Quantum and classical relaxation rates from classical simulations

Joel S. Bader and B. J. Berne
Department of Chemistry, Columbia University, New York, New York 10027

(Received 4 January 1994; accepted 22 February 1994)

The time correlation function for a harmonic quantum mechanical system can be related to the time correlation function for a corresponding classical system. Although straightforward to derive and well known in other contexts, this relationship has been unappreciated in the context of vibrational relaxation, where time correlation functions obtained from classical molecular dynamics have been used to predict relaxation rates for a quantum solute in a classical solvent. This inconsistent treatment—quantum solute, classical solvent—predicts a relaxation rate which is slower than if the entire system, both solute and solvent, were treated classically. We demonstrate that if the classical time correlation functions are rescaled to account for the ratio of quantum to classical fluctuations, providing a quantum mechanical treatment for the solute and the solvent, the relaxation rates and the entire absorption spectrum are the same as for a purely classical treatment. Our conclusions are valid when the solute and solvent can be described by a set of effective harmonic normal modes, and can also be valid when anharmonicities are present.

I. INTRODUCTION

A very successful melding of theory and simulation has been the use of classical simulations to predict properties of quantum systems, such as reaction rates, population relaxation rates, and dephasing rates. For condensed phase systems involving many degrees of freedom, direct quantum simulations to determine such rates are far too computationally expensive to be feasible. Instead, perturbation theory can be used with quantum correlation functions to predict these properties. Although quantum correlation functions are difficult to obtain, classical molecular dynamics can often be used to obtain the analogous correlation function for a corresponding classical system.

There is no general prescription for relating a classical correlation function to a quantum correlation function. The precise relationship depends on the underlying Hamiltonian generating the classical and quantum dynamics. When the classical and quantum systems are both characterized by identical effective harmonic Hamiltonians, the underlying set of effective normal modes of the quantum and classical systems are identical, and it is then possible to relate quantum and classical correlation functions. This restriction to a harmonic solvent is implicit in theoretical treatments which truncate a solvent response function at the level of the second cumulant (in the context of vibrational relaxation see, for example, Refs. 1–8). Furthermore, simulation studies of velocity relaxation,[9] vibrational relaxation,[10] photon echoes,[11] spectroscopic line shapes,[12] and dielectric relaxation[13–15] have demonstrated that complicated classical atomic and molecular solvents can be approximated very well by harmonic baths.

With the restriction to an effective harmonic Hamiltonian for the solvent, we show how a correlation function obtained for a classical system can be used to obtain the corresponding quantum correlation function. Along with the detailed balance factor, we find an additional factor which is related to the ratio of quantum fluctuations to classical fluctuations. These well-known formal results for effective harmonic systems provide a useful approximation for more general systems, but have not always been appreciated when classical time correlation functions obtained from molecular dynamics have been used to estimate quantum rates. An application to absorption spectroscopy is given in Sec. II, where we show that the absorption line shape for a linearly responding system is identical under a classical or quantum treatment. This implies that T_1, T_2, and the absorption frequency shift for a harmonic vibrational mode are the same for a classical and corresponding quantum mechanical system. In Sec. III we further investigate the rate of population relaxation, $1/T_1$, for a quantum oscillator in a quantum fluid, as well as the state-to-state transition rates. We find that some recent studies of vibrational relaxation have been inconsistent in their treatment of a tagged excited vibrational mode, described quantum mechanically, and the remaining degrees of freedom, treated classically. Our analysis indicates that if the classical bath modes can be described as an effective set of normal modes, and if the bath is treated quantum mechanically rather than classically, the energy relaxation of the quantum oscillator in a quantum bath is the same as the energy relaxation of a corresponding classical oscillator in a classical bath.

II. ABSORPTION SPECTRA

Real-time correlation functions can be used to predict condensed phase absorption line shapes.[16–19] Here we show that the line shape predicted by a quantum mechanical treatment is exactly the same as a classical absorption spectrum, provided that the absorbing modes are effectively harmonic. Making the approximation that the radiation field can be treated classically, the Hamiltonian describing the system is

$$H = H_0 - \mathbf{M} \cdot \mathbf{E}(t), \tag{1}$$

where $\mathbf{M}$ is the net system dipole and $\mathbf{E}(t)$ is a spatially homogeneous, time dependent electric field along the $\hat{x}$ axis,

0021-9606/94/100(11)/8359/8/$6.00

$\mathbf{E}(t)=\hat{x}E_0\cos(\omega t)$. According to the golden rule, the rate for transitions from eigenstate $|i\rangle$ of H_0 to eigenstate $|f\rangle$ is

$$k^{\rm qm}_{f\leftarrow i}=(\pi|M_{fi}|^2E_0^2/2\hbar^2)[\delta(\omega+\omega_{fi})+\delta(\omega-\omega_{fi})], \quad (2)$$

where $\omega_{fi}=(E_f-E_i)/\hbar$ and $M_{fi}=\langle f|\mathbf{M}\cdot\hat{x}|i\rangle$. Assuming that the perturbation $\mathbf{E}(t)$ is small and that each state $|i\rangle$ is initially populated according to a Boltzmann distribution, the absorption coefficient $\alpha_{\rm qm}(\omega)$ in the Beer–Lambert law is

$$\alpha_{\rm qm}(\omega)=\frac{8\pi^2\omega}{V\hbar c}\tanh(\beta\hbar\omega/2)\times\int_{-\infty}^{\infty}\frac{dt}{2\pi}\,e^{-i\omega t}\langle\tfrac{1}{2}[M(t),M(0)]_+\rangle_{\rm qm}, \quad (3)$$

where V is the total volume of the system, c is the speed of light, and $[A,B]_+=AB+BA$ is the anticommutator. Thus it is important to compute the time correlation function for the anticommutator,

$$G^{\rm qm}_{MM}(t)\equiv\langle\tfrac{1}{2}[M(t),M(0)]_+\rangle_{\rm qm}, \quad (4)$$

and its power spectrum,

$$\hat{G}^{\rm qm}_{MM}(\omega)=\frac{1}{2\pi}\int_{-\infty}^{\infty}dt\,e^{-i\omega t}G^{\rm qm}_{MM}(t). \quad (5)$$

It is straightforward to compute this function in the case that M can be expressed as a linear combination of the effective normal modes $\{x_\alpha\}$ of the system, with frequencies $\{\omega_\alpha\}$ and effective masses $\{m_\alpha\}$,

$$M=\sum_\alpha g_\alpha x_\alpha. \quad (6)$$

Because there is no coupling between normal modes,

$$G^{\rm qm}_{MM}(t)=\sum_\alpha\langle x_\alpha^2\rangle_{\rm qm}\cos(\omega_\alpha t)=\sum_\alpha(\hbar\omega_\alpha/2)\coth(\beta\hbar\omega_\alpha/2)\frac{g_\alpha^2}{m_\alpha\omega_\alpha^2}\cos(\omega_\alpha t). \quad (7)$$

From this it follows that

$$\hat{G}^{\rm qm}_{MM}(\omega)=\sum_\alpha(\hbar\omega_\alpha/2)\coth(\beta\hbar\omega_\alpha)\frac{g_\alpha^2}{2m_\alpha\omega_\alpha^2}\times[\delta(\omega+\omega_\alpha)+\delta(\omega-\omega_\alpha)]=(\hbar\omega/2)\coth(\beta\hbar\omega/2)J_0(\omega), \quad (8)$$

where $J_0(\omega)$ is the spectral density function for the normal modes in H_0,

$$J_0(\omega)=\sum_\alpha\frac{g_\alpha^2}{2m_\alpha\omega_\alpha^2}[\delta(\omega+\omega_\alpha)+\delta(\omega-\omega_\alpha)]. \quad (9)$$

This property of the system is independent of Planck's constant. Substitution of Eq. (8) into Eq. (3) gives the absorption coefficient,

$$\alpha_{\rm qm}(\omega)=\frac{8\pi^2\omega}{V\hbar c}\tanh(\beta\hbar\omega/2)\times(\hbar\omega/2)\coth(\beta\hbar\omega/2)J_0(\omega)=\frac{4\pi^2\omega^2}{Vc}J_0(\omega). \quad (10)$$

Thus the absorption coefficient is independent of Planck's constant and it immediately follows that for a harmonic system the absorption coefficient is the same for a fully quantum system as for a fully classical system,

$$\alpha_{\rm qm}(\omega)=\alpha_{\rm cl}(\omega). \quad (11)$$

Furthermore, since the absorption lineshape for an oscillator coupled to a bath is determined parametrically by the population relaxation time T_1, the dephasing time T_2, and the frequency shift, these relaxation times must also be identical under a fully quantum and fully classical treatment as long as the complete system is effectively harmonic.

To make this discussion more concrete, we will assume that the radiation field couples directly to a tagged oscillator q, which is then coupled bilinearly to a harmonic bath. The absorption line shape is related to T_1 and T_2 for the tagged oscillator. The total Hamiltonian for the system is $H=H_q+H_b+H_{qb}$, with

$$H_q=\frac{p^2}{2\mu}+\frac{1}{2}\mu\omega_0^2q^2, \quad (12a)$$

$$H_b=\sum_\alpha\left(\frac{p_\alpha^2}{2m_\alpha}+\frac{1}{2}m_\alpha\omega_\alpha^2x_\alpha^2\right), \quad (12b)$$

and

$$H_{qb}=-q\sum_\alpha g_\alpha x_\alpha=-qF. \quad (12c)$$

The rate that the system absorbs energy due to a time-dependent perturbation $V(t)=-qE_0\cos(\omega t)$ is the same classically and quantum mechanically:

$$(dE/dt)_{\rm qm}=(dE/dt)_{\rm cl}=(E_0^2\omega^2/4k_BT)\int_{-\infty}^{\infty}dt\,e^{-i\omega t}\langle q(t)q(0)\rangle_{\rm cl}. \quad (13)$$

The transform of the classical correlation function,

$$\hat{C}^{\rm cl}_{qq}(\omega)=\int_{-\infty}^{\infty}dt\,e^{-i\omega t}\langle q(t)q(0)\rangle_{\rm cl}, \quad (14)$$

can be obtained by analyzing a generalized Langevin equation which produces stochastic dynamics for q which are equivalent to the dynamics under H,

$$\ddot{q}(t)=-\bar{\omega}^2q(t)+\mu^{-1}\xi(t)-\mu^{-1}\int_0^t dt'\,\zeta_{\rm cl}(t-t')\dot{q}(t'). \quad (15)$$

The friction kernel is related to $J_b(\omega)$, the spectral density of bath modes in H_b, by a cosine transform,

$$\zeta_{\mathrm{cl}}(t)=\int_{-\infty}^{\infty} d\omega\, J_b(\omega)\cos(\omega t). \tag{16}$$

The friction kernel $\zeta_{\mathrm{cl}}(t)$ also characterizes the Gaussian random force $\xi(t)$ by a classical fluctuation-dissipation theorem, $\langle \xi(t)\xi(0)\rangle = k_B T \zeta_{\mathrm{cl}}(t)$. The renormalized frequency $\tilde{\omega}^2$ is $\omega_0^2-\mu^{-1}\zeta_{\mathrm{cl}}(0)$. The spectrum $\hat{C}^{\mathrm{cl}}_{qq}(\omega)$ can be obtained by Laplace transform methods, giving

$$\hat{C}^{\mathrm{cl}}_{qq}(\omega)=(1/\beta\mu\tilde{\omega}^2)\,\frac{2\gamma'(\omega)\tilde{\omega}^2}{[\tilde{\omega}^2-\omega^2+\omega\gamma''(\omega)]^2+\omega^2\gamma'(\omega)^2}, \tag{17}$$

where $\gamma'(\omega)=\mu^{-1}\,\mathrm{Re}\,\tilde{\zeta}_{\mathrm{cl}}(i\omega)$, $\gamma''(\omega)=-\mu^{-1}\,\mathrm{Im}\,\tilde{\zeta}_{\mathrm{cl}}(i\omega)$, and

$$\tilde{\zeta}_{\mathrm{cl}}(i\omega)=\int_0^{\infty} dt\, e^{-i\omega t}\zeta_{\mathrm{cl}}(t). \tag{18}$$

It is important to note that in the quantum mechanical analog of Eq. (17), $\gamma'(\omega)$, $\gamma''(\omega)$, and $\tilde{\omega}^2$ are exactly the same as in the classical expression,

$$\begin{aligned}\hat{C}^{\mathrm{qm}}_{qq}(\omega)&=\int_{-\infty}^{\infty} dt\, e^{-i\omega t}\langle \tfrac{1}{2}[q(t),q(0)]_+\rangle_{\mathrm{qm}}\\&=(\beta\hbar\omega/2)\coth(\beta\hbar\omega/2)\hat{C}^{\mathrm{cl}}_{qq}(\omega).\end{aligned} \tag{19}$$

This is because $\gamma'(\omega)$, $\gamma''(\omega)$, and $\tilde{\omega}^2$ should be thought of as elements of a normal mode transformation[7] rather than as response functions per se. The normal mode transformation is made by first transforming to mass-weighted coordinates, $X_\alpha=\sqrt{m_\alpha}x_\alpha$ and $X_0=\sqrt{\mu}q$. We also take $P_\alpha=p_\alpha/\sqrt{m_\alpha}$, where α includes q as well as the bath modes. The Hamiltonian $H_q+H_b+H_{qb}$ can be diagonalized by a unitary transformation $\mathbf{U}$, $Y_i=\Sigma_\alpha U_{i\alpha}X_\alpha$, as

$$H=\frac{1}{2}\sum_i (P_i^2+\lambda_i^2 Y_i^2). \tag{20}$$

All the frequencies λ_i are real and positive. The transformation back to the mode q coupled directly to the radiation field is $q=(1/\sqrt{\mu})\Sigma_i U_{0i}Y_i$. Since the normal modes are uncoupled,

$$\langle [q(t),q(0)]_+\rangle_{\mathrm{qm}}=(1/\mu)\sum_i U_{0i}^2\langle [Y_i(t),Y_i(0)]_+\rangle_{\mathrm{qm}}. \tag{21}$$

In terms of the normal modes,

$$\begin{aligned}\hat{C}^{\mathrm{qm}}_{qq}(\omega)&=(1/\mu)\sum_i U_{0i}^2(\hbar/2\lambda_i)\coth(\beta\hbar\lambda_i/2)\pi\delta(\lambda_i-|\omega|)\\&=(\hbar/2\mu\omega)\coth(\beta\hbar\omega/2)\pi\sum_i U_{0i}^2\delta(\lambda_i-|\omega|).\end{aligned} \tag{22}$$

In comparison with Eq. (19), we see explicitly that

$$\begin{aligned}&\frac{\gamma'(\omega)\omega^2}{[\tilde{\omega}^2-\omega^2+\omega\gamma''(\omega)]^2+\omega^2\gamma'(\omega)^2}\\&\quad=(\pi/2)\sum_i U_{0i}^2\delta(\lambda_i-|\omega|).\end{aligned} \tag{23}$$

Since the transformation $\mathbf{U}$ and the normal mode frequencies λ_i are the same classically and quantum mechanically, the quantity in Eq. (23) must also be the same classically or quantum mechanically.

It follows that the line shape of the quantum absorption is exactly the same as the classical line shape. In particular, the dephasing time T_2 and the population relaxation time T_1 are identical to the classical results. These relaxation times are well-defined when the absorption spectrum is sharply peaked, which indicates a separation of time scales between the tagged oscillator and the bath modes. From Eq. (17), the peak is at frequency $\Omega=\tilde{\omega}+\gamma''(\tilde{\omega})$. For $\omega\approx\Omega$,

$$\hat{C}^{\mathrm{cl}}_{qq}(\omega)=(2/\beta\mu\tilde{\omega}^2)\,\frac{\gamma'(\Omega)}{(\Omega-\omega)^2+\gamma'(\Omega)^2}. \tag{24}$$

The population relaxation time T_1 can be estimated as $\gamma'(\Omega)^{-1}$, and the dephasing time T_2 is $2T_1$ with either a quantum or classical treatment. The solvent-induced frequency shift $\gamma''(\Omega)$ is also the same quantum mechanically and classically.

Our derivation of the result that T_1, T_2, and the frequency shift are the same classically and quantum mechanically has relied on an underlying harmonic Hamiltonian for the tagged oscillator and the solvent. It is likely that even if the oscillator or the oscillator-bath coupling is anharmonic, the relaxation rates predicted by classical mechanics and quantum mechanics will still be almost identical. To lowest order, anharmonicity will lead to pure dephasing, decreasing T_2 while leaving T_1 unchanged:

$$\frac{1}{T_2}=\frac{1}{2T_1}+\frac{1}{T_2^*}, \tag{25}$$

where T_1 is that for a harmonic reference system and T_2^* corresponds to pure dephasing. (Higher order perturbation theory for the relaxation of a two-level system coupled to a stochastic bath can sometimes predict $T_2>2T_1$, see Refs. 20–23.) The result of Eq. (25) has recently been derived starting from a classical generalized Langevin equation[10] using H_b and H_{qb} from Eqs. (12b) and (12c), and taking an anharmonic potential for H_q,

$$H_q=\frac{p^2}{2\mu}+\frac{1}{2}\mu\omega_0^2q^2+\frac{1}{6}fq^3. \tag{26}$$

The pure dephasing time is given by the Kubo formula[1–4]

$$\frac{1}{T_2^*}=\mathrm{Re}\int_0^{\infty} dt\langle \delta\omega(t)\delta\omega(0)\rangle_b^{\mathrm{qm}}, \tag{27}$$

where $\delta\omega(t)$ is the instantaneous shift in the frequency of the oscillator due to solvent fluctuations. Since the Laplace transform is taken at zero frequency, it involves only the classical, low-frequency portion of the bath spectral density; consequently, the classical and quantum predictions for T_2^* are identical as long as H_b is harmonic.[7]

Another anharmonic model which illustrates that T_2^* can be the same classically and quantum mechanically is to introduce a nonlinear coupling between the tagged oscillator and the bath,

$$H_{qb}=\frac{1}{2}mq^2\sum_\alpha f_\alpha x_\alpha, \tag{28}$$

while keeping the harmonic forms for H_q and H_b from Eqs. (12a) and (12b). The instantaneous frequency of the tagged oscillator is $(\omega_0^2+\delta\omega(t)^2)^{1/2}$. To lowest order in the coupling constants $\{f_\alpha\}$, the frequency shift is

$$\delta\omega(t)=\frac{1}{2\omega_0}\sum_\alpha f_\alpha x_\alpha. \tag{29}$$

Evaluating the Kubo formula, Eq. (27), for this model gives

$$\begin{aligned}\frac{1}{T_2^*}&=\mathrm{Re}\,\frac{1}{4\omega_0^2}\sum_\alpha f_\alpha^2\int_0^\infty dt\langle x_\alpha(t)x_\alpha(0)\rangle_b^{\mathrm{qm}}\\&=\frac{1}{4\omega_0^2}k_BT\pi\sum_\alpha\frac{f_\alpha^2}{m_\alpha\omega_\alpha^2}\,\delta(\omega_\alpha),\end{aligned} \tag{30}$$

which is independent of $\hbar$ because it measures the fluctuations of only the low frequency, classical bath modes. The same result can also be derived from Bloch–Redfield theory[24–26] if the connection is made that T_2^* is the relaxation time for the coherence between pairs of adjacent oscillator states n and $n+1$. The dominant contribution to the relaxation rate is

$$\begin{aligned}\frac{1}{T_2^*}&=\mathrm{Re}\left(\frac{\mu}{2\hbar}\right)^2[\langle n+1|q^2|n+1\rangle-\langle n|q^2|n\rangle]^2\\&\quad\times\int_0^\infty dt\sum_\alpha f_\alpha^2\langle x_\alpha(t)x_\alpha(0)\rangle_b^{\mathrm{qm}},\end{aligned} \tag{31}$$

which is exactly equivalent to Eq. (30) upon evaluation of the harmonic oscillator matrix elements. Consequently, the lowest order classical and quantum mechanical predictions for T_2^* are identical for this anharmonic model.

III. VIBRATIONAL RELAXATION

Here we concentrate on the rate of relaxation of a tagged vibrationally excited solute in a solvent. The relaxation rate serves as a probe of solute-solvent interactions. The interactions which contribute to vibrational relaxation are also important in determining a wide variety of closely related condensed phase properties, such as chemical reaction rates and transport coefficients. In this section, we show how classical simulation data can be used to determine the rate of relaxation, including both the population relaxation time T_1 and the quantum state-to-state rates, of a quantum mechanical solute in a quantum mechanical solvent. We do this by defining a correlation function for the classical bath, converting it to a correlation function for a corresponding quantum bath, and using the quantum correlation function in a perturbation theory expression for the rate of vibrational transitions for a quantum solute.

Correlation function expressions for the vibrational relaxation rate are useful even for classical systems because relaxation can be so slow that the energy loss of a solvated oscillator can be negligible over a long simulation. The classical limit of the expression we obtain for T_1 for a quantum solute-quantum solvent agrees with previous results for the relaxation of a classical solute in a classical solvent. Furthermore, we predict that when the tagged oscillator and the bath can be described by a set of effective harmonic normal modes, T_1 for a quantum solute in a quantum solvent is the same as T_1 for a classical solute in a classical solvent.

Recent simulation studies have shown that the energy relaxation rate predicted using a classical force–force autocorrelation function can agree well with that observed in a simulation of a classical oscillator in a classical molecular fluid.[10,27,28] Correlation functions from a simulation of a classical solvent were later used to predict the relaxation of a quantum oscillator, with either Bloch–Redfield theory[29,30] or a Fermi golden rule, Landau–Teller–Zener treatment.[31] We reinterpret these existing results for the relaxation of classical and quantum solutes in a classical bath to account for the quantum mechanics of the solvent molecules, and find that the changes in reported lifetimes and relaxation rates can be considerable.

We first review how to obtain an expression for the rate of transitions between vibrational levels using time-dependent perturbation theory. We then describe how this approach can be generalized to give the relaxation rate of a quantum solute in a quantum solvent. Only when the real classical bath can be represented by an effective harmonic bath will it be possible to accurately infer the quantum behavior from a classical simulation. The result we obtain should be accurate under the reasonable assumption that the corresponding classical solvent exhibits linear response.

The perturbation theory, Fermi golden rule, Landau–Teller–Zener expression for the rate of vibrational transitions is derived starting from a Hamiltonian of the form $H=H_q+H_b+H_{qb}$.[5,24,32] The Hamiltonian for a solute vibrational mode with frequency ω and reduced mass μ is H_q,

$$H_q=\frac{p^2}{2\mu}+\frac{\mu\omega^2q^2}{2}. \tag{32}$$

The bath Hamiltonian H_b describes solvent molecules as well as any solute modes not included in H_q, and H_{qb} couples the solute vibrational mode and the bath. The eigenstate $|n\rangle$ of H_q has energy $E_n=\hbar\omega(n+1/2)$. A straightforward application of Fermi's golden rule gives the rate of transitions from solute state i to state j as

$$k_{j\leftarrow i}^{\mathrm{qm}}=\frac{1}{\hbar^2}\int_{-\infty}^{\infty}dt\,e^{i\omega_{ij}t}\langle V_{ij}(t)V_{ji}(0)\rangle_b^{\mathrm{qm}}. \tag{33}$$

The average $\langle\cdots\rangle_b^{\mathrm{qm}}$ is over states of the quantum mechanical bath with thermal weight $\exp(-\beta H_b)$. The perturbation matrix element is defined as

$$V_{ij}(t)=\langle i|\exp(iH_bt/\hbar)V\exp(-iH_bt/\hbar)|j\rangle, \tag{34}$$

and $\omega_{ij}=(E_i-E_j)/\hbar$.

It is possible to rewrite $k_{j\leftarrow i}^{\mathrm{qm}}$ in a slightly different form involving a time-symmetrized correlation function,

$$k^{\mathrm{qm}}_{j\leftarrow i}=\frac{2}{\hbar^2[1+\exp(-\beta\hbar\omega_{ij})]}\times\int_{-\infty}^{\infty}dt\; e^{i\omega_{ij}t}\langle\tfrac{1}{2}[V_{ij}(t),V_{ji}(0)]_+\rangle^{\mathrm{qm}}_b. \tag{35}$$

We will assume that the coupling term V is linear in the solute coordinate, $V=-qF$, where the force F exerted on the vibrational mode by the bath involves bath terms only. We will also assume that $\langle F\rangle^{\mathrm{qm}}_b=0$, i.e., any systematic force due to the bath has already been absorbed into the definition of q and the value of the frequency ω, which might differ from the gas-phase solute vibrational frequency ω_0. For a harmonic solute, only transitions between eigenstates n and $n\pm 1$ are allowed. Using the harmonic oscillator matrix element $\langle n|q|n-1\rangle=\sqrt{n\hbar/2\mu\omega}$,

$$k^{\mathrm{qm}}_{n-1\leftarrow n}=\frac{n}{\mu\hbar\omega[1+\exp(-\beta\hbar\omega)]}\times\int_{-\infty}^{\infty}dt\; e^{i\omega t}\langle\tfrac{1}{2}[F(t),F(0)]_+\rangle^{\mathrm{qm}}_b. \tag{36}$$

With $\zeta_{\mathrm{qm}}(t)\equiv(1/2k_BT)\langle[F(t),F(0)]_+\rangle^{\mathrm{qm}}_b$, the Fourier–Laplace transform of $\zeta_{\mathrm{qm}}(t)$ is

$$\tilde{\zeta}_{\mathrm{qm}}(i\omega)=\int_0^{\infty}dt\; e^{-i\omega t}\zeta_{\mathrm{qm}}(t)=\tilde{\zeta}'_{\mathrm{qm}}(\omega)-i\tilde{\zeta}''_{\mathrm{qm}}(\omega), \tag{37}$$

with $\tilde{\zeta}'_{\mathrm{qm}}(\omega)$ and $\tilde{\zeta}''_{\mathrm{qm}}(\omega)$ both pure real. These definitions for $\zeta_{\mathrm{qm}}(t)$ and $\tilde{\zeta}_{\mathrm{qm}}(i\omega)$ follow the conventions used to define the friction kernel in the context of generalized Langevin equations and reaction rate theories.[33,34] The final equation for the transition rate is

$$k^{\mathrm{qm}}_{n-1\leftarrow n}=\frac{2n}{\mu\beta\hbar\omega[1+\exp(-\beta\hbar\omega)]}\tilde{\zeta}'_{\mathrm{qm}}(\omega)=e^{\beta\hbar\omega}k^{\mathrm{qm}}_{n\leftarrow n-1}. \tag{38}$$

According to Eq. (38), the rate of transitions between states diverges in the classical limit as the dimensionless energy difference between states $\hbar\omega/k_BT$ approaches 0. The quantity related to a transition rate which survives in the classical limit is the energy or population relaxation time T_1. The average energy at time t of a distribution of oscillators is defined through the oscillator density matrix as $\langle E(t)\rangle_{\mathrm{qm}}=\Sigma_n\rho_{nn}(t)E_n$. The rate of change of the average oscillator energy is

$$\frac{d\langle E(t)\rangle_{\mathrm{qm}}}{dt}=\sum_n E_n\dot{\rho}_{nn}(t). \tag{39}$$

Assuming that the bath relaxes much faster than the timescale of transitions between quantum states of the tagged oscillator, the rate of change of ρ_{nn} is

$$\dot{\rho}_{nn}(t)=\sum_{n'\neq n}[k^{\mathrm{qm}}_{n\leftarrow n'}\rho_{n'n'}(t)-k^{\mathrm{qm}}_{n'\leftarrow n}\rho_{nn}(t)], \tag{40}$$

which is the result of Bloch–Redfield theory along with a secular approximation decoupling the diagonal and off-diagonal matrix elements.[24–26] This approximation is equivalent to a master equation description for the populations of the oscillator energy levels. It should be a reasonable approximation because off-diagonal coherences in the density matrix contribute mostly to pure dephasing and not to population relaxation. Since only adjacent oscillator states are coupled, the rate of change of the energy is

$$\frac{d\langle E\rangle_{\mathrm{qm}}}{dt}=-\hbar\omega\sum_n\rho_{nn}(t)(k^{\mathrm{qm}}_{n-1\leftarrow n}-k^{\mathrm{qm}}_{n+1\leftarrow n})=-\frac{2\tilde{\zeta}'_{\mathrm{qm}}(\omega)\hbar\omega}{\mu\beta\hbar\omega[1+\exp(-\beta\hbar\omega)]}\sum_n\rho_{nn}(t)[n-e^{-\beta\hbar\omega}(n+1)]$$
$$=\frac{\tilde{\zeta}'_{\mathrm{qm}}(\omega)}{\mu}\frac{2}{\beta\hbar\omega}\tanh\left(\frac{\beta\hbar\omega}{2}\right)\sum_n\rho_{nn}(t)\left[\hbar\omega(n+\tfrac{1}{2})-\frac{\hbar\omega}{2}\coth\left(\frac{\beta\hbar\omega}{2}\right)\right]. \tag{41}$$

Noting that $\Sigma_n\rho_{nn}(t)=1$ and that $(\hbar\omega/2)\coth(\beta\hbar\omega/2)$ is the thermal equilibrium average $\langle E\rangle^{\mathrm{qm}}_{\mathrm{eq}}$, the relaxation time T_1 is defined by the relation

$$\frac{d\langle E(t)\rangle_{\mathrm{qm}}}{dt}=T_1^{-1}[\langle E(t)\rangle_{\mathrm{qm}}-\langle E\rangle^{\mathrm{qm}}_{\mathrm{eq}}] \tag{42}$$

as

$$T_1^{-1}=\frac{\tanh(\beta\hbar\omega/2)}{\beta\hbar\omega/2}\frac{\tilde{\zeta}'_{\mathrm{qm}}(\omega)}{\mu}. \tag{43}$$

The equation for T_1 is not the same as that given as Eq. (3) of Ref. 29: Our expression is in terms of $\tilde{\zeta}'_{\mathrm{qm}}(\omega)$, whereas that expression is in terms of $\tilde{\zeta}'_{\mathrm{cl}}(\omega)$. When our expression involving $\tilde{\zeta}'_{\mathrm{qm}}(\omega)$ is used, T_1^{-1} has the correct limits for small and large $\hbar\omega/k_BT$. In the classical limit, $\hbar\omega\ll k_BT$, $T_1^{-1}\approx\tilde{\zeta}'_{\mathrm{qm}}(\omega)/\mu$.[10,35] In the opposite limit, $\hbar\omega\gg k_BT$, T_1^{-1} and $k^{\mathrm{qm}}_{0\leftarrow 1}$ both approach $2\tilde{\zeta}'_{\mathrm{qm}}(\omega)/\mu\beta\hbar\omega$.

In several recent simulation studies of the relaxation of quantum solutes[29–31] the time correlation function $\zeta_{\mathrm{cl}}(t)$ and its corresponding spectrum $\tilde{\zeta}'_{\mathrm{cl}}(\omega)$ are determined from classical molecular dynamics. These workers have determined T_1 by substituting $\tilde{\zeta}'_{\mathrm{cl}}(\omega)$ directly for $\tilde{\zeta}'_{\mathrm{qm}}(\omega)$ in expressions corresponding to Eq. (43). To assess this approximation it is useful to consider an explicit harmonic bath Hamiltonian where $\zeta(t)$ and its transform may be computed exactly, both classically and quantum mechanically. The most general forms for harmonic H_b and H_{qb}, assuming that F is linear in the bath modes and $\langle F\rangle^{\mathrm{qm}}_b=0$, are those given in Eqs. (12b) and (12c). It immediately follows that

TABLE I. State-to-state rates $k^{qm}_{n-1\leftarrow n}$ for a quantum solute.

Classical solvent	Quantum solvent
$\dfrac{2n\tilde{\zeta}'_{\mathrm{cl}}(\omega)}{\mu\beta\hbar\omega(1+e^{-\beta\hbar\omega})}$	$\dfrac{\beta\hbar\omega}{2}\coth\left(\dfrac{\beta\hbar\omega}{2}\right)\dfrac{2n\tilde{\zeta}'_{\mathrm{cl}}(\omega)}{\mu\beta\hbar\omega(1+e^{-\beta\hbar\omega})}$

$$\tilde{\zeta}'_{\mathrm{qm}}(\omega)=(\beta\hbar\omega/2)\coth(\beta\hbar\omega/2)\tilde{\zeta}'_{\mathrm{cl}}(\omega). \tag{44}$$

In terms of the classical correlation function measured in a simulation, the rate of vibrational transitions for a quantum solute in a quantum bath is

$$k^{\mathrm{qm}}_{n-1\leftarrow n}=\frac{2n}{\mu\beta\hbar\omega[1+\exp(-\beta\hbar\omega)]}\frac{\beta\hbar\omega}{2}\coth\left(\frac{\beta\hbar\omega}{2}\right)\tilde{\zeta}'_{\mathrm{cl}}(\omega). \tag{45}$$

The vibrational energy relaxation time for a quantum solute in a quantum bath, again in terms of the classical bath correlation function, is given by Eqs. (43) and (44) as

$$T_1^{-1}=\frac{\tilde{\zeta}'_{\mathrm{cl}}(\omega)}{\mu}. \tag{46}$$

This result indicates that T_1 for a quantum solute in a quantum solvent is exactly the same as T_1 for a classical solute in a classical solvent. Expressions for $k^{\mathrm{qm}}_{n-1\leftarrow n}$ are summarized in Table I and those for T_1^{-1} are summarized in Table II. For ease of application to classical simulation data, the rates for a solute in a quantum solvent are expressed in terms of $\tilde{\zeta}'_{\mathrm{cl}}(\omega)$, the real part of the Fourier–Laplace transform of $\zeta_{\mathrm{cl}}(t)$ of the corresponding classical solvent which can be obtained directly from molecular dynamics. The relaxation rate for a classical solute in a quantum solvent is included for completeness.

Quantizing the solvent enhances state-to-state rates and energy relaxation rates by a factor of $(\beta\hbar\omega/2)\coth(\beta\hbar\omega/2)$. This rate enhancement is a consequence of the solute-bath coupling $\langle F(t)F(0)\rangle_b^{\mathrm{qm}}$ scaling as $\langle x_\alpha^2\rangle_b^{\mathrm{qm}}$ for solvent mode x_α. The coupling is only capable of inducing vibrational transitions when the solvent mode frequency ω_α is close to the solute frequency ω. For these solvent modes, the ratio of the quantum coupling to the classical coupling, $\langle x_\alpha^2\rangle_b^{\mathrm{qm}}/\langle x_\alpha^2\rangle_b^{\mathrm{cl}}$, is exactly the factor $(\beta\hbar\omega/2)\coth(\beta\hbar\omega/2)$. The asymptotic limits of the ratio of the relaxation rate for a quantum solute in a quantum solvent to the relaxation rate of a quantum solute in a classical solvent are

$$\frac{T_1^{-1},\ \text{quantum solvent}}{T_1^{-1},\ \text{classical solvent}}=\begin{cases}1, & \hbar\omega\ll k_BT\\ \hbar\omega/2k_BT, & \hbar\omega\gg k_BT\end{cases} \tag{47}$$

as a function of the solute frequency ω. The ratio of state-to-state rates scales the same way.

TABLE II. Vibrational energy relaxation rates T_1^{-1}.

	Classical solvent	Quantum solvent
Classical solute	$\dfrac{\tilde{\zeta}'_{\mathrm{cl}}(\omega)}{\mu}$	$\dfrac{\beta\hbar\omega}{2}\coth\left(\dfrac{\beta\hbar\omega}{2}\right)\dfrac{\tilde{\zeta}'_{\mathrm{cl}}(\omega)}{\mu}$
Quantum solute	$\dfrac{2}{\beta\hbar\omega}\tanh\left(\dfrac{\beta\hbar\omega}{2}\right)\dfrac{\tilde{\zeta}'_{\mathrm{cl}}(\omega)}{\mu}$	$\dfrac{\tilde{\zeta}'_{\mathrm{cl}}(\omega)}{\mu}$

For a molecular solvent, the rate of relaxation has been expressed formally in terms of a kernel $\zeta_{\mathrm{cl}}(t)$ which depends on the detailed intermolecular and intramolecular interactions between the solute and solvent. When the solvent is classical, $\tilde{\zeta}'_{\mathrm{cl}}(\omega)$ can be determined by a transform of the classical fluctuating forces on the solute vibration,[10,27–30]

$$\tilde{\zeta}'_{\mathrm{cl}}(\omega)=\beta\int_0^\infty dt\,\cos(\omega t)\langle\delta F(t)\,\delta F(0)\rangle_{\mathrm{cl}}. \tag{48}$$

In such simulations the solute vibrational mode is held fixed at its equilibrium position while the fluctuating forces are autocorrelated. An alternate method is to allow the solute to vibrate and to obtain $\langle\dot{q}(t)\dot{q}(0)\rangle_{\mathrm{cl}}$, which may be inverted to give $\zeta_{\mathrm{cl}}(t)$.[36] The parameter ζ defined by others[27–29,31] corresponds to $2k_BT\tilde{\zeta}'_{\mathrm{cl}}(\omega)$ in our notation. One can view Eq. (48) as essentially extracting the density of normal modes in the solvent at the frequency ω. This normal mode picture is actually implicit in the perturbation theory that has been employed, since the bath terms are only included to second order. Thus, one can construct an effective harmonic Hamiltonian which, when treated classically, produces the same results for $\zeta_{\mathrm{cl}}(t)$ and $\tilde{\zeta}_{\mathrm{cl}}(i\omega)$ as are obtained from the actual molecular solvent. Furthermore, when the harmonic bath is treated quantum mechanically, $\tilde{\zeta}'_{\mathrm{qm}}(\omega)$ is related to $\tilde{\zeta}'_{\mathrm{cl}}(\omega)$ through Eq. (44). Therefore, assuming linear response, the vibrational transition rates $k^{\mathrm{qm}}_{n-1\leftarrow n}$ and the energy relaxation time T_1 for a quantum solute with frequency ω in a quantum solvent can be obtained using $\tilde{\zeta}'_{\mathrm{cl}}(\omega)$ from the corresponding classical solvent and the relations in Tables I and II.

The possibility of using $\tilde{\zeta}'_{\mathrm{cl}}(\omega)$ from a classical simulation to estimate $\tilde{\zeta}'_{\mathrm{qm}}(\omega)$ for the corresponding quantum mechanical system has been discussed by Berne in the general context of time correlation functions.[16] In related applications to electron transfer reaction rates, it has been shown how spectral densities can be extracted from classical simulations[37] and used to accurately predict the response of corresponding quantum solvents.[38]

We now reanalyze relaxation rates which have been recently reported for a variety of molecular models. Wilson, Whitnell, and Hynes (WWH) investigated the vibrational relaxation of the C–Cl stretch in a model of $\mathrm{CH_3Cl}$ in water. Treating all the modes classically, they obtained relaxation rates in two ways. First, using nonequilibrium molecular dynamics, energy was placed in the C–Cl stretch instantaneously and the decay of energy was fit to the form $\exp(-t/T_1)$. In a second set of simulations, the C–Cl bond was held fixed at its equilibrium position and the autocorrelation function $\langle\delta F(0)\,\delta F(t)\rangle_{\mathrm{cl}}$ of the fluctuating forces on the bond was averaged. The relaxation time T_1 was estimated using Eq. (46) and a frequency of 676 cm^{-1} for the bond.

WWH found that both methods gave similar results, $T_1 \approx 4.7$ ps. The good agreement between nonequilibrium simulations and classical perturbation theory indicates that the relaxation is in the linear response regime. If the solute vibrational mode and the solvent were both quantized, we would predict that there would be little change to T_1.

It is possible that linear response would be violated for a sufficiently large excitation of the C–Cl bond, since it is treated as a Morse potential in the simulation. Tuckerman and Berne have detected the effects of the anharmonicity of the Morse potential in their simulations of the vibrational relaxation of a highly excited Morse oscillator.[10] The excitation energies which were used by WWH were not large enough to sample the anharmonic tail of the potential, however, and anharmonic effects were not important in their simulations.

Figueirido and Levy (FL) have studied the relaxation of a quantum C–Cl stretch in a model of CH_3Cl in water,[29] similar to the model used by WWH. The fluctuating forces on the C–Cl bond were Fourier analyzed at the C–Cl stretch frequency of 673 cm^{-1} to give $\tilde{\zeta}'_{\text{cl}}(\omega)$. The imaginary part of the transform, $\tilde{\zeta}''_{\text{cl}}(\omega)$, was set to zero. The real part, $\tilde{\zeta}'_{\text{cl}}(\omega)$, was used in a Bloch–Redfield propagation of the density matrix for the C–Cl vibrational mode. Neglecting the imaginary part of the transform corresponds to neglecting solvent-induced frequency shifts. Population relaxation is dominated by the real part of the transform, which to some extent justifies the omission of the imaginary part of the transform.

The type of perturbation theory used by FL, in which the correlation function from a classical simulation is used directly, corresponds to treating the bath classically and the solute quantum mechanically. Under this mixed treatment of solute and solvent, FL predict a relaxation time of $T_1 \approx 10$ ps for the C–Cl stretch. The same time is predicted whether or not the off-diagonal density matrix elements are included in the calculation. If the molecular solvent can be considered to be an effective harmonic bath, then a consistent quantum mechanical treatment of both the solvent and the solute decreases the relaxation time to 5.7 ps. This is the same T_1 as predicted using classical perturbation theory and the value of $\tilde{\zeta}'_{\text{cl}}(\omega)$ reported by FL.

Classical, nonequilibrium simulations analogous to those of WWH were also performed by FL. From these simulations of excited C–Cl stretches, the relaxation time for the classical solute vibrational mode in a classical solvent was found to be about 4 ps, rather than the value 5.7 ps which would be predicted by classical linear response theory. The disagreement between the nonequilibrium classical simulations and the classical perturbation theory might be due to anharmonicities in the C–Cl Morse potential. These anharmonicities would be expected to decrease the relaxation time in nonequilibrium molecular dynamics relative to the decay of equilibrium fluctuations in the energy, which is the same direction as the FL results. However, since these anharmonicities did not seem to be important for WWH, it is not clear that they are solely responsible for the difference in the rate obtained by FL using direct nonequilibrium molecular dynamics and the rate predicted by classical perturbation theory. It is also possible that the anharmonic nature of the molecular solvent is contributing to the difference between the value of T_1 calculated from perturbation theory and the actual T_1 observed in the nonequilibrium simulations. It should be noted, however, that simulation studies of vibrational relaxation in a Lennard-Jones fluid have indicated that a harmonic bath can serve as a good representation of the solvent.[10]

There is also a small difference between the results of FL from classical nonequilibrium simulations and the nonequilibrium simulation results of WWH, 4 ps vs 4.7 ps for T_1. This difference is most likely due to small differences in the molecular models which were used by each.

The effects of quantizing the bath modes are quite considerable when the quantum solute mode is a very high frequency vibration, such as a proton stretch. The Si–H stretching mode on the H/Si(111)1×1 surface was recently studied by Gai and Voth (GV).[30] The experimentally determined lifetime for the $\nu=1$ state is about 0.95 ns.[39,40] From their simulation data, GV obtained $\tilde{\zeta}'_{\text{cl}}(\omega)$ for use with Bloch–Redfield theory. The imaginary part of the transform, $\tilde{\zeta}''_{\text{cl}}(\omega)$, was neglected in their implementation of the Bloch–Redfield equations, just as was done by FL. GV find a lifetime of 1.7±0.1 ns for the Si–H stretch, almost twice the experimental lifetime. Based on the frequency of this stretch, 2084 cm^{-1}, we predict that quantizing the bath modes in the simulation model of the Si surface would reduce the Si–H lifetime to about 0.34 ns, one-third of the experimentally observed lifetime. This substantial difference in the predicted relaxation rate is important to consider when using data such as relaxation times to optimize the parameters of a specific molecular model. We further note that the harmonic treatment of the substrate modes and their couplings to the Si–H stretch on which our predictions are based might not be entirely appropriate, since GV have suggested that the important couplings are highly nonlinear.

Bruehl and Hynes (BH) have recently studied relaxation times for various stretching modes in a model of an AH···B hydrogen bonding complex in a CH_3Cl-like solvent.[31] Holding the atoms of the hydrogen-bonded complex fixed, they allowed the solvent molecules to fluctuate and autocorrelated the fluctuating forces acting on various stretching modes of the AH···B complex. The lifetime for each of the modes, estimated as the inverse of the rate for the $\nu=1$ to $\nu=0$ transition for each mode, was calculated using the data from classical simulations. The lifetime for the symmetric (AH)–B stretch was reported as 0.04 to 0.14 ps for a symmetric-stretch frequency range of 100 to 300 cm^{-1}. The frequency is low because this mode involves motion of the heavy A and B particles. Quantizing the solvent modes would not produce a substantial change in the lifetime of the $\nu=1$ state for this low frequency mode. The next higher frequency mode considered was the doubly degenerate AHB bending mode. A lifetime of 2–35 ps was estimated for bend frequencies in the range 1000–1700 cm^{-1}. If the solvent can be treated as effectively harmonic, quantizing the solvent modes should decrease the lifetime of this mode to the range 0.8–8.4 ps, a factor of 2.5 decrease in the lifetimes at the lower frequencies to a factor of 4 at the high end of the frequency range. Even more dramatic are the changes to the relaxation times for the AH proton stretch. Assuming a frequency range of 2500–3500 cm^{-1} for this mode, BH calculated lifetimes ranging from 4–44 ns for the $\nu=1$ to $\nu=0$ transition. We find that with a quantized solvent, the corresponding lifetimes are 0.7–5.2 ns, a decrease in the lifetime by factors of 6 to 9 relative to a classical solvent.

IV. CONCLUSION

We have provided a theoretic framework for extracting relaxation times for quantum solutes in quantum solvents from classical simulation data. Using an effective harmonic Hamiltonian, we find that T_1 for a classical solute-classical solvent is exactly the same as T_1 for a quantum solute-quantum solvent, and is faster than T_1 for a quantum solute-classical solvent by a factor of $(\hbar\omega/2k_BT)\coth(\hbar\omega/2k_BT)$. This factor can represent an order of magnitude enhancement to a relaxation rate. We also find, again for a harmonic model, that T_2, the frequency shift, and indeed the entire absorption line shape, are also the same classically and quantum mechanically. Even when anharmonicities are present, quantum and classical perturbation theory predictions for T_1 and T_2 can still be identical. Our results suggest the strong possibility that a purely classical study of vibrational energy relaxation might provide an accurate representation of important aspects of the relaxation dynamics of a fully quantum mechanical system.

ACKNOWLEDGMENTS

We thank Professor R. A. Friesner and Dr. W. T. Pollard for helpful discussions. This research was supported by a grant from the National Science Foundation (NSF CHE-91-22-506).

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