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Decoherence and quantum-classical dynamics in a dissipative bath

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The dynamics of a mixed quantum-classical system, in which the classical subsystem interacts with a dissipative bath, is investigated. This description of the dynamics will be appropriate if the details of the bath dynamics are unimportant but its presence plays an important role in the dissipation of energy to the environment. In this dynamical description, which can be simulated employing an ensemble of stochastic surface-hopping trajectories, the strength of the dissipation is controlled by a friction coefficient. We show that if decoherence, whose effects are controlled by the bath friction, is sufficiently rapid, the equation of motion can be reduced to a master equation. Thus, decoherence and the validity of master equation models may be explored as a function of bath friction. We use this framework to study the mechanism of decoherence in a simple model nonadiabatic chemical reaction. © *2010 American Institute of Physics*. [doi:10.1063/1.3310811]

I. INTRODUCTION

When modeling quantum processes in the condensed phase, one often partitions the many degrees of freedom into several sets destined for different treatment, according to the characteristics of the system under consideration. This division is motivated both by reasons of computational efficiency, and by the potential to gain greater insight into the dynamics of the system through the judicious choice of modeling techniques. Often, we are only interested in the dynamics of a subset of the total degrees of freedom. Thus, we can divide the complete system into a subsystem of interest and an environment which influences its dynamics. Such open quantum systems have been studied extensively.[1–3]

In some cases it is useful and physically reasonable to approximate the dynamics of some of the degrees of freedom with classical mechanics.[4,5] This is the case for systems where light particles interact with much more massive particles; for example, proton and electron transfers in the condensed phase and in biomolecules. In fact, here, we can introduce a third partition, since the quantum degrees of freedom (e.g., the protons) couple directly only with a subset of the classical degrees of freedom (specific functional groups) which in turn couple with the remainder of the classical degrees of freedom (the remainder of the biomolecule, or the extended solvent). Thus, we speak of a mixed quantum-classical subsystem coupled to a bath.

We are interested only in the dynamics of this bath because it affects the quantum-classical subsystem. In some cases, the dynamics of the quantum-classical subsystem may depend on the detailed dynamics of the bath. Here we consider the case where the bath can be adequately modeled as a dissipative environment.

While there is a variety of approaches that combine quantum dynamics of a subsystem with classical dynamics of the environment, in this article we base our analysis on the quantum-classical Liouville (QCL) equation description of such systems.[5–14] More specifically, the starting point for our analysis is the dissipative backward quantum-classical Liouville (QCL) equation[15] for an operator $\hat{\mathcal{A}}(X,t)$,

$$\frac{d\hat{\mathcal{A}}(X,t)}{dt} = \frac{i}{\hbar}[\hat{H},\hat{\mathcal{A}}(X,t)] - \frac{1}{2}(\{\hat{H},\hat{\mathcal{A}}(X,t)\} - \{\hat{\mathcal{A}}(X,t),\hat{H}\}) - \zeta\left(\frac{P}{M} - k_B T\frac{\partial}{\partial P}\right)\frac{\partial}{\partial P}\hat{\mathcal{A}}(X,t) \equiv i\mathcal{L}^{DB}\hat{\mathcal{A}}(X,t), \tag{1}$$

which specifies the dynamics of a quantum-classical system coupled to a bath modeled as a dissipative environment described by a Fokker–Planck operator. In this equation, the second equality defines the dissipative backward QCL operator, $i\mathcal{L}^{DB}$. The Hamiltonian of the subsystem is $\hat{H}(X) = P^2/2M + \hat{p}^2/2m + \hat{V}(\hat{q},R) \equiv P^2/2M + \hat{h}(R)$. All operators in this paper are partially Wigner transformed quantities[14,16] and $X=(R,P)$ is used to denote the phase space coordinates of the subsystem's classical particles with characteristic mass M, while $\hat{q}$ and $\hat{p}$ stand for the position and momentum operators of the quantum subsystem whose particles have characteristic mass m.

The first three terms of this equation correspond to the evolution of the subsystem in the absence of the bath, and methods are available to simulate the dynamics described by these terms.[17,18] The last term is the Fokker–Planck operator that accounts for the dissipative bath characterized by a friction coefficient ζ. In Sec. II, we show that the evolution described by Eq. (1) can be computed using an average over an ensemble of stochastic surface-hopping trajectories.

Decoherence in the subsystem occurs as a result of the interaction with the bath. Quantum-classical descriptions can be justified by arguments based on decoherence arising from environmental interactions[19] and decoherence plays an im-

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portant role in establishing the validity of surface-hopping descriptions of the dynamics[20,21] and the construction of simulation algorithms.[22–25] In particular, environmental decoherence can lead to the reduction of the QCL equation to a master equation whose simulation involves propagation on single adiabatic surfaces interspersed with quantum transitions between surfaces,[20,21] similar to that in many surface-hopping schemes. Here we consider the same problem from the perspective of the dissipative QCL equation which accounts for the bath through the Fokker–Plank operator in Eq. (1). Analysis of this equation allows one to explore the role of bath friction on the decay of the memory kernel more systematically and provides a means to investigate the dynamics of open quantum-classical systems where details of the bath are unimportant for the phenomena under study.

In Sec. II A we show that Eq. (1) in the adiabatic basis can be reduced to a Markovian master equation if decoherence is strong enough to cause the rapid decay of a memory term related to the quantum coherences in the subsystem. In Sec. III, we illustrate the results by considering decoherence in a simple nonadiabatic reaction model. In particular, we examine the effect of friction on the decay time of the memory term and determine the mechanism of the decay. The conclusions of the study are given in Sec. IV.

II. QUANTUM-CLASSICAL DYNAMICS IN A DISSIPATIVE BATH

In order to study decoherence induced by the bath and especially to make connections to decoherence in surface-hopping schemes for nonadiabatic chemical dynamics, it is convenient to represent the dynamics in an adiabatic basis, which is given by the solution of the eigenvalue equation, $\hat{h}(R)|\alpha;R\rangle = E_\alpha(R)|\alpha;R\rangle$. In this basis the structure of the dissipative backward QCL equation is similar to that presented earlier for the QCL equation,[14]

$$\frac{d\mathcal{A}^{\alpha\alpha'}(X,t)}{dt} = \sum_{\beta\beta'} i\mathcal{L}^{DB}_{\alpha\alpha',\beta\beta'}\mathcal{A}^{\beta\beta'}(X,t), \tag{2}$$

where

$$i\mathcal{L}^{DB}_{\alpha\alpha',\beta\beta'} = (i\omega_{\alpha\alpha'} + iL^{KB}_{\alpha\alpha'})\delta_{\alpha\beta}\delta_{\alpha'\beta'} - \mathcal{J}_{\alpha\alpha',\beta\beta'}, \tag{3}$$

with $\omega_{\alpha\alpha'} = \Delta E_{\alpha\alpha'}/\hbar$ and $\Delta E_{\alpha\alpha'} = E_\alpha - E_{\alpha'}$. The matrix elements of the backward Kramers operator, $iL^{KB}_{\alpha\alpha'}$, are given by

$$iL^{KB}_{\alpha\alpha'} = \frac{P}{M}\frac{\partial}{\partial R} + \frac{1}{2}(F^\alpha + F^{\alpha'})\frac{\partial}{\partial P} - \zeta\left(\frac{P}{M} - k_BT\frac{\partial}{\partial P}\right)\frac{\partial}{\partial P}. \tag{4}$$

The Hellmann–Feynmann force[26] for state α is $F_\alpha = \langle\alpha;R|\partial\hat{V}(\hat{q},R)/\partial R|\alpha;R\rangle$. The $\mathcal{J}$ operator is responsible for quantum transitions and the accompanying momentum changes in the classical subsystem and has the form[14,17,27] $\mathcal{J}_{\alpha\alpha',\beta\beta'} = \mathcal{C}_{\alpha\beta}\delta_{\alpha'\beta'} + \mathcal{C}^*_{\alpha'\beta'}\delta_{\alpha\beta}$, where $\mathcal{C}_{\alpha\beta} = -D_{\alpha\beta}(X) \times (1 + (1/2)S_{\alpha\beta}\cdot(\partial/\partial P))$, the nonadiabatic coupling matrix element is given by $d_{\alpha\beta} = \langle\alpha;R|\nabla_R|\beta;R\rangle$, $S_{\alpha\beta} = \Delta E_{\alpha\beta}d_{\alpha\beta}/D_{\alpha\beta}(X)$, and $D_{\alpha\beta}(X) = (P/M)\cdot d_{\alpha\beta}$.

From the classical theory of random processes, evolution under the backward Kramers operator can be computed from an average over realizations of stochastic trajectories evolving under Langevin dynamics.[28] Similarly, dissipative backward QCL dynamics can be simulated from averages over realizations of stochastic surface-hopping trajectories determined by the QC Langevin–Liouville equation,

$$\frac{dA^{\alpha\alpha'}(X,t)}{dt} = \sum_{\beta\beta'} i\mathcal{L}^{L}_{\alpha\alpha',\beta\beta'}(t)A^{\beta\beta'}(X,t), \tag{5}$$

where $A^{\alpha\alpha'}(X,t)$ is now to be interpreted as a random variable. The matrix elements of the QC Langevin–Liouville operator are

$$i\mathcal{L}^{L}_{\alpha\alpha',\beta\beta'}(t) = (i\omega_{\alpha\alpha'} + iL^{L}_{\alpha\alpha'}(t))\delta_{\alpha\beta}\delta_{\alpha'\beta'} - \mathcal{J}_{\alpha\alpha',\beta\beta'}. \tag{6}$$

The form of the operator is unchanged, except that the backward Kramers operator is replaced with the classical Langevin–Liouville operator,

$$iL^{L}_{\alpha\alpha'}(t) = \frac{P}{M}\frac{\partial}{\partial R} + \frac{1}{2}(F^\alpha + F^{\alpha'})\frac{\partial}{\partial P} - \left(\zeta\frac{P}{M} - \xi(t)\right)\frac{\partial}{\partial P}. \tag{7}$$

The time dependence of this operator is due to the random force, $\xi(t)$, which is a Gaussian white-noise process with first and second moments given by

$$\begin{aligned}&\langle\xi(t)\rangle = 0,\\ &\langle\xi(t)\xi(t')\rangle = 2k_BT\zeta\delta(t-t').\end{aligned} \tag{8}$$

The equivalence of the Langevin–Liouville and Kramers operators and is easily shown by writing the integral series solution of Eq. (5) and averaging over realizations of the stochastic process, indicated by $\langle\cdots\rangle_r$:

$$\begin{aligned}&\langle A^{\alpha\alpha'}(X,t)\rangle_r\\ &\quad = A^{\alpha\alpha'}(X,0) + \int_0^t dt_1 \sum_{\mu_1\mu_1'} \langle i\mathcal{L}^L_{\alpha\alpha',\mu_1\mu_1'}(t_1)\rangle_r A^{\mu_1\mu_1'}(X,0)\\ &\qquad + \int_0^t dt_1\int_0^{t_1} dt_2 \sum_{\mu_1\mu_1'\mu_2\mu_2'} \langle i\mathcal{L}^L_{\alpha\alpha',\mu_1\mu_1'}(t_1) i\mathcal{L}^L_{\mu_1\mu_1',\mu_2\mu_2'}(t_2)\rangle_r\\ &\qquad \times A^{\mu_2\mu_2'}(X,0) + \cdots .\end{aligned} \tag{9}$$

Using the properties of the random force given in Eq. (8) to evaluate the average over realizations in this equation, the result for $\langle A^{\alpha\alpha'}(X,t)\rangle_r$ in Eq. (9) can be shown to be identical, term by term to each order in t, to that for $\mathcal{A}^{\alpha\alpha'}(X,t)$ obtained from the series solution of Eq. (2). The prescribed initial condition is $A^{\alpha\alpha'}(X,0) = \mathcal{A}^{\alpha\alpha'}(X,0)$. This establishes the equivalence of the Fokker–Planck and Liouville–Langevin descriptions and the equality $\langle A^{\alpha\alpha'}(X,t)\rangle_r = \mathcal{A}^{\alpha\alpha'}(X,t)$ for this quantum-classical system.

A. Master equation dynamics

The derivation of a dissipative master equation for the diagonal elements of an operator is formally very similar to that for a system where the explicit dynamics of the environment is retained.[20] Equation (5) can be written as a pair of coupled equations for the diagonal and off-diagonal elements of an operator. Formally solving the equation for the off-diagonal elements and substituting the result in to the equation for the diagonal elements, one obtains a generalized master equation,[20,29]

$$\frac{dA_d^\alpha(X,t)}{dt} = iL_\alpha^L(t)A_d^\alpha(X,t) + \int_0^t dt' \sum_\beta \mathcal{M}_{\alpha\beta}(t')A_d^\beta(X,t-t'), \tag{10}$$

where the memory kernel *operator* $\mathcal{M}_{\alpha\beta}(t)$ is given by

$$\mathcal{M}_{\alpha\beta}(t) = \sum_{\mu\mu',\nu\nu'} \mathcal{J}^{d,o}_{\alpha,\mu\mu'}\left[\mathcal{T}e^{\int_0^t dt' i\mathcal{L}^o(t')}\right]_{\mu\mu',\nu\nu'}\mathcal{J}^{o,d}_{\nu\nu',\beta}. \tag{11}$$

In these equations the symbols d and o are used to denote diagonal $\alpha\equiv(\alpha\alpha)$ and off-diagonal $((\alpha\alpha'),\ \alpha\neq\alpha')$ pairs of quantum indices, respectively, and $\mathcal{T}$ is the time-ordering operator.

The expression for the memory kernel operator can be simplified and reduced to a memory *function* if the action of the $\mathcal{C}$ operator in the $\mathcal{J}$ operator is computed in the momentum-jump approximation,[14,30,31] $\mathcal{C}_{\alpha\beta} \approx -D_{\alpha\beta}(X)j_{\alpha\beta}(X)$, where $j_{\alpha\beta}(X)$ is the momentum shift operator. These shifts occur in conjunction with quantum transitions and depend on the quantum states involved. Thus, if $f(X)$ is an arbitrary function of the phase space coordinates X, we denote the shifted momentum resulting from a transition $\alpha\to\beta$ as $\bar{X}_{\alpha\beta}=(R,\bar{P}_{\alpha\beta})=(R,P+\Delta P_{\alpha\beta})$ such that $j_{\alpha\beta}(X)f(X)=f(\bar{X}_{\alpha\beta})$. The actual momentum shift is given by $\Delta P_{\alpha\beta}=\hat{d}_{\alpha\beta}(\mathrm{sgn}(P\cdot\hat{d}_{\alpha\beta})[(P\cdot\hat{d}_{\alpha\beta})^2+\Delta E_{\alpha\beta}M]^{1/2}-P\cdot\hat{d}_{\alpha\beta})$. The argument in the square root must be positive. This restriction ensures that a quantum transition occurs only if there is sufficient kinetic energy in the classical degrees of freedom to effect it.

Using this approximation for $\mathcal{J}$ and neglecting direct transitions between different coherently coupled states,[32] we find

$$\begin{aligned}\frac{dA_d^\alpha(X,t)}{dt} &= iL_\alpha^L(t)A_d^\alpha(X,t)\\ &\quad+\int_0^t dt'\left(\sum_\beta M_{\alpha\beta}^{\alpha\beta}(X,t')A_d^\beta(\bar{X}^{\alpha\beta}_{\alpha\beta,t'},t-t')\right.\\ &\quad\left.+\sum_\nu M_{\alpha\nu}^{\nu\alpha}(X,t')A_d^\alpha(\bar{X}^{\nu\alpha}_{\alpha\nu,t'},t-t')\right),\end{aligned} \tag{12}$$

where the memory function is given by

$$M_{\alpha\nu}^{\nu\alpha}(X,t) = 2\,\mathrm{Re}(\mathcal{W}_{\alpha\nu}(t))D_{\alpha\nu}(X)D_{\nu\alpha}(\bar{X}_{\alpha\nu,t}). \tag{13}$$

These memory function matrix elements couple the time evolution of different diagonal elements of the $\hat{A}(X,t)$ operators. Transitions between diagonal states occur via intermediate coherently coupled pairs of states in QCL dynamics. The subscripts and superscripts on the memory function refer to the indices on the first and second D functions, respectively, which give rise to the transitions between single adiabatic states. In writing Eq. (13) we used the fact that the off-diagonal propagator can be expressed as the product of a phase factor and a classical propagator,

$$\begin{aligned}\mathcal{T}e^{\int_0^t dt'(i\omega_{\alpha\alpha'}+iL^L_{\alpha\alpha'}(t'))} &= e^{\int_0^t dt' i\omega_{\alpha\alpha'}(R_{t'})}\mathcal{T}e^{\int_0^t dt' iL^L_{\alpha\alpha'}(t')}\\ &\equiv \mathcal{W}_{\alpha\alpha'}(t)\mathcal{T}e^{\int_0^t dt' iL^L_{\alpha\alpha'}(t')}.\end{aligned} \tag{14}$$

In Eq. (13) the coordinate has been updated according to

$$\bar{X}^{\nu\alpha}_{\alpha\nu,t'} = j_{\alpha\nu}(X)\mathcal{T}e^{\int_0^{t'} dt'' iL^L_{\alpha\nu}(t'')}j_{\nu\alpha}(X)X, \tag{15}$$

i.e., it has undergone a momentum shift corresponding to a first quantum transition $\alpha\to\nu$; it has evolved for a time t' under Langevin dynamics on the mean surface $\alpha\nu$, and it has undergone a second momentum shift corresponding to a final transition $\nu\to\alpha$.

The time evolution specified by Eq. (12) consists of stochastic classical evolution along single adiabatic surfaces and two memory terms which account for the aforementioned transition process to new surfaces. For example, the transition from diagonal state $\alpha\alpha$ to diagonal state $\beta\beta$ occurs with rate $M_{\alpha\beta}^{\alpha\beta}$ that arises from a concatenation of two events: a transition from $\alpha\alpha$ to $\alpha\beta$ (subscript), evolution on the coherently coupled $\alpha\beta$ surface, and transition from $\alpha\beta$ (superscript) to $\beta\beta$. A similar interpretation applies to the rate $M_{\alpha\nu}^{\nu\alpha}$ where the system is returned to the original $\alpha\alpha$ state after transition to the intermediate coherently coupled $\alpha\nu$ surface. Therefore, the dynamics of the generalized master equation is separated into diagonal and off-diagonal contributions, providing a framework to investigate environment-induced decoherence in the quantum-classical subsystem.

The principal differences between this equation and that derived earlier[20] for a many-body deterministic bath are the presence of time-ordered exponentials arising from the explicit time dependence of the Langevin–Liouville operator and the fact that the dynamics is stochastic rather than Newtonian for the propagator governing the dynamics between the quantum transitions.

B. Decoherence and Markov approximation

For dissipative QC Langevin–Liouville dynamics all quantities of physical interest are obtained from averages over realizations of the stochastic process governing the evolution. Averaging Eq. (12) over realizations, we obtain

$$\begin{aligned}\frac{d\langle A_d^\alpha(X,t)\rangle_r}{dt} &= \langle iL_\alpha^L(t)A_d^\alpha(X,t)\rangle_r\\ &\quad+\int_0^t dt'\left(\sum_\beta \langle M_{\alpha\beta}^{\alpha\beta}(X,t')\rangle_r\langle A_d^\beta(\bar{X}^{\alpha\beta}_{\alpha\beta,t'},t-t')\rangle_r\right.\\ &\quad\left.+\sum_\nu \langle M_{\alpha\nu}^{\nu\alpha}(X,t')\rangle_r\langle A_d^\alpha(\bar{X}^{\nu\alpha}_{\alpha\nu,t'},t-t')\rangle_r\right).\end{aligned} \tag{16}$$

In writing this equation we made the additional approximation that terms involving correlations of fluctuations of the memory kernel from its average over realizations, $\delta M_{\alpha\nu}^{\nu\alpha}(X,t)\equiv M_{\alpha\nu}^{\nu\alpha}(X,t)-\langle M_{\alpha\nu}^{\nu\alpha}(X,t)\rangle$, are small. For short times, where different realizations of the stochastic process have not strongly separated, $\delta M_{\alpha\nu}^{\nu\alpha}(X,t)$ will be small. For long times it will be a highly oscillatory function and will lead to a small contribution to the memory integral. Consequently, to a good approximation, its effect may be neglected. This is the stochastic analog of the approximation made in the derivation of a master equation for a system coupled to a deterministic bath where terms involving correlations in bath projections of the memory term were neglected.[20]

The memory function involves classical evolution on the mean surface, under the influence of friction and a random force arising from the presence of the dissipative environment. As a result of the ensemble average over many different realizations of the stochastic dynamics, we expect that the memory function will decay due to environment-induced decoherence. If the timescale of this decay, τ_d, is short compared to the rate of change of the observable, we can make a Markovian approximation

$$\begin{aligned}\langle M^{\alpha\beta}_{\alpha\beta}(X,t)\rangle_r &\approx 2\left[\int_0^\infty dt'\langle M^{\alpha\beta}_{\alpha\beta}(X,t')\rangle_r\right]\delta(t)\\ &\equiv 2m_{\alpha\beta}(X)\,\delta(t). \qquad (17)\end{aligned}$$

Using this result in Eq. (16) yields

$$\begin{aligned}\frac{\partial\langle A^{\alpha}_{d}(X,t)\rangle_r}{\partial t} &= \langle iL^{L}_{\alpha}(t)A^{\alpha}_{d}(X,t)\rangle_r - m_{\alpha\alpha}(X)\langle A^{\alpha}_{d}(X,t)\rangle_r\\ &\quad + \sum_{\beta} m_{\alpha\beta}(X)\,j_{\alpha\to\beta}\langle A^{\beta}_{d}(X,t)\rangle_r, \qquad (18)\end{aligned}$$

where

$$m_{\alpha\alpha}(X) = -\sum_{\nu}\int_0^\infty dt'\langle M^{\nu\alpha}_{\alpha\nu}(X,t')\rangle_r. \qquad (19)$$

The Markovian approximation leads to the instantaneous action of both momentum shift operators on the observable; they accompany a transition from one single adiabatic surface (α) directly to another single surface (β). Accordingly, the second term in Eq. (18) was rewritten in terms of a single momentum shift operator, $j_{\alpha\to\beta}$, where the double momentum shift differs from that given earlier by a factor of 2 in front of the energy difference.

Rather than dealing directly with Eq. (18), in order to compute the evolution of operators, it is more convenient to simulate the evolution governed by the stochastic equation,

$$\begin{aligned}\frac{\partial A^{\alpha}_{d}(X,t)}{\partial t} &= iL^{L}_{\alpha}(t)A^{\alpha}_{d}(X,t) - m_{\alpha\alpha}(X)A^{\alpha}_{d}(X,t)\\ &\quad + \sum_{\beta} m_{\alpha\beta}(X)\,j_{\alpha\to\beta}A^{\beta}_{d}(X,t), \qquad (20)\end{aligned}$$

which does not involve the average $\langle iL^{L}_{\alpha}(t)A^{\alpha}_{d}(X,t)\rangle_r$. Once the solution to Eq. (20) is obtained the average over realizations may be computed and the result will be the same as if Eq. (18) was simulated directly. The removal of the average in this derivation is analogous to the lifting of the non-Markovian subsystem master equation to the full phase space in the case of the deterministic bath.[20]

The evolution described by this equation is as follows. The classical degrees of freedom evolve according to Langevin dynamics on single adiabatic surfaces, while quantum transitions take the system from one single adiabatic surface directly to another, without passing through a coherently coupled surface. In the master equation, the contribution to the dynamics from the coherent states, including decoherence, is accounted for in the transition rates; $m_{\alpha\beta}$ corresponds to transitions from one surface to a different one while $m_{\alpha\alpha}$ accounts for transitions from the mean surface back to the original adiabatic surface.

The simulation of Eq. (20) by an ensemble of surface-hopping trajectories can be carried out easily using the same Trotter-based algorithm as in the deterministic case. The only difference is that the dynamics between nonadiabatic transitions is stochastic rather than deterministic. In the next section we use this master equation formalism to examine decoherence in a simple model nonadiabatic chemical reaction.

III. NONADIABATIC REACTION MODEL

We now apply the formalism developed above to a simple model for a quantum rate process.[20,27,33] The model consists of a two-level quantum system coupled to a classical, one-dimensional quartic oscillator with phase space coordinates (R,P). This quantum-classical system is embedded in a dissipative environment characterized by the friction ζ and inverse temperature β. Using a diabatic representation, the Hamiltonian for the quantum-classical subsystem is

$$\mathbf{H} = \begin{pmatrix} V_q(R)+\hbar\gamma_0 R & -\hbar\Omega \\ -\hbar\Omega & V_q(R)-\hbar\gamma_0 R \end{pmatrix} + \frac{P^2}{2M}\mathbf{I}, \qquad (21)$$

where $V_q(R)=aR^4/4-bR^2/2$ is the potential of the quartic oscillator. The adiabatic eigenstates of this system, $|\alpha;R\rangle$, have energy eigenvalues $E_\alpha=V_q(R)\mp\hbar\sqrt{\Omega^2+(\gamma_0 R)^2}$. The adiabatic energy gap is 2Ω. The values of the model parameters are $a=0.25$, $b=1.00$, $\gamma_0=1.25$, $\omega=0.51$, and $\beta=0.50$. The friction, ζ, was varied over a range of 0.1–10. All quantities are reported in dimensionless units.[27]

For these parameters, the ground state free energy surface has a double-well form with the barrier top at $R=0$; to its left is the reactant species A, and to its right, the product species B. The expression for the forward time dependent rate coefficient of the reaction $A\rightleftharpoons B$ is given by[34]

$$\begin{aligned}k(t) &= \frac{1}{n_A^{eq}}\sum_{\alpha}\sum_{\alpha'\geq\alpha}(2-\delta_{\alpha'\alpha})\\ &\quad\times\int dX\,\mathrm{Re}\big(N_B^{\alpha\alpha'}(X,t)W_A^{\alpha'\alpha}(X,\beta)\big), \qquad (22)\end{aligned}$$

where $N_B^{\alpha\alpha'}(X,t)$ is a matrix element of the time-evolved number operator for the product state B and n_A^{eq} is the equilibrium number density of the reactant A state. At $t=0$, the number operator is diagonal and its elements are given by $N_B^{\alpha\alpha'}(R)=\Theta(-R)\delta_{\alpha 1}\delta_{\alpha' 1}$, where $\Theta(R)$ is the Heaviside function. $W_A^{\alpha'\alpha}(X,\beta)$ is the subsystem spectral density function. It accounts for the quantum equilibrium structure of the quantum-classical subsystem.[34] Thus, for this reaction model the operator of interest is the number operator for the product state: $\mathcal{A}^{\alpha\alpha'}(X,t)=N_B^{\alpha\alpha'}(X,t)$.

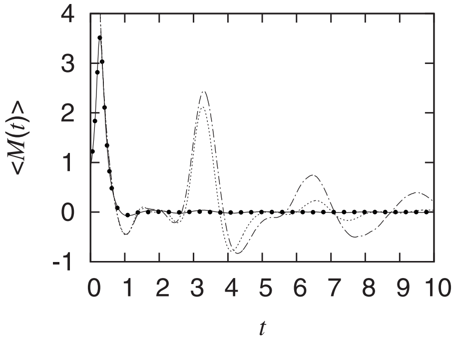

FIG. 1. Comparison of the ensemble averaged memory function, $\langle M_{12}^{12}(X,t)\rangle_r$, and the factorized form for $R=1$, $P=-4$, $\zeta=1$ (solid line and dots, respectively), and $R=0$, $P=-2$, $\zeta=0.1$ (dot-dashed line and dotted line).

A. Memory function

We are interested in the decay properties of the ensemble-averaged memory function [Eq. (13)]. The memory function accounts for all evolution which occurs in coherently coupled states and, thus, its decay is related to the environment-induced decoherence of these states. Furthermore, the validity of the dissipative master equation [Eq. (20)] rests on the rapid decay of the memory function, allowing the use of a Markovian approximation.

We studied the memory function as a function of time, for various initial phase space coordinates, (R,P), and a range of values of the friction coefficient, ζ. We found that the qualitative behavior of the memory function depends on whether the initial position is close to or far from $R=0$, the nonadiabatic coupling maximum, and whether the magnitude of the initial momentum is large or small. This suggested that that the behavior of the memory function is primarily due to the second D factor, $D_{\nu\alpha}(\bar{X}_{\alpha\nu,t})=(\bar{P}_{\alpha\nu,t}/M)\cdot d_{\alpha\beta}(R_t)$, which involves the product of the time-evolved momentum and nonadiabatic coupling.

To determine the exact cause of the decay, we examined the importance of correlations between the factors in the memory function. We found that the correlations between the phase factor and the second D factor could be neglected to a good approximation,

$$\langle M_{\alpha\nu}^{\nu\alpha}(X,t)\rangle_r = 2D_{\alpha\nu}(X)\langle \mathrm{Re}(\mathcal{W}_{\alpha\nu}(t))D_{\nu\alpha}(\bar{X}_{\alpha\nu,t})\rangle_r$$
$$\approx 2D_{\alpha\nu}(X)\langle \mathrm{Re}(\mathcal{W}_{\alpha\nu}(t))\rangle_r\langle D_{\nu\alpha}(\bar{X}_{\alpha\nu,t})\rangle_r. \quad (23)$$

In Fig. 1, we plot the ensemble-averaged memory functions for two initial phase points with different friction coefficients and compare them with the factorized form. We see that the short time behavior of the averaged memory function is very similar to the approximate factored form. Consider the results in Fig. 1 for $R=1$, $P=-4$, and $\zeta=1$. The ensemble of trajectories starts to the right of the barrier top but the initial momentum is directed to the left. The ensemble averaged memory function starts at a fairly small value since the nonadiabatic coupling is small; it increases as the phase point moves into the barrier region where the coupling is strong. (The friction is not large enough to completely randomize the velocity in this time interval.) Then the memory function decays rapidly to zero when the phase point leaves the vicinity of the strong coupling region. This agreement was observed for various initial phase points and a range of friction coefficient values. Similar considerations apply to the $\zeta=0.1$ results in the figure except that now the ensemble starts from the barrier top and the memory function exhibits a strong initial decay. The long time behavior of the memory function for very low friction deviates somewhat from the factorized form. For very low friction values the Markovian description is not expected to be valid.

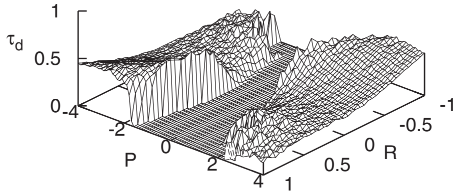

FIG. 2. Decoherence time τ_d as a function of R and P for $\zeta=2$ estimated from the decay of the $\langle M_{12}^{12}(X,t)\rangle_r$ for upward transitions. Transitions in the zero-value region of the figure are not allowed due to insufficient energy in the environment.

We estimated the decay times of the averaged memory function, phase factor, and D factor by finding the time after which the magnitude of the functions remained below a specified fraction of their maximum values. Figure 2 plots the decoherence time as a function of R and P for $\zeta=2$, estimated by the time needed for the memory function to reach 0.8 of its asymptotic value. The structure of τ_d as a function of (R,P) reflects the behavior of the memory function discussed above. The decoherence time is short when the ensemble starts near the barrier top. Larger values of τ_d for large negative (positive) R and positive (negative) P reflect the passage through the barrier region before final decay as described in connection with the results in Fig. 1. It is also larger for positive (negative) R and positive (negative) P since the decay of the phase factor controls the behavior in this region. (The memory function has a small value in these regions where the nonadiabatic coupling is very small.)

For various values of ζ, we found that for most initial phase points, the timescale of the decay of the memory function was close to that of the D factor, while the decay of the phase factor occurred at considerably longer times. The decay of D is a result of the quartic oscillator moving away from the nonadiabatic coupling maximum at $R=0$ and thermalization of the momenta. The exceptions were for phase points initially far from $R=0$ with low momenta; in this case, all three decays occurred on similar timescales.[35] However, the behavior of the memory function for these phase points is of limited interest: for these points, the magnitudes of D and the memory function are small, even initially. Consequently, the corresponding transition rates are quite small and do not contribute much to the dynamics of the system.

Figure 3 shows the mean decoherence time, averaged over the phase points (R,P), as a function of the friction. We expect that a stronger interaction with the environment will accelerate decoherence, and this is indeed what we observe: the decoherence time decreases as friction is increased.

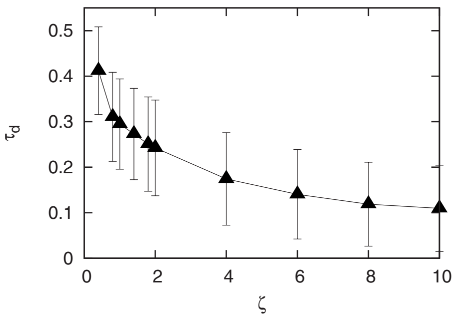

FIG. 3. Mean decoherence time vs friction coefficient. For each value of the friction coefficient, the average was performed over the ensemble of phase points at which the first quantum transition $1 \rightarrow 2$ occurred in mixed quantum-classical Langevin–Liouville dynamics. The error bars show the standard deviation across this ensemble.

B. Transition rates and decoherence times

The calculation of the transition rates involves evaluating the integral $m_{\alpha\beta}(X) = \int_0^\infty dt' \langle M_{\alpha\beta}^{\alpha\beta}(X,t') \rangle_r$. To simulate the master equation we need the rates of the upward and downward transitions. The calculation of these transition rates involves classical, stochastic evolution, on the mean surface. The stochastic evolution is responsible for the spread in the ensemble of realizations, leading to decoherence. Thus, while master equation dynamics involves only single adiabatic surfaces, the probabilities of transitions between these surfaces is calculated with evolution on coherent surfaces, introducing the effect of decoherence. This can be seen in Fig. 4, which shows that the average transition rate decreases with increasing friction.

For the Markovian approximation to be valid, the decoherence time must be short compared to the decay time of the process under consideration. In the present application, the decoherence time should be much shorter than the time it takes for the time dependent rate coefficient to decay to its plateau value. We estimated the microscopic decay time, τ_{mic}, by the time at which $k(t) = k(0)/e$. The results are shown as a function of friction in Fig. 5. Comparing Figs. 3 and 5, we see that this condition is satisfied so that a Markovian description of this model rate process should yield a good approximation to full quantum-classical Langevin–Liouville dynamics. The reaction model in a dissipative bath is related to the same reaction model in a harmonic oscillator bath with Ohmic spectral density investigated earlier.[20] There it was shown by comparisons of simulations on the QCL and the master equations that when the memory kernel decays rapidly and the Markov approximation is valid the master equation provides a good description of the dynamics. Our investigations of the decay of the memory kernel and computations of the decoherence and microscopic times provide the conditions for which the inequality, $\tau_d \ll \tau_{\text{mic}}$, is valid and, thus, a master equation description will be applicable.

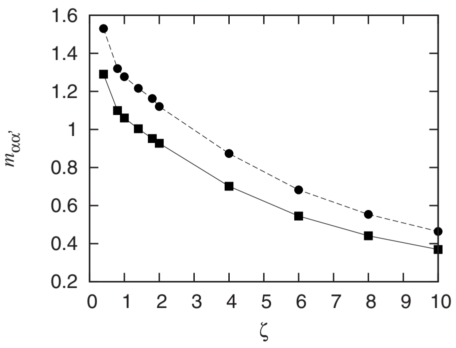

FIG. 4. Average transition rates vs friction coefficient: solid line, m_{12}, dashed line, m_{21}. These are unweighted averages across the range of R and P studied.

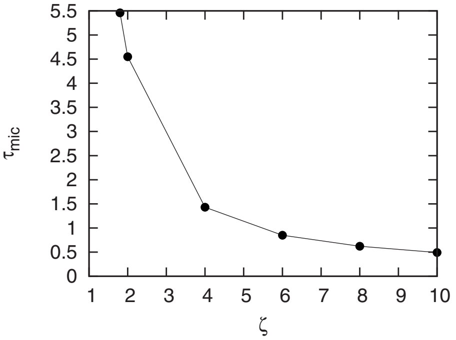

FIG. 5. Microscopic decay time vs ζ. For the purpose of extracting τ_{mic}, we calculated $k(t)$ with an absorbing boundary, located at the product well minimum on the ground state surface. Values were not obtained for friction coefficients lower than 1.8 because $k(t)$ never drops to $k(0)/e$ and the presence of oscillations renders reliable estimation difficult.

IV. CONCLUSION

The dissipative quantum-classical Liouville–Langevin equation is a useful framework for the study of open quantum systems in situations where a portion of the environment need not be described in full dynamical detail. In the present study, it allowed us to investigate the role decoherence plays in the reduction of the dynamics to a master equation and how the behavior varies with bath friction. As expected the decoherence time decreases with increased friction.

Perhaps more surprising is the mechanism of the decay of the memory function that characterizes this decoherence. The memory kernel contains an oscillatory factor that reflects the dynamics on the coherently coupled adiabatic mean surface. Normally, one ascribes decoherence to the interference of oscillations of this phase factor when averages over an ensemble of bath realizations is considered. This is indeed the case. However, as our comparisons with the factored form of the memory kernel in Eq. (23) show, the main decay mechanism is due to the time variation of $\langle D_{\nu\alpha}(\bar{X}_{\alpha\nu,t}) \rangle_r$ as discussed above. The average of the phase factor over realizations decays more slowly than this quantity. We expect this result to be application specific. In the time dependent rate coefficient calculation considered here, trajectories are initiated at the barrier top where the nonadiabatic coupling is strong. The system rapidly moves away from the barrier top to configuration space regions where the nonadiabatic coupling is small. This, in conjunction with the thermalization of the velocity, leads to a rapid fall of $\langle D_{\nu\alpha}(\bar{X}_{\alpha\nu,t}) \rangle_r$ with time. In other applications, it is the average of the phase factor that will control the decay of the memory function.

The results discussed here could form the basis for alternative algorithms for quantum-classical dynamics based on master equation descriptions. To do this computationally efficient ways need to be devised to compute the appropriate phase-space-dependent transition rates. Investigations of the conditions under which master equation descriptions are valid also allow one to assess the accuracy of simple surface-hopping schemes where trajectories evolve on single adiabatic surfaces between nonadiabatic transitions.

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