP equation in the Markovian limit reads therefore as

$$\dot{\rho}(t) = -\frac{i}{\hbar}[H,\rho(t)] - \frac{\eta k_B T}{\hbar^2}[Q,[Q,\rho(t)]]$$

$$+ \frac{\eta}{2\hbar^2}[Q,[[H,Q],\rho(t)]_+]. \quad (5.13)$$

In the case of the Cartesian coordinate $Q=q$, we have $[H,Q]=\hbar p/iM$ with p being the conjugate momentum and M the mass. In this case, Eq. (5.13) recovers the conventional FP equation [34–36,52]

$$\dot{\rho}(t) = -\frac{i}{\hbar}[H,\rho(t)] - \frac{\eta k_B T}{\hbar^2}[q,[q,\rho(t)]]$$

$$- \frac{i\eta}{2\hbar M}[q,[p,\rho(t)]_+]. \quad (5.14)$$

Equation (5.14) can further be recast explicitly in the quantum Wigner phase-space (p,q) representation as [29,34]

$$\frac{\partial}{\partial t}\rho_w(p,q,t) = -\frac{i}{\hbar}[H,\rho(t)]_w + \eta k_B T\frac{\partial^2}{\partial p^2}\rho_w(p,q,t)$$

$$+ \frac{\eta}{M}\frac{\partial}{\partial p}p\rho_w(p,q,t). \quad (5.15)$$

The classical FP equation can further be recovered from the above equation by replacing $-(i/\hbar)[H,\rho(t)]_w$ with the Poisson bracket $\{H,\rho(t)\}$.

C. Comments on the hierarchical relaxation operators

The key step to the development of generalized FP theory in the non-Gaussian-Markovian bath is the construction of hierarchical series of bath-induced relaxation operators in Hilbert space (Sec. IV). We shall in this subsection discuss the possible physical implication of these relaxation operators. For simplicity, the hierarchical relaxation operators in the POP reduction scheme $\{K_n(t), n=0,...,N\}$ [cf. Eqs. (4.8) and (4.10)] will be discussed explicitly. The resulting arguments will also be valid for the COP relaxation operators $\{K_n^{COP}(t), n=0,...,N\}$ [cf. Eqs. (4.1) and (4.7)].

As seen from Eq. (4.10b), the time evolution of $K_n(t)$ depends explicitly only on $K_{n+1}(t)$ and itself. As a result, $K_n(t)$ at time t depends on all $K_m(\tau)$ with $n<m\leq N$ and $\tau <t$. Physically, $K_0(t),...,K_N(t)$ may be responsible for the progressively detailed and short-time information on quantum relaxation processes. The relevant time scale in the non-Gaussian-Markovian bath model [Eq. (3.1)] is characterized by t_c. From Eq. (4.10b) we may argue that the survival time of a given $K_n(t)$ is of the order of $(n/t_c+\Delta^2 t_c)^{-1}$. The dynamics at a later time depends in general on the system at earlier times to a certain degree of accuracy depending on the nature of the bath. An appropriate truncation at N should therefore correlate the degree of memory being required by the quantum relaxation dynamics. In the Gaussian-Markovian limit ($t_c=0$), the resulting exponential form of the correlation function provides a single coarse-grained relaxation time. In this case, our hierarchy of bath induced relaxation operators $\{K_n, n=0,...,N\}$ can be truncated at the $N=0$ level, resulting in a pair of equations of motion for $\rho(t)$ and $K(t)=K_0(t)$ (cf. Sec. V A). In the extreme case of the Markovian (white-noise) limit in which the bath correlation is a δ function, no memory is involved and we do not need any bath-induced operator at all. This is the case for the single conventional quantum Fokker-Planck equation (Sec. V B).

Our bath model [cf. Eq. (3.1)] allows a smooth interplay between both the long- [Eq. (3.4)] and short-time [Eq. (3.5)] behaviors of the bath correlation function. This implies that the bath can be effectively considered as in the Gaussian-Markovian limit when $t\gg t_c$. Moreover, the Markovian white noise becomes applicable in the hydrodynamic limit as $t\to\infty$. We may therefore expect the number of operators in $\{K_n, n=0,...,N\}$ that can affect $\rho(t)$ decreases progressively. Note the survival time of a given $K_n(t)$ is of the order of $(n/t_c+\Delta^2 t_c)^{-1}$ [cf. Eq. (4.10b)]. As t becomes large with respect to t_c, it reaches the Gaussian-Markovian regime and we may need the pair of equations for $\rho(t)$ and $K_0(t)$ [Eq. (5.8)]. Furthermore, as $t\to\infty$, it becomes applicable for the Markovian (white-noise) relaxation theory [cf. Eq. (5.13)] and we do not need any K_n at all.

The above comments recall the ''inverse snowball'' picture of Onsage in his study of the effect of polar fluid on electrons [53]. In his picture, an excess electron induces initially a long-range structural change in the bath; the bath rearrangement follows and propagates inward toward the electron [53]. In this sense, the relaxation operator set $\{K_n(t), n=0,...,N\}$ describes the inverse snowball structure, in which the survival time of an individual K_n that can affect the dynamics of the open quantum system decreases as n increases.

D. Detailed balance relation in the bath model

As the form of bath model [Eq. (3.1)] is crucial to the development of generalized FP theory, we shall examine to what extent this model satisfies the exact detailed balance or fluctuation-dissipation relation. Note that the exact quantum fluctuation-dissipation theorem can be recast as [cf. Eqs. (2.27) and (3.1a)]

$$g_{exact}(t-i\beta)-g_{exact}^*(t)=0. \qquad (5.16)$$

However, our bath model gives [cf. Eq. (3.1b) with (3.3)]

$$g(t-i\beta)-g^*(t)=-i(\beta\Delta^2-2\lambda)t_c$$
$$+(\zeta e^{i\beta/t_c}-\zeta^*)t_c e^{-t/t_c}. \qquad (5.17)$$

By applying the semiclassical fluctuation-dissipation relation of Eq. (3.1c) and further denoting

$$\chi\equiv(\zeta e^{i\beta/t_c}-\zeta^*)t_c=(\Delta^2 t_c)[(t_c-i\beta/2)e^{i\beta/t_c}-(t_c+i\beta/2)], \qquad (5.18)$$

we have the relation

$$g(t-i\beta)-g^*(t)=\chi e^{-t/t_c}. \qquad (5.19)$$

We are now in the position to analyze the conditions at which Eq. (5.19) approaches the exact fluctuation-dissipation relation of Eq. (5.16). Let us start with the exponential factor in Eq. (5.19). It is obvious that for $t\gg t_c$ the right-hand side of Eq. (5.19) drops exponentially to zero. In particular, in the Gaussian-Markovian limit in which $t_c\to 0$ while $\Delta^2 t_c=D$ remains finite, the exponential factor vanishes at all times except for the singularity point at $t=0$. We now turn to the pre-exponential parameter χ in Eq. (5.19). It can be shown that in the small-β/t_c (high-temperature) regime, χ [Eq. (5.18)] vanishes as

$$\chi\sim\frac{i}{12}\Delta^2\beta^3/t_c. \qquad (5.20)$$

The above analysis concludes that our model of non-Gaussian-Markovian bath [Eq. (3.1)] satisfies the fluctuation-dissipation relation under the condition (3.2). It is in this sense that the fluctuation-dissipation relation is incorporated into our model [Eq. (3.1)] in a semiclassical manner.

VI. SUMMARY AND CONCLUSION

In this paper we have constructed a hierarchical approach and developed a generalized Fokker-Planck theory (Sec. IV) in a non-Gaussian-Markovian medium. We have also presented a thorough discussion (cf. Sec. V) on several theoretical issues, such as the physical implication of the hierarchical bath induced relaxation operators in Hilbert space and the semiclassical fluctuation-dissipation relation in the model bath.

The model bath [Eq. (3.1)] adopted in this paper is characterized by three parameters Γ, Δ, and t_c, together with a semiclassical fluctuation-dissipation relation [Eq. (3.1c)]. Here Γ denotes the system-bath coupling strength, while Δ and t_c interpolate smoothly the relaxation dynamics between the long- and short-time regimes. The Gaussian-Markovian bath is a special case of the present model with $t_c = 0$.

The final results of the generalized FP theory are expressed in terms of two sets of $N+2$ operator equations of motion, i.e., Eqs. (4.7) and (4.10). These two sets of FP equations stem, respectively, from the reduced Liouville equations in two distinct (the COP and the POP) prescriptions in the weak system-bath interaction limit. They are, however, not equivalent due to the different approximations for the partial resummation of contributions from the higher-order system-bath interaction. In the generalized COP-FP theory [cf. Eq. (4.7)], it requires a simultaneous integration of the $(N+2)$-coupled equations of motion for $\{\rho^{\mathrm{COP}}(t), K_0^{\mathrm{COP}}(t), \ldots, K_N^{\mathrm{COP}}(t)\}$. However, the $N+2$ POP FP equations [cf. Eq. (4.10)] can in principle be integrated one by one in inverse order, first for $K_N(t)$, then $K_{N-1}(t), \ldots, K_0(t)$, and finally for $\rho^{\mathrm{POP}}(t)$. The hierarchical truncation number N depends on the relative bath time scale t_c with respect to the system dynamics. The larger t_c is, the larger N should be. In the limit of the Gaussian-Markovian bath in which $t_c = 0$, the truncation number is $N = 0$. In this case, we need only a pair of FP equations for $\{\rho^{\mathrm{COP}}(t), K^{\mathrm{COP}}(t)\}$ or $\{\rho^{\mathrm{POP}}(t), K(t)\}$ (cf. Sec. V A).

In general, we may expect from Eq. (4.7b) or (4.10b) that the survival time of K_n^{COP} or K_n is at the order of $(n/t_c + \Delta^2 t_c)^{-1}$. This suggests the possibility of an efficient scheme of integrating the set of FP equations. As time evolves, the required number of FP equations in Eq. (4.7) or (4.10) is progressively decreasing. It is expected that in the hydrodynamic limit ($t \to \infty$) the conventional single FP equation (cf. Sec. V B) becomes adequate.

The key step in the theoretical development is to construct a hierarchical series of bath induced relaxation operators that allows the set of $N+2$ FP equations to be closed at a rather small value of N. The hierarchical approach developed in this paper (cf. Sec. IV) is expected to meet this criterion for a small or moderate value of Δt_c. However, the required N could become very large as the bath approaches the slow modulation limit in which $\Delta t_c \gg 1$. Thus it might be worth at least in the short-time region constructing an alternative hierarchical set of FP equations, which are more suitable for the case of $\Delta t_c \gg 1$. We shall consider this case elsewhere.

For simplicity, the present generalized FP theory is reported explicitly in terms of a single system-bath coupling mode. It is obvious that the effect of statistically independent system-bath coupling modes, in which [cf. Eq. (2.26)]

$$C_{ab}(t) \equiv \langle F_a(t)F_b(0)\rangle = \delta_{ab}C_{aa}(t) \qquad (6.1)$$

is additive. In this case, Eqs. (4.7a) and (4.10a) should be replaced, respectively, by

$$\dot{\rho}^{\mathrm{COP}}(t) = -(i/\hbar)[H(t), \rho^{\mathrm{COP}}(t)]$$

$$-\sum_a (\Gamma_a/\hbar)^2\{[Q_a, K_0^{a,\mathrm{COP}}(t)] + \mathrm{H.c.}\}$$

$$(6.2)$$

and

$$\dot{\rho}^{\mathrm{POP}}(t) = -(i/\hbar)[H(t), \rho^{\mathrm{POP}}(t)]$$

$$-\sum_a (\Gamma_a/\hbar)^2\{[Q_a, K_0^a(t)\rho^{\mathrm{POP}}(t)] + \mathrm{H.c.}\}.$$

$$(6.3)$$

Here Q_a is the system coordinate that couples with the bath via the Langevin force F_a. Each non-Gaussian-Markovian (macroscopic) bath mode a is characterized by three parameters Γ_a, Δ_a, and t_c^a. The hierarchical FP equations for $K_n^{a,\mathrm{COP}}$ and K_n^a, with $n = 0, \ldots, N_a$, will remain as the same forms as those in Sec. IV. Here N_a is the truncation number for the given system-bath coupling mode a. The total number of FP equations in either the COP or POP form is therefore $\mathcal{N} = 1 + \Sigma_a(N_a + 1)$. Note that in the COP form, the equation of motion for each $K_n^{a,\mathrm{COP}}$ [cf. Eq. (4.7b)] depends on ρ^{COP}, whose time evolution is given by Eq. (6.2). As a result, the time evolution of relaxation operator $K_n^{a,\mathrm{COP}}$ induced by the bath mode a depends indirectly on the relaxation operators induced by all other bath modes. All the $\mathcal{N}$ COP FP equations are therefore coupled and shall be solved simultaneously. On the other hand, the $\mathcal{N}$ POP FP equations can be solved one by one as we mentioned before. The relaxation operator K_n^a contains no feedback information from the reduced density matrix ρ^{POP} and is completely independent of other statistically independent bath modes.

The operator formulation of the present generalized FP theory can be easily recast in various representations. Moreover, it constitutes a unified background for a quantum, classical, or semiclassical implementation of relaxation dynamics. For example, consider an optical process in a molecular system involving the electronic ground g and an excited e surfaces. We may adopt a mixed representation scheme in which the molecular electronic dynamics is described in the state representation, while the nuclear motion is considered in the Wigner phase space. The reduced density matrix is therefore of the form

$$\rho(t) = \begin{bmatrix} \rho_{gg}(p,q,t) & \rho_{ge}(p,q,t) \\ \rho_{eg}(p,q,t) & \rho_{ee}(p,q,t) \end{bmatrix}. \qquad (6.4)$$

The bath induced relaxation operators can be treated in the same manner. In this case, each of the generalized FP equations in Eqs. (4.7) and (4.10) contains actually four electronic components with the indices of gg, ge, eg, and ee. We just mentioned that the effect of a stochastically independent bath mode is additive. The present generalized FP theory can thus provide a convenient way to study the dephasing and relaxation dynamics in both electronic and nuclear degrees of freedom, such as that which occurs in spectroscopic or curve-crossing processes in condensed phases.

APPENDIX: REDUCED LIOUVILLE EQUATIONS IN TERMS OF THE FORCE-FORCE CORRELATION FUNCTION

Let us consider the relaxation term $\gamma(t,\tau)\rho^{\text{COP}}(\tau)$ in the COP reduced Liouville equation. Making use of Eqs. (2.3), (2.7b), (2.9), and (2.20), we have

$$\gamma(t,\tau)\rho^{\text{COP}}(\tau) = \text{tr}_B[\mathcal{L}'(t)\mathcal{G}(t,\tau)\mathcal{L}'(\tau)\rho_B(0)\rho^{\text{COP}}(\tau)]$$
$$= \hbar^{-2}\,\text{tr}_B[H'(t)G(t,\tau)H'(\tau)\rho_B(0)\rho^{\text{COP}}(\tau)$$
$$\times G^\dagger(t,\tau) - G(t,\tau)H'(\tau)\rho_B(0)\rho^{\text{COP}}(\tau)$$
$$\times G^\dagger(t,\tau)H'(t)] + \text{H.c.}$$
$$= \hbar^{-2}\sum_{a,b}\{I - II + \text{H.c.}\}. \tag{A1}$$

Here

$$I \equiv \text{tr}_B[F_a(t)F_b(\tau)\rho_B(0)]Q_aG(t,\tau)Q_b\rho^{\text{COP}}(\tau)G^\dagger(t,\tau)$$
$$= C_{ab}(t-\tau)Q_aG(t,\tau)Q_b\rho^{\text{COP}}(\tau)G^\dagger(t,\tau) \tag{A2}$$

and

$$II \equiv \text{tr}_B[F_b(\tau)\rho_B(0)F_a(t)]G(t,\tau)Q_b\rho^{\text{COP}}(\tau)G^\dagger(t,\tau)Q_a$$
$$= C_{ab}(t-\tau)G(t,\tau)Q_b\rho^{\text{COP}}(\tau)G^\dagger(t,\tau)Q_a. \tag{A3}$$

In deriving Eqs. (A2) and (A3) we have used Eq. (2.26) and the trace cyclic invariance

$$C_{ab}(t-\tau) = \text{tr}_B[F_a(t)F_b(\tau)\rho_B(0)] = \text{tr}_B[F_b(\tau)\rho_B(0)F_a(t)]. \tag{A4}$$

By substituting Eqs. (A2) and (A3) into Eq. (A1) followed by integration, we obtain

$$\int_0^t d\tau\,\gamma(t,\tau)\rho^{\text{COP}}(\tau) = \hbar^{-2}\sum_a \{[Q_a,\tilde{Q}_a^{\text{COP}}(t)] + \text{H.c.}\}, \tag{A5}$$

with $\tilde{Q}_a(t)$ being defined by Eq. (2.30b). The COP Liouville equation (2.30) now can be recovered by substituting Eqs. (A4) and (2.7a) for Eq. (2.20a). The POP Liouville equation (2.31) can also be derived using a similar approach.

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