

Vibrational energy relaxation in the condensed phases: Quantum vs classical bath for multiphonon processes

S. A. Egorov and B. J. Berne

Department of Chemistry, Columbia University, New York, New York 10027

(Received 20 May 1997; accepted 22 July 1997)

We develop a theory for relating quantum and classical time correlation functions in the context of vibrational energy relaxation. The treatment is based on the assumption that both the quantum and the classical systems are characterized by effective harmonic Hamiltonians with identical normal modes; and the solute-solvent interaction is taken to be linear in the solute vibrational coordinate, but nonlinear in the bath coordinates. We propose an approximate “quantum correction” which allows the determination of the quantum energy relaxation rates from the classical force-force time correlation functions in the limit of large solute’s vibrational frequency. We test the accuracy of this approximate correction against exact numerical results for two forms of the solute-solvent interaction (exponential and power law), and find it to be accurate for a wide range of solute vibrational frequencies and for different solvent thermodynamic states. A simple form of the “quantum correction” is proposed for the models based on Lennard-Jones interactions. In all cases it is found that the vibrational relaxation time in a fully quantum system is better approximated by a fully classical theory (classical oscillator in classical bath) than by a mixed quantum-classical theory (quantum oscillator in classical bath). © 1997 American Institute of Physics.
[S0021-9606(97)51540-6]

I. INTRODUCTION

Numerous processes in condensed phases involve dissipation of energy from vibrationally excited modes. A profound understanding of this phenomenon is of major importance for developing a theory of reaction dynamics. As such, vibrational energy relaxation (VER) has been actively studied experimentally,^{1–30} and the results have been reviewed on several occasions.^{31–39}

Experimental data on VER have been analyzed with various theoretical approaches.^{5,40–80} Most of these^{48–80} are based on the low-order perturbation theory, and involve partitioning the total Hamiltonian into three terms: the vibrational Hamiltonian for the excited mode of the solute (guest, impurity), the Hamiltonian for all other degrees of freedom (solvent, host, bath), and the interaction between these two subsystems, which induces the transitions between the solute’s vibrational states. Within this formalism, the state-to-state transition rates, are determined by the Fourier transform (at the vibrational frequency of the solute) of the time correlation function (TCF) of the force exerted by the solvent on the solute’s vibrational mode. When studying VER in low-temperature solids, this TCF can be evaluated quantum mechanically. At the same time, a full quantum treatment of dynamics in liquid hosts is not feasible, and a common approach is to treat the translational degrees of freedom in liquids classically. However, for certain experimental conditions (e.g., vibrational relaxation of molecular oxygen in liquid mixtures with argon in the temperature range 60–90 K³) a classical treatment of the solvent may be questionable. In order to account for the quantum nature of the bath, one needs to relate the classical TCF to its quantum analogue. Once the potential energy in the Hamiltonian is specified, the classical and quantum TCFs (and their power spectra) are

uniquely defined. In general, however, it is not possible to find (in a closed analytical form) the exact relationship between the two, and various approximate prescriptions have been proposed in the literature for obtaining the quantum results from the classical ones.^{31,81–88} The first issue which needs to be addressed is related to the fact that the classical TCF is a real even function of time, while the one-sided quantum TCF is a complex function. The direct consequence of this is that the classical power spectrum is symmetric, while its quantum analogue satisfies the detailed balance condition, and is thus asymmetric. At the same time, one can relate the quantum power spectrum to the Fourier transform of the symmetrized quantum TCF, which shares the property of being a real even function of time with the classical TCF. This suggests comparing the classical TCF with the symmetrized quantum one in the time domain, which has been done in Ref. 85 for the one-dimensional rigid rotor. The two functions disagreed slightly at short times and very significantly at long times.⁸⁵ Nevertheless, if one simply replaces the symmetrized quantum TCF with the classical one, the resulting power spectrum will at least satisfy the detailed balance condition. Such an approach has been widely used in the context of vibrational energy relaxation,^{31,63,69} although it has been recognized that simply obtaining Boltzmann equilibrium is not a sufficient justification for the above replacement.^{68,80,89}

A different approach to relating quantum and classical TCFs was introduced by Schofield,⁸¹ and involves modifying the classical TCF in the time domain. Schofield⁸¹ suggested approximating the one-sided quantum mechanical TCF evaluated at time t by the classical TCF evaluated at $(t - i\beta\hbar/2)$. The resulting power spectrum satisfies detailed balance, but does not satisfy any moment sum rules. For the latter reason Egelstaff⁸² proposed an alternative approxima-

tion, where the argument t of the classical TCF is replaced by $[t(t - i\beta\hbar/2)]^{1/2}$. When the Egelstaff transformation is applied to the normalized classical TCF, the resulting function satisfies both the condition of detailed balance and the first few sum rules.⁸³ The accuracy of the Egelstaff approximation was tested in Ref. 85 for the one-dimensional rigid rotor; it was found to agree well with the exact quantum result at short times, but to disagree at longer times.⁸⁵ Later the Egelstaff transformation was modified in order to account for the change in the zero-time value of the (unnormalized) TCF in going from classical to quantum case.⁸⁸ Of course, one can equally well apply the aforementioned transformations in the time domain to approximate the symmetrized quantum TCF instead of the one-sided function.⁶⁸

To summarize, numerous prescriptions have been proposed for relating quantum and classical TCFs both in the time and in the frequency domains. However, due to approximations involved in these treatments, two different prescriptions may lead to two different predictions of the quantum power spectra, both of which satisfy the detailed balance requirement, but differ greatly from each other, especially in the high-frequency region.^{86,88} Furthermore, it may well be the case that neither of these spectra agrees with the true quantum result.

In view of that, it is of great importance to assess the accuracy of various approximations by studying exactly solvable models.^{90,91} In the context of vibrational energy relaxation, such a possibility is provided when the classical and quantum solvents are described by effective harmonic Hamiltonians with the same set of normal modes. If the solute-bath coupling is taken to be linear both in the solute and bath coordinates, one can obtain an exact relationship between the force-force TCF for a classical bath and its quantum counterpart.⁸⁹ However, due to the assumption of bilinear coupling, the applicability of this result is limited to single-phonon relaxation processes. At the same time, it is often the case that the excitation energy of the solute's vibrational mode is much larger than the typical energy associated with the solvent's thermal motion. In the absence of intra- and intermolecular vibration-vibration (excitonic) energy transfer, the nonradiative relaxation process is necessarily multiphonon, i.e., the solute's vibrational energy is dissipated into many quanta of bath excitations. In order to allow for multiphonon processes, one can either treat the bilinear system-bath coupling within high-order perturbation theory, or introduce a coupling which is more realistically nonlinear in the bath coordinates, while retaining the lowest-order Fermi's golden rule formalism. It was recently shown,⁹² that the latter mechanism generally gives the dominant contribution to the relaxation rate. For an arbitrary nonlinear system-bath coupling, it is not possible to derive an exact relationship between the classical and quantum TCFs. However, for sufficiently large solute vibrational energies (relative to the bath thermal energy scale) an approximate relation between the two can be obtained. In addition to that, for a given spectral density of the effective harmonic bath (which is the same for classical and quantum systems) one can obtain exact numerical results for both classical and quantum TCFs, which al-

lows us to assess the accuracy of this approximate relationship.

The purpose of this paper is to carry out the program outlined above. In Section II we consider a somewhat simplified model where the system-bath coupling is modeled with an exponential function of a scalar collective bath coordinate. In the asymptotic case of large solute's vibrational energy gap, we derive an approximate relation between the power spectra of quantum and classical TCFs, which leads to a relation between the energy relaxation rates for a classical solute in a classical bath and for a quantum solute in a quantum bath. Assuming a particular model for the bath spectral density, we calculate these relaxation rates exactly and test the accuracy of our approximate result. In Section III we perform similar calculations for a more realistic problem involving vibrational relaxation of a diatomic Lennard-Jones solute in monatomic Lennard-Jones fluid. We again obtain an approximate "correction factor" (which is somewhat different from the one obtained for the exponential interaction) and assess its accuracy by performing exact numerical calculations. In both cases (exponential and Lennard-Jones interactions) our approximation gives a very accurate estimate of the ratio between quantum and classical energy relaxation rates. We also test various prescriptions for relating quantum and classical TCFs which have been proposed earlier in the literature, and find that neither of these is robust enough to handle different functional forms of the system-bath coupling. In Section IV we conclude.

II. MODEL HAMILTONIAN: LINEAR AND EXPONENTIAL COUPLING

A. Model Hamiltonian: Linear coupling

We consider the relaxation rate of a vibrationally excited solute in a solvent. As discussed in the Introduction, we assume that the total Hamiltonian can be written as follows:

$$H = H_q + H_b + V. \quad (1)$$

In the above, H_q is the (harmonic) Hamiltonian associated with the solute's vibrational coordinate, q , whose conjugate momentum is p , reduced mass is μ , and angular frequency is ω_0

$$H_q = \frac{p^2}{2\mu} + \frac{\mu\omega_0^2 q^2}{2}. \quad (2)$$

The bath Hamiltonian H_b describes the solvent molecules and all the remaining (apart from q) degrees of freedom of the solute. In what follows, we take H_b to be harmonic and write it as a sum over normal modes with frequencies ω_k and Boson creation and annihilation operators b_k^\dagger and b_k

$$H_b = \sum_k \hbar\omega_k (b_k^\dagger b_k + 1/2). \quad (3)$$

Finally, the interaction term V , which couples the solute's vibrational mode to the bath, is taken to be linear in q : $V = -q\gamma F$, where γF is the force exerted by the solvent on the

vibrational coordinate, the coupling constant γ has units of force, and F is a dimensionless function of the bath normal coordinates.

Using the golden rule lowest-order perturbation theory, one can express⁸⁹ the solute vibrational energy relaxation rate in terms of the Fourier transform of the symmetrized quantum force-force time correlation function (TCF) evaluated at the solute vibrational frequency

$$\left(\frac{1}{T_1}\right)_{qm} = \frac{\tanh(\beta\hbar\omega_0/2)}{\beta\hbar\omega_0/2} \frac{\bar{\zeta}'_{qm}(\omega_0)}{\mu} \quad (4)$$

with

$$\begin{aligned} \bar{\zeta}'_{qm}(\omega_0) &= \beta\gamma^2 \int_0^\infty dt \cos(\omega_0 t) \\ &\times \left\langle \frac{1}{2} [\delta F(t), \delta F(0)]_+ \right\rangle_{qm}, \end{aligned} \quad (5)$$

where $\delta F(t) = F(t) - \langle F \rangle_{qm}$, $\langle \cdots \rangle_{qm} = \text{Tr}_b[\cdots \rho_b]$ denotes a trace over the quantum bath states, $\rho_b = e^{-\beta H_b} / \text{Tr}_b[e^{-\beta H_b}]$ is the equilibrium bath density matrix, and $\beta = 1/k_B T$.

The calculation of the quantum TCF is feasible for low-temperature solids, but is extremely difficult in liquids. In the latter case, a common approach is to obtain the TCF for a corresponding classical system — either from molecular dynamics simulations or from analytical theories. One is then faced with a problem of relating the classical TCF to its quantum counterpart, and various prescriptions have been suggested for this procedure in the literature.^{31,81–88} For the Hamiltonian described above, this problem has been considered by Bader and Berne⁸⁹ for the particular case of bilinear solute-solvent coupling, i.e., the force exerted by the solvent on the solute vibrational coordinate was written as a linear function of the bath dimensionless collective coordinate Q

$$F = Q = \sqrt{\hbar} \sum_k c_k (b_k^\dagger + b_k), \quad (6)$$

where c_k are real expansion coefficients. Provided the classical and quantum systems are described by identical effective harmonic Hamiltonians, they are characterized by the same spectral density

$$J(\omega) = \sum_k c_k^2 \delta(\omega - \omega_k). \quad (7)$$

From Eqs. (4), (5), (6) and (7), one obtains

$$\left(\frac{1}{T_1}\right)_{qm} = \frac{\pi\gamma^2}{\mu\omega_0} J(\omega_0). \quad (8)$$

The above result does not depend on \hbar , and therefore the energy relaxation rate for a quantum solute in a quantum bath is identical to the relaxation rate for a classical solute in a classical solvent, as discussed in Ref. 89. This result is valid for the bilinear system-bath coupling, which corresponds to single phonon relaxation processes. We next consider the case when the coupling between the solute vibra-

tional coordinate and the solvent is nonlinear in the bath coordinates, i.e., allow for multiphonon processes.

B. Exponential coupling

We model the solute-solvent interaction with an exponential function of the bath collective coordinate: $F = \exp(Q)$. With the above form of the system-bath coupling, the thermal averaging over the bath states in Eq. (5) can be performed using standard boson algebra operator identities,^{93,94} and the integral in Eq. (5) can be evaluated approximately using saddle point method⁹³ to yield

$$\begin{aligned} \bar{\zeta}'_{qm}(\omega_0) &= \frac{\beta\gamma^2}{2} \exp(C_{qm}(0)) \sqrt{\frac{2\pi}{\omega_0\omega_{ph}}} \cosh \\ &\times (\beta\hbar\omega_0/2) \exp\left(-\frac{\omega_0}{\omega_{ph}} [\ln(2\phi_{qm}) - 1]\right), \end{aligned} \quad (9)$$

with

$$\phi_{qm} = \frac{\omega_0}{\lambda\hbar\omega_{ph}} \sinh(\beta\hbar\omega_{ph}/2), \quad (10)$$

and

$$C_{qm}(0) = \hbar \int_0^\infty d\omega J(\omega)(2n(\omega) + 1), \quad (11)$$

where $n(\omega) = [\exp(\hbar\omega/kT) - 1]^{-1}$ is the phonon thermal occupation number. In the above we have defined an ‘‘average’’ phonon frequency according to the relation

$$\omega_{ph} = \frac{1}{\lambda} \int_0^\infty d\omega \omega J(\omega); \quad \lambda = \int_0^\infty d\omega J(\omega). \quad (12)$$

Taking the limit $\hbar \rightarrow 0$ in Eq. (9) gives the following expression for the classical friction:

$$\begin{aligned} \bar{\zeta}'_{cl}(\omega_0) &= \frac{\beta\gamma^2}{2} \exp(C_{cl}(0)) \sqrt{\frac{2\pi}{\omega_0\omega_{ph}}} \\ &\times \exp\left(-\frac{\omega_0}{\omega_{ph}} [\ln(2\phi_{cl}) - 1]\right), \end{aligned} \quad (13)$$

with

$$\phi_{cl} = \frac{\beta\omega_0}{2\lambda}, \quad (14)$$

and

$$C_{cl}(0) = \frac{2}{\beta} \int_0^\infty d\omega \frac{J(\omega)}{\omega}. \quad (15)$$

From Eqs. (4), (9), (13) and the relation $(T_1^{-1})_{cl} = \bar{\zeta}'_{cl}(\omega_0)/\mu$ it follows that energy relaxation rate T_1^{-1} for a quantum solute in a quantum bath is no longer equal to its classical counterpart; their ratio is given by

$$R_1 = \frac{(T_1^{-1})_{qm}}{(T_1^{-1})_{cl}} = \frac{\exp(C_{qm}(0))}{\exp(C_{cl}(0))} \frac{\sinh(\beta\hbar\omega_0/2)}{\beta\hbar\omega_0/2} \times \left(\frac{\beta\hbar\omega_{ph}}{2 \sinh(\beta\hbar\omega_{ph}/2)} \right)^{\omega_0/\omega_{ph}}. \quad (16)$$

C. Numerical results for the exponential coupling

Certain approximations (mean value theorem, saddle point method) have been involved in arriving at the Eq. (16). In order to assess their accuracy, we now assume a particular functional form for the spectral density $J(\omega)$ and evaluate the quantum and classical energy relaxation rates exactly (numerically). Although the main goal of the present work is to relate classical and quantum TCF in liquids, we defer the discussion of the form for $J(\omega)$ appropriate for liquid hosts until the next section where we consider vibrational relaxation of a Lennard-Jones solute in a Lennard-Jones fluid. In the present section, for the purpose of testing the result in Eq. (16), we consider the following super-Ohmic spectral density:

$$J(\omega) = 2\lambda \alpha^2 \omega^3 \exp(-\alpha\omega^2), \quad (17)$$

which behaves as the Debye model coupled with the deformation potential approximation (for numerical convenience we have replaced a sharp cut-off at the Debye frequency with a smooth Gaussian cut-off). This form for $J(\omega)$ would be appropriate in studying vibrational relaxation by acoustic phonons in a crystalline host.

Anticipating the study of LJ fluid in the next section, we define dimensionless time and frequency variables in terms of the LJ parameters of Ar and the mass of Ar atom: $t^* = t(\epsilon_{Ar}/m_{Ar}\sigma_{Ar}^2)^{1/2}$ and $\omega^* = \omega(m_{Ar}\sigma_{Ar}^2/\epsilon_{Ar})^{1/2}$. With the values⁹⁵ $\epsilon_{Ar}/k_B = 119.8$ K, $\sigma_{Ar} = 3.405$ Å, and $m_{Ar} = 6.634 \times 10^{-23}$ g, $\omega^* = 1$ corresponds to $\omega/2\pi c = 2.46$ cm⁻¹.

In performing the calculations, we take $\alpha^* = 2.5 \times 10^{-3}$. From Eq. (12), this gives the average phonon frequency $\omega_{ph}/2\pi c = 65.4$ cm⁻¹. The temperature is taken to be $T = 75$ K, i.e., comparable to a characteristic phonon frequency. We set the dimensionless normalization constant $\lambda\hbar$ equal to unity, and take $\gamma = \epsilon_{Ar}/\sigma_{Ar}$ and $\mu = m_{Ar}$.

With the above parameters, we calculate the energy relaxation rate T_1^{-1} for a quantum solute in a quantum bath and for a classical solute in a classical bath as a function of the solute vibrational frequency ω_0 ; the corresponding results are shown in Fig. 1. One sees that in the contrast to the case of linear coupling, where the fully quantum and the fully classical results are identical, in the case of exponential solute-bath interaction, the fully classical treatment underestimates the relaxation rate. Also shown in Fig. 1 is the ‘‘corrected’’ classical approximation given by $(T_1^{-1})_{cl} \times R_1$ with R_1 calculated from Eq. (16). This ‘‘corrected’’ classical approximation follows the quantum result quite closely for a wide range of the ‘‘energy gaps’’ ω_0 , thus confirming that the approximations involved in arriving at Eq. (16) are reasonable. Finally, we plot in Fig. 1 the energy relaxation rate for a quantum solute in a classical bath calculated by multiplying the fully classical rate by the factor

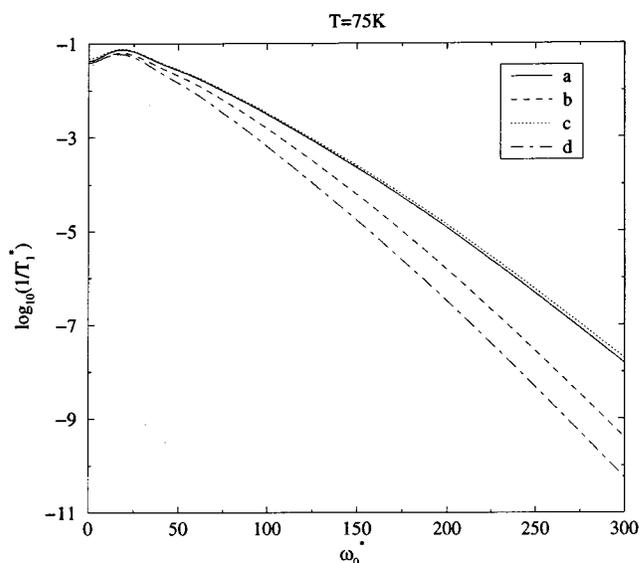


FIG. 1. $\log_{10}(1/T_1^*)$ vs ω^* for the exponential solute-solvent interaction. The solid line (a) is the fully quantum result, the dashed line (b) is the fully classical result, and the dotted line (c) is the classical result corrected according to the approximation from Eq. (16). The dash-dotted line (d) is for a quantum solute in a classical solvent.

$\tanh(\beta\hbar\omega_0/2)/(\beta\hbar\omega_0/2)$. This factor is less than unity for any frequency ω_0 , which suggests that the fully classical treatment gives consistently better results for the rates than the ‘‘mixed’’ one (although the former rates still need to be corrected to get agreement with the quantum rates).

It would be of some interest to analyze the nature of the three factors in R_1 . The first factor is independent of the energy gap ω_0 , it depends only on the temperature and the spectral density. For $k_B T \gg \hbar\omega_{ph}$, $C_{qm}(0) \approx C_{cl}(0)$ and the first factor in R_1 is close to unity. The second factor coincides with the Schofield transformation⁸¹ when the latter is combined with the symmetrization of the quantum TCF. This factor has the strongest dependence on ω_0 of all three; it approaches 1 only for $k_B T \gg \hbar\omega_0$. At the same time, a more typical situation in high-order relaxation processes corresponds to $\hbar\omega_{ph} \leq k_B T \leq \hbar\omega_0$, in which case the second factor in R_1 is much greater than unity. Finally, the third factor is always less than 1, for $k_B T \sim \hbar\omega_{ph}$ it displays a weak (albeit exponential) decrease with the energy gap; for $k_B T \gg \hbar\omega_{ph}$ it remains on the order of 1 for all physically realistic values of ω_0 .

It is also of interest to compare the results obtained with the correction factor R_1 [cf. Eq. (16)] to other approximations suggested in the literature. For this purpose, we apply the Schofield,⁸¹ the Egelstaff,⁸² and the ‘‘scaled’’ Egelstaff⁸⁸ transformations to our classical results. The Schofield approximation has been discussed above, it amounts to replacing R_1 with $\sinh(\beta\hbar\omega_0/2)/(\beta\hbar\omega_0/2)$. The Egelstaff procedure⁸² can be obtained as a product of two transformations.⁸³ One first replaces the argument t of the classical TCF with $[t^2 - (\beta\hbar/2)^2]^{1/2}$, and then performs the Schofield transformation on the resulting function. The ‘‘scaled’’ Egelstaff transformation⁸⁸ is the same as the Egel-

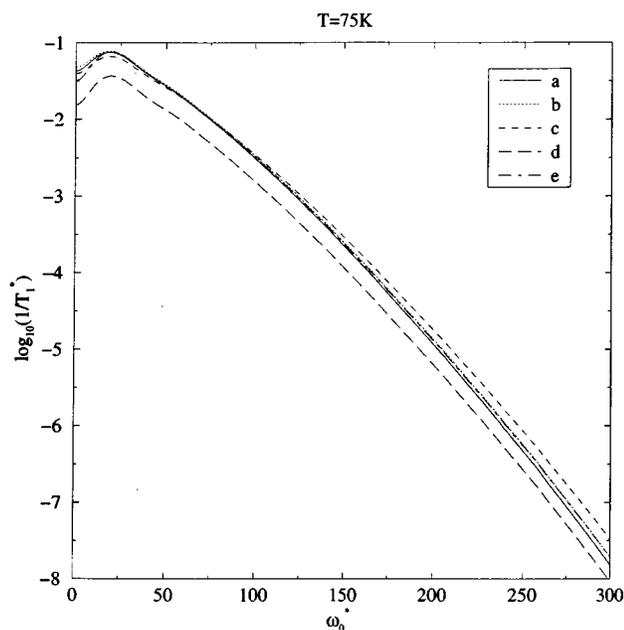


FIG. 2. $\log_{10}(1/T_1^*)$ vs ω^* for the exponential solute-solvent interaction. The solid line (a) is the fully quantum result, the dotted line (b) is the classical result corrected according to the approximation from Eq. (16). The dashed line (c) is the Schofield approximation, the long-dashed line (d) is the Egelstaff approximation, and the dash-dotted line (e) is the “scaled” Egelstaff approximation, as described in the text.

staff transformation⁸² except for the rescaling of the classical TCF by the following factor: $\langle \delta F^2 \rangle_{cl} / \langle \delta F(\beta\hbar/\sqrt{2}) \delta F(0) \rangle_{cl}$.

The results of applying these three procedures to the classical VER rates are shown in Fig. 2 together with the quantum result; also plotted are the rates obtained with the approximate correction R_1 . One sees that the Schofield transformation overestimates the quantum correction somewhat (especially at the higher frequencies), the Egelstaff approximation gives the rates which are too low, and the “scaled” Egelstaff procedure is generally as accurate as the approximate correction given by the factor R_1 . We defer the discussion of these results until the next section, where we perform a similar analysis for a force-force TCF with another functional form of the force, namely, inverse power law type interaction.

We close this section by noting that similar calculations have been performed for a wide range of temperatures and parameters $\lambda\hbar$ and α^* ; the “quantum correction” given by R_1 was found to be consistently accurate for all values of parameters tested.

III. VIBRATIONAL RELAXATION FOR LENNARD-JONES COUPLING BETWEEN SOLUTE AND SOLVENT

In this section, we discuss the relation between the quantum and the classical TCF for the problem of vibrational relaxation of a Lennard-Jones solute (a solute molecule whose sites interact through the Lennard-Jones potential with

the solvent atoms) in a Lennard-Jones host (a solvent whose molecules interact through the Lennard-Jones potential). Although we focus on the Lennard-Jones potential here, it is important to note that the same procedure can be used for an arbitrary continuous form of the solute-solvent interaction. To simplify the analysis, we consider a single diatomic solute immersed in a monatomic solvent, and assume that the diatomic interacts with the solvent particles with a spherically symmetric pair potential, and that its vibrational coordinate also has spherical symmetry. Such a “breathing sphere” model has been used to study vibrational relaxation of diatomic molecules both in crystalline⁸⁰ and liquid⁷⁹ Lennard-Jones hosts. In crystalline hosts, the total microscopic Hamiltonian for the system can be easily reduced to the form of Eq. (1) by treating the crystalline lattice in the harmonic approximation. In liquid hosts, on the other hand, the Hamiltonian for the translational degrees of freedom of the solvent and the solute is anharmonic. Thus, for liquids one is usually confined to a classical treatment of the translational degrees of freedom in calculating of the TCF. The results obtained in this way have to be corrected by accounting for the quantum nature of the solvent.

The relation between $\tilde{\zeta}'_{qm}(\omega_0)$ and $\tilde{\zeta}'_{cl}(\omega_0)$ obtained in the previous section was based on the assumption that both quantum and classical systems are described by identical effective harmonic Hamiltonians. Thus, to obtain a similar relation for a Lennard-Jones fluid, one needs to map this system onto an effective harmonic bath. We achieve this by introducing an effective quantum harmonic Hamiltonian for the translational degrees of freedom of the solute and the solvent, and by requiring that in the classical limit this Hamiltonian reproduces the results for the LJ fluid obtained from the classical MD simulations.

Starting from a microscopic Hamiltonian for a single diatomic in a monatomic fluid and assuming pairwise interactions, we follow the procedure outlined in Ref. 80 to reduce it to the following form:

$$H = H_q + H_b + V. \quad (18)$$

The solute vibrational Hamiltonian H_q is given by Eq. (2). H_b is the quantum-mechanical Hamiltonian for the translational degrees of freedom of the solute and all solvent particles (the bath)

$$H_b = T + U_0, \quad (19)$$

with

$$T = \frac{p_0^2}{2m_0} + \sum_i \frac{p_i^2}{2m_s}, \quad (20)$$

$$U_0 = \sum_i \phi(r_i) + \sum_{i < j} \phi_s(r_{ij}). \quad (21)$$

T is the total translational kinetic energy of the solute and solvent atoms; the solute has momentum \mathbf{p}_0 and mass m_0 , the summation indices refer to solvent atoms, and the i th solvent atom has momentum \mathbf{p}_i and mass m_s . The potential energy U_0 involves the solute-solvent pair potential $\phi(r)$,

which is independent of q , and the solvent-solvent pair potential $\phi_s(r)$; r_i is the distance between the i th solvent atom and the center of mass of the diatomic, r_{ij} is the distance between the i th and j th solvent atoms.

In the spirit of the lattice theories of liquids^{96,97} we represent the medium by a harmonic lattice, which amounts to replacing H_b by an effective harmonic Hamiltonian. As a first approximation, we will assume that the diatomic's mass is sufficiently close to that of the solvent atoms, and that the solute-solvent interaction is sufficiently similar to the solvent-solvent interactions. Therefore, as far as the phonons are concerned, we take $m_0 = m_s$ and $\phi(r) = \phi_s(r)$, and introduce normal modes in the usual fashion⁹⁸

$$H_b = \sum_{\mathbf{k}l} \hbar \omega_{\mathbf{k}l} \left(b_{\mathbf{k}l}^\dagger b_{\mathbf{k}l} + \frac{1}{2} \right), \quad (22)$$

where $b_{\mathbf{k}l}$ and $b_{\mathbf{k}l}^\dagger$ are the phonon annihilation and creation operators, the sum over wave vector \mathbf{k} is restricted to the first Brillouin zone, the summation index l runs over the three acoustic phonon polarization branches, and $\omega_{\mathbf{k}l}$ is the phonon frequency.

As before, the coupling term has the form $V = -q\gamma F$, but in contrast to the previous Section, the total (dimensionless) force F exerted by the solvent on the solute vibrational coordinate q is explicitly written as a sum of forces from all solvent atoms, thus avoiding the "collective coordinate" assumption:

$$F = \sum_i f(r_i). \quad (23)$$

We now write $r_i = |\mathbf{r}_i + \mathbf{u}_{i0}|$, where the vector \mathbf{r}_i is the equilibrium position of the i th host atom in the effective harmonic lattice relative to the diatomic, and $\mathbf{u}_{i0} = \mathbf{u}_i - \mathbf{u}_0$ is the difference of the displacements of the two atoms from equilibrium due to the lattice vibrations. Expanding the function $f(r_i)$ in a Taylor series around \mathbf{r}_i and following the procedure outlined in Ref. 79, one obtains the following result for the symmetrized quantum force-force TCF:

$$G_{qm}(t) = \left\langle \frac{1}{2} [\delta F(t), \delta F(0)]_+ \right\rangle_{qm} = \frac{1}{2} \sum_{ij} \sum_{k=1}^{\infty} \sum_{l=0}^{\infty} \sum_{m=0}^{\infty} \frac{(r_i)^{2l+k} (r_j)^{2m+k} (C_{qm}(t)^k + C_{qm}^*(t)^k)}{k!l!m!} \left[\frac{C(0)}{2} \right]^{l+m} \\ \times (\hat{r}_i^{\circ} \hat{r}_j^{\circ})^k \left[\frac{d^k}{dr_i^k} \frac{1}{r_i} \frac{d^{2l}}{dr_i^{2l}} r_i f(r_i) \right] \Bigg|_{r_i=r_i^{\circ}} \left[\frac{d^k}{dr_j^k} \frac{1}{r_j} \frac{d^{2m}}{dr_j^{2m}} r_j f(r_j) \right] \Bigg|_{r_j=r_j^{\circ}}, \quad (24)$$

with

$$C_{qm}(t) = \hbar \int_0^{\infty} d\omega J(\omega) \{ (n(\omega) + 1) \exp(-i\omega t) + n(\omega) \exp(+i\omega t) \}, \quad (25)$$

and $C_{qm}(0)$ given by Eq. (11). For the reasons that will become clear below, we focus on the normalized quantum TCF given by

$$\bar{G}_{qm}(t) = \frac{G_{qm}(t)}{G_{qm}(0)}. \quad (26)$$

In the case of Lennard-Jones potentials the solute-solvent interaction is sufficiently short-ranged, and the summation over the solvent atoms in Eq. (24) can be restricted to nearest neighbors only. In lattice theories of liquids one usually allows for a possibility of vacant lattice sites, and employs some kind of a smearing procedure in order to smooth out the details of the arrangement of the solvent particles around the solute.⁹⁹ We account for both these effects by introducing an "average" number of nearest neighbors \bar{Z} and by keeping only diagonal terms in the sum over the solvent atoms. We assume (see below) an inverse power law for the force on the solute vibrational coordinate

$$f(r) = \Phi r^{-p}. \quad (27)$$

In this case the derivatives in Eq. (24) can be evaluated, and we find that

$$\bar{G}_{qm}(t) = \left(\frac{1}{2} \sum_{k=1}^{k_{\max}} (C_{qm}(t)^k + C_{qm}^*(t)^k) \frac{S_{qm}(k,p)}{k!} \right) / \left(\sum_{k=1}^{k_{\max}} C_{qm}(0)^k \frac{S_{qm}(k,p)}{k!} \right), \quad (28)$$

with

$$S_{qm}(k,p) = \left[\sum_{l=0}^{l_{\max}} \left(\frac{C_{qm}(0)}{2} \right)^l \frac{\Gamma(p+2l+k)}{\Gamma(l+1)\Gamma(p-1)(p+2l-1)} \right]^2, \quad (29)$$

where $\Gamma(n) = (n-1)!$. Note that this result for the normalized TCF does not depend on the parameters r° (the nearest neighbor separation) and \bar{Z} (average number of nearest neighbors). As discussed in Ref. 79, the upper limits on the k and l summations have been set to k_{\max} and l_{\max} , respectively. In fact, if these were taken to be ∞ , both sums would diverge no matter how small $C_{qm}(0)$ is, which ultimately results from the singularity of $f(r)$ at the origin. In practice,

however, for $C_{qm}(0) \ll 1$ the summand decreases with increasing k and l , and becomes essentially zero over a wide range of k and l . At this point one can simply truncate the sums, obtaining a well-defined result for the TCF (and avoiding the unphysical divergence).

From Eqs. (5), (24) and (28), the quantum friction can be written as

$$\begin{aligned} \tilde{\zeta}'_{qm}(\omega_0) &= \beta \gamma^2 G_{qm}(0) \int_0^\infty dt \cos(\omega_0 t) \bar{G}_{qm}(t) \\ &= \sum_{k=1}^{k_{\max}} W_k^{qm}(\omega_0), \end{aligned} \quad (30)$$

with

$$\begin{aligned} W_k^{qm}(\omega_0) &= \beta \gamma^2 \bar{Z} \Phi^2 \frac{S_{qm}(k, p)}{2k!(r^\circ)^{2p}} \int_0^\infty dt \cos(\omega_0 t) [C_{qm}(t)]^k \\ &\quad + C_{qm}^*(t)^k. \end{aligned} \quad (31)$$

As shown in Ref. 94, for a given (and sufficiently large) ω_0 the dominant contribution to $\tilde{\zeta}'_{qm}(\omega_0)$ comes from the term $W_{\bar{k}}^{qm}$ with $\bar{k} \approx \omega_0/\omega_{ph}$, and to a good approximation is given by

$$\begin{aligned} \tilde{\zeta}'_{qm}(\omega_0) &\approx \beta \gamma^2 \bar{Z} \Phi^2 \frac{S_{qm}(\bar{k}, p) \hbar^{\bar{k}}}{2\bar{k}!(r^\circ)^{2p}} [(n(\omega_0/\bar{k}) + 1)^{\bar{k}} \\ &\quad + n(\omega_0/\bar{k})^{\bar{k}}] \int_0^\infty dt \cos(\omega_0 t) \\ &\quad \times \left[\int_0^\infty d\omega J(\omega) \exp(-i\omega t) \right]^{\bar{k}}. \end{aligned} \quad (32)$$

We now consider a classical harmonic lattice characterized by the same spectral density $J(\omega)$ as its quantum analogue introduced above. The corresponding normalized classical force-force TCF is given by

$$\begin{aligned} \bar{G}_{cl}(t) &= \frac{G_{cl}(t)}{G_{cl}(0)} = \frac{\langle \delta F(t) \delta F(0) \rangle_{cl}}{\langle \delta F^2 \rangle_{cl}} \\ &= \left(\sum_{k=1}^{k_{\max}} C_{cl}(t)^k \frac{S_{cl}(k, p)}{k!} \right) / \\ &\quad \left(\sum_{k=1}^{k_{\max}} C_{cl}(0)^k \frac{S_{cl}(k, p)}{k!} \right), \end{aligned} \quad (33)$$

with

$$\begin{aligned} S_{cl}(k, p) &= \left[\sum_{l=0}^{l_{\max}} \left(\frac{C_{cl}(0)}{2} \right)^l \right. \\ &\quad \left. \times \frac{\Gamma(p+2l+k)}{\Gamma(l+1)\Gamma(p-1)(p+2l-1)} \right]^2, \end{aligned} \quad (34)$$

$$C_{cl}(t) = \frac{2}{\beta} \int_0^\infty d\omega \frac{J(\omega)}{\omega} \cos(\omega t), \quad (35)$$

and $C_{cl}(0)$ given by Eq. (15). The classical friction is given by

$$\tilde{\zeta}'_{cl}(\omega_0) = \beta \gamma^2 G_{cl}(0) \int_0^\infty dt \cos(\omega_0 t) \bar{G}_{cl}(t), \quad (36)$$

which is equivalent to the classical limit of Eq. (30). Hence, to obtain the corresponding approximate result, we take the classical limit directly in Eq. (32) to get

$$\begin{aligned} \tilde{\zeta}'_{cl}(\omega_0) &\approx \beta \gamma^2 \bar{Z} \Phi^2 \frac{S_{cl}(\bar{k}, p)}{\bar{k}!(r^\circ)^{2p}} \left(\frac{\bar{k}}{\beta \omega_0} \right)^{\bar{k}} \int_0^\infty dt \cos(\omega_0 t) \\ &\quad \times \left[\int_0^\infty d\omega J(\omega) e^{-i\omega t} \right]^{\bar{k}}. \end{aligned} \quad (37)$$

In Eqs. (32) and (37) \bar{k} has the meaning of the integer number closest to the ratio ω_0/ω_{ph} . In fact, to a good approximation,⁹² one can simply replace \bar{k} by this ratio. This yields the following result for the ratio R_2 of the quantum and classical energy relaxation rates:

$$\begin{aligned} R_2 &= \frac{(T_1^{-1})_{qm}}{(T_1^{-1})_{cl}} = \frac{S_{qm}(\omega_0/\omega_{ph}, p)}{S_{cl}(\omega_0/\omega_{ph}, p)} \frac{\sinh(\beta \hbar \omega_0/2)}{\beta \hbar \omega_0/2} \\ &\quad \times \left(\frac{\beta \hbar \omega_{ph}}{2 \sinh(\beta \hbar \omega_{ph}/2)} \right)^{\omega_0/\omega_{ph}}. \end{aligned} \quad (38)$$

Note that the second and the third factors in the above expression are identical with those in the formula for R_1 [Eq. (16)]. However, the first factor is no longer independent of the solute's vibrational frequency; in fact, we find below from the model calculations that it increases with ω_0 . Thus, our approximate result for the quantum correction in the case of the power law solute-solvent interaction has a different overall dependence on the "energy gap" as compared to the case of the exponential interaction.

In order to test the above result, we need to specify the spectral density $J(\omega)$. As discussed earlier, we choose a phenomenological form for $J(\omega)$, and adjust its parameters to obtain the best possible agreement between $\bar{G}_{cl}(t)$ calculated from Eq. (33) and the exact one obtained from the MD simulations. In fact, since we are mostly interested in the high-frequency Fourier components of the TCF, which determine the relaxation rates for high-order processes, we will perform the fit in the frequency domain, i.e., we fit $\hat{G}_{cl}(\omega_0) = \int_0^\infty dt \cos(\omega_0 t) \bar{G}_{cl}(t)$. We take the following simple two-parameter form for $J(\omega)$:

$$J(\omega) = \lambda \alpha \omega \exp\left(-\frac{\alpha \omega^2}{2}\right). \quad (39)$$

A similar (but slightly more complicated) form has been used by Singwi¹⁰⁰ to fit the spectrum of the velocity time autocorrelation function for Ar fluid.

The above form for the spectral density gives the following result for the Fourier transform of the normalized classical force-force TCF:

TABLE I. Solvent thermodynamic parameters and zero-time values of TCFs.

ρ^*	T^*	α^*	$\lambda\hbar$	$G_{cl}(0)$ from sim.
0.50	1.41	0.30×10^{-2}	0.12×10^{-2}	144 ± 2
0.85	1.41	0.26×10^{-2}	0.13×10^{-2}	382 ± 2
0.85	0.80	0.42×10^{-2}	0.99×10^{-3}	173 ± 1

$$\hat{G}_{cl}(\omega_0) = \sqrt{\frac{\pi\alpha}{2}} \frac{\sum_{k=1}^{k_{\max}} \frac{C_{cl}(0)^k}{\sqrt{k}k!} \exp\left(-\frac{\alpha\omega_0^2}{2k}\right) S_{cl}(k,p)}{\sum_{k=1}^{k_{\max}} \frac{C_{cl}(0)^k}{k!} S_{cl}(k,p)}, \quad (40)$$

with

$$C_{cl}(0) = \frac{\lambda}{\beta} \sqrt{2\pi\alpha}. \quad (41)$$

We now determine the parameters λ and α by fitting $\hat{G}_{cl}(\omega_0)$ given by Eq. (40) to the corresponding simulation results. The classical force-force TCFs and their Fourier transforms have been calculated from MD simulations in Ref. 80 for the model of a ‘‘breathing sphere’’ LJ solute in LJ fluid for a variety of thermodynamic conditions. The solute-solvent and solvent-solvent LJ potentials were taken to be the same

$$\phi(r) = \phi_s(r) = 4\epsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6 \right], \quad (42)$$

and the solute mass was set equal to the solvent mass: $m_0 = m_s$. Note that the same assumptions have been used in constructing the effective harmonic bath Hamiltonian in Eq. (22).

The ‘‘breathing sphere’’ model⁸⁰ gives the following expression for the force on the solute vibrational coordinate:

$$f(r) = -12 \left[2 \left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6 \right] \quad (43)$$

(we set the coupling constant γ equal to ϵ/σ). The high-frequency Fourier components of the force-force TCF are dominated by the r^{-12} term in $f(r)$, which gives a power law force of the form of Eq. (27), where $\Phi = -24\sigma^{12}$ and $p = 12$. It is worth emphasizing that the MD simulations have been performed with the full form of $f(r)$ given by Eq. (43). However, in constructing the effective harmonic Hamiltonian [i.e., in choosing the parameters for $J(\omega)$], we are only interested in reproducing the simulation results for $\hat{G}_{cl}(\omega_0)$, for which purpose it is sufficient to keep the simplified form of $f(r)$ from Eq. (27).

We now proceed to construct the spectral density by fitting the simulation data. We consider three points on the LJ phase diagram, for which the simulations have been performed in Ref. 80. The corresponding sets of thermodynamic parameters are listed in Table I, with dimensionless density and temperature defined according to $\rho^* = \rho\sigma^3$ and T^*

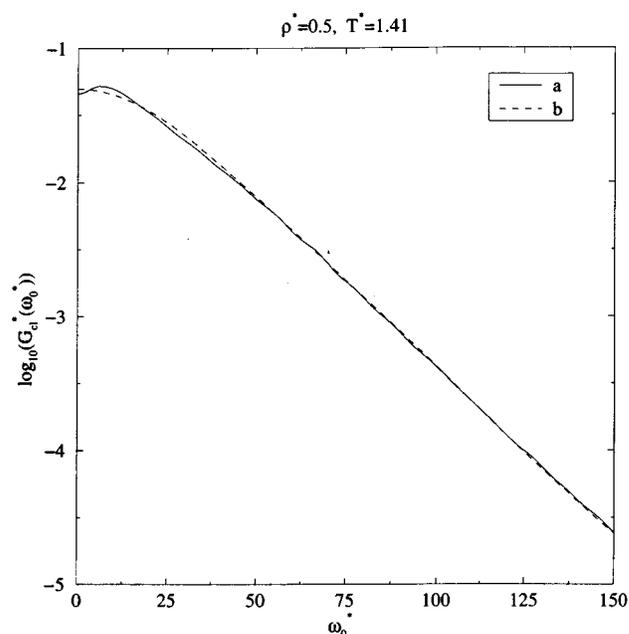


FIG. 3. $\log_{10}(\hat{G}_{cl}^*(\omega^*))$ vs ω^* . The solid line (a) is the simulation result, and the dashed line (b) is obtained from Eq. (40) with the best-fit parameters α^* and $\lambda\hbar$ listed in Table I. The solvent density and temperature are $\rho^* = 0.5$ and $T^* = 1.41$.

$= k_B T/\epsilon$. Due to the anharmonic nature of the LJ potential, the spectral density for an effective harmonic bath depends on the density and temperature of the solvent, and we perform a separate fit for each thermodynamic point. The values of the parameters α^* and $\lambda\hbar$ obtained by fitting the simulation results for $\hat{G}_{cl}(\omega_0)$ are listed in Table I. To illustrate the quality of the fit, we plot in Fig. 3 the $\hat{G}_{cl}(\omega_0)$ obtained from the simulation and calculated from Eq. (40) for the first thermodynamic point listed in Table I. The quality of the fit is satisfactory except for the low-frequency region. Thus, the spectral density given by Eq. (39) is suitable for reproducing the exact results for the TCFs in LJ fluid.

In addition to $J(\omega)$, the calculation of quantum and classical relaxation rates requires the knowledge of the zero-time values of the corresponding TCFs [see Eqs. (30) and (36)]. For the harmonic lattice model, these are given by

$$G_{qm}(0) = \frac{\bar{Z}\Phi^2}{(r^\circ)^{2p}} \sum_{k=1}^{k_{\max}} \frac{C_{qm}(0)^k}{k!} S_{qm}(k,p), \quad (44)$$

and

$$G_{cl}(0) = \frac{\bar{Z}\Phi^2}{(r^\circ)^{2p}} \sum_{k=1}^{k_{\max}} \frac{C_{cl}(0)^k}{k!} S_{cl}(k,p). \quad (45)$$

The above expressions contain two unknown parameters: r° and \bar{Z} . At the same time, $G_{cl}(0)$ can be calculated directly from the MD simulations; the corresponding values are listed in Table I. In calculating the relaxation rates, we will use the simulation results for $G_{cl}(0)$, and calculate $G_{qm}(0)$ according to

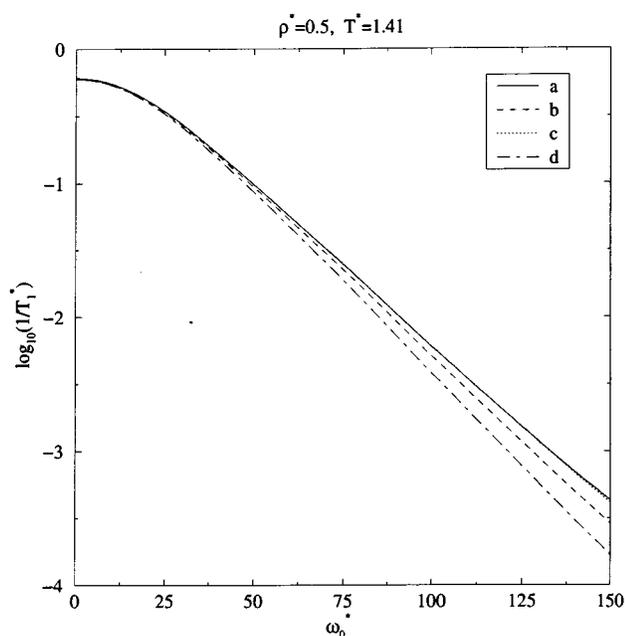


FIG. 4. $\log_{10}(1/T_1^*)$ vs ω_0^* for LJ solute in LJ solvent. The solid line (a) is the fully quantum result, the dashed line (b) is the fully classical result, and the dotted line (c) is the classical result corrected according to the approximation from Eq. (38). The dash-dotted line (d) is for a quantum solute in a classical solvent. The solvent density and temperature are $\rho^*=0.5$ and $T^*=1.41$.

$$G_{qm}(0) = G_{cl}(0) \frac{\sum_{k=1}^{k_{\max}} \frac{C_{qm}(0)^k}{k!} S_{qm}(k,p)}{\sum_{k=1}^{k_{\max}} \frac{C_{cl}(0)^k}{k!} S_{cl}(k,p)}, \quad (46)$$

thus avoiding the necessity to determine r° and \bar{Z} .

For each thermodynamic point listed in Table I, we calculate the fully quantum energy relaxation rates and the fully classical ones. All the integrations and summations are performed numerically, without involving any approximations except for truncating the summations in order to avoid unphysical divergences, as discussed above. In performing the calculations we take $\mu = m_{Ar}/4$. The results are shown in Figs. 4, 5, and 6. As in the case of the exponential interaction, the fully classical treatment underestimates the relaxation rates. Also shown are the “corrected” classical results given by $(T_1^{-1})_{cl} \times R_2$ with R_2 calculated from Eq. (38); they are in good agreement with the quantum rates. Finally, we plot the results of the “mixed” treatment (quantum solute in a classical bath) which, as expected, deviate more from the fully quantum rates than do the fully classical results.

As in the previous section, we now compare the results obtained with the correction factor R_2 to other transformations proposed in the literature, namely, the Schofield,⁸¹ the Egelstaff,⁸² and the “scaled” Egelstaff⁸⁸ procedures. The general trends are the same for all three thermodynamic points, and for the purpose of presenting the results we choose the first point listed in Table I. In Fig. 7 we plot the results of applying the three transformations listed above to-

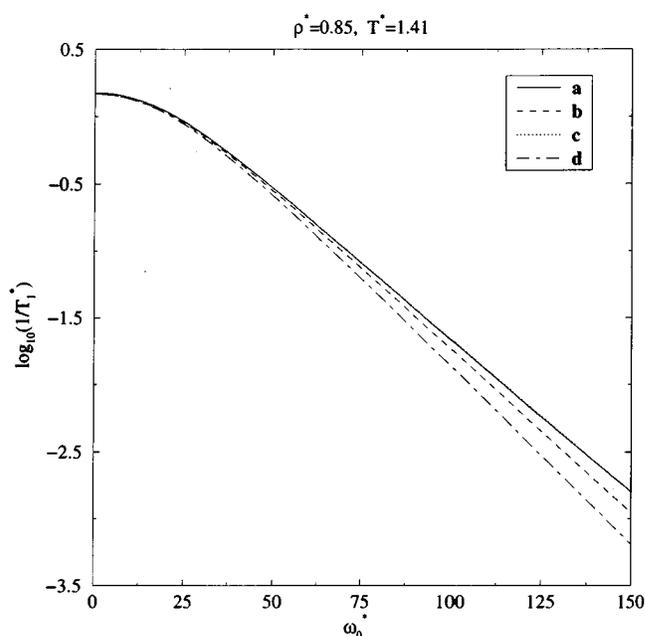


FIG. 5. Same as Fig. 4 but for $\rho^*=0.85$ and $T^*=1.41$.

gether with the fully quantum result and the classical result corrected by the factor R_2 . In contrast to the case of the exponential interaction, the Schofield approximation is clearly the best of the three, and is nearly as good as the presently proposed procedure (involving R_2). Both original and “scaled” Egelstaff transformations give incorrect exponents in the (apparently) exponential dependence of the rates on the energy gap ω_0 ; in the energy range considered, the

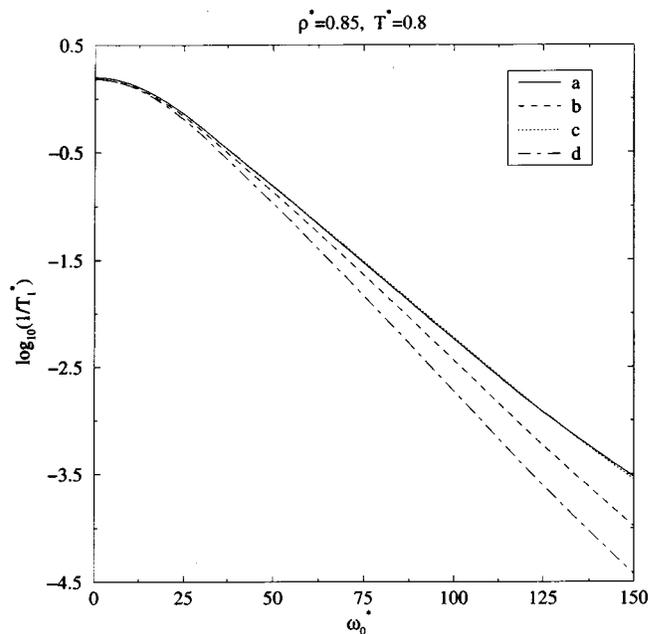


FIG. 6. Same as for Fig. 4 but for $\rho^*=0.85$ and $T^*=0.8$.

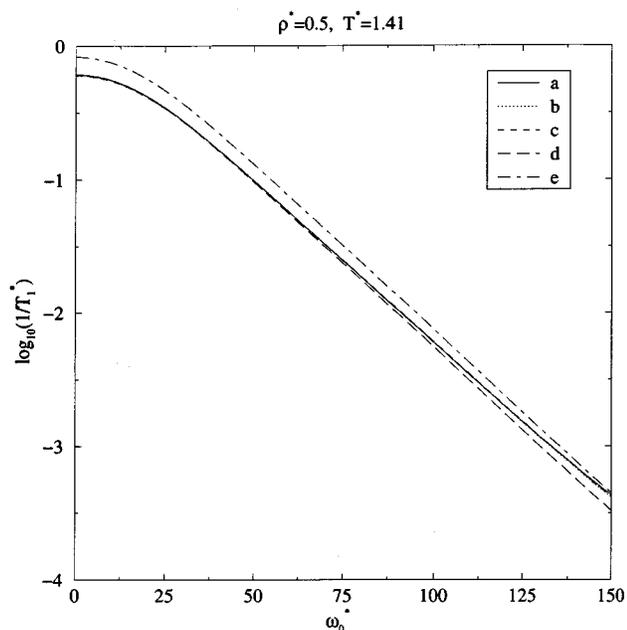


FIG. 7. $\log_{10}(1/T_1^*)$ vs ω_0^* for LJ solute in LJ solvent. The solid line (a) is the fully quantum result, the dotted line (b) is the classical result corrected according to the approximation from Eq. (38). The dashed line (c) is the Schofield approximation, the long-dashed line (d) is the Egelstaff approximation, and the dash-dotted line (e) is the “scaled” Egelstaff approximation, as described in the text. The solvent density and temperature are $\rho^* = 0.5$ and $T^* = 1.41$.

former underestimates, and the latter overestimates the quantum correction.

From the above results one can draw the following conclusions. For the present problem of relating the quantum force-force TCF to its classical analogue, the correction factor depends on the functional form of the solute-solvent interaction: The first factor in the expression for R_1 is different from the first factor in the expression for R_2 . Both corrections perform nearly equally well in their respective cases (although for the LJ interaction the agreement with the fully quantum result is somewhat better than in the case of the exponential interaction). At the same time, the approximate transformations previously proposed in the literature do not depend on the quantity for which the TCF is calculated, and thus cannot perform equally well for two different types of interactions. This is indeed observed: while for the exponential interaction the “scaled” Egelstaff approximation gives the best results of the three procedures, for the LJ interaction it happens to be the Schofield transformation which is the best of the three.

It is worth emphasizing that there is nothing profound in the fact that the Schofield approximation works so well for the LJ interaction, it is simply a consequence of fortuitous cancellation of the first and the third factors in the expression for R_2 . However, since this correction has a particularly simple form (it depends only on the temperature and the solute’s vibrational frequency, but does not depend on the spectral density of the bath), and performs well over a wide range of the solvent’s densities and temperatures, it would be reasonable to use this simple transformation in treating the

models based on LJ potentials. Strictly speaking, our result for R_2 from Eq. (38) has been obtained for a “breathing sphere” model of LJ diatomic. Its generalization to more realistic systems will be the subject of future investigations. At the same time, a microscopic theory of VER for a “breathing sphere” LJ diatomic in LJ monatomic solvent has been developed in Ref. 80; it was applied to analyze the experimental data¹³ on VER of molecular iodine in liquid xenon for a wide range of densities and temperatures. In view of this, it would be appropriate to check how the theoretical results obtained in Ref. 80 are affected by incorporating the approximate “quantum correction.” In the spirit of the above discussion, we use the simplified form of the correction factor (i.e., the one originally due to Schofield), which depends only on the solute vibrational frequency and on the solvent temperature, and does not depend on the solvent density. The theoretical results for VER rates of I_2 in Xe presented in Ref. 80 were obtained for a quantum solute in a classical solvent (see, however, Notes added in proof in Ref. 80). Therefore, the correction factor which has to be applied is equal to $\cosh(\beta\hbar\omega_0/2)$. The vibrational frequency of molecular iodine is $\omega_0/2\pi c = 214.6 \text{ cm}^{-1}$,¹⁰¹ and at the temperature $T = 280 \text{ K}$ (for which the density dependence of VER rates was measured) the correction factor is equal to 1.16. At the lowest experimental temperature ($T = 253 \text{ K}$) it is equal to 1.27, and at the highest temperature ($T = 323 \text{ K}$) it is equal to 1.12. Thus, applying the quantum correction and performing a new fit to the experimental data would result in a slightly smaller value of the adjustable parameter, which accounts for the non-spherical nature of molecular I_2 (see Ref. 80). It would also lead to a slightly less steep temperature dependence of the calculated rates. However, the changes will not be significant enough to noticeably affect the level of agreement with the experimental results, and will not change any conclusions reached in Ref. 80.

IV. CONCLUSION

In this paper we have considered the problem of relating quantum and classical time correlation functions in the context of vibrational energy relaxation in condensed phases. The treatment was based on the assumption that both quantum and classical systems are characterized by effective harmonic Hamiltonians with identical set of normal modes. The solute-solvent interaction was taken to be linear in the solute vibrational coordinate, but nonlinear in the bath coordinates, thereby allowing for high-order multiphonon relaxation processes. Thus, the present work extends the previous treatment of the same problem by Bader and Berne,⁸⁹ which was limited to the bilinear system-bath coupling, i.e., single-phonon processes. In that case,⁸⁹ an exact relationship between quantum and classical TCFs was obtained, and it was shown that the VER rates for a classical solute in a classical solvent and for a quantum solute in a quantum solvent are identical.

The situation is considerably different in the case of nonlinear system-bath coupling. First, it is only possible to obtain an approximate relationship between quantum and clas-

sical TCFs, which is valid in the limit of large solute's vibrational energy gap. Second, the fully quantum and fully classical VER rates are no longer identical, but can be related using the above approximate relationship. Having chosen a functional form for the bath spectral density, we have performed exact numerical calculations of the quantum and classical rates, and found that the accuracy of the approximate "quantum correction" is satisfactory. The calculations were performed for two forms of system-bath coupling: an exponential repulsion and a power law form. The latter case is applicable to studying vibrational relaxation of a "breathing sphere" LJ solute in LJ solvent. The accuracy of various "quantum corrections" previously proposed in the literature has also been tested; it was found that for the model based on Lennard-Jones interactions, a simple approximation due to Schofield provides an accurate estimate of the "quantum correction."

In all cases studied it was found that the fully classical VER rates, while being lower than the fully quantum ones, are higher than the "mixed" rates for a quantum solute in a classical solvent. Thus, in the absence of results for more realistic systems (i.e., beyond "breathing sphere") it would be more accurate to treat both the solute and the solvent classically, instead of employing a "mixed" model of a quantum solute in a classical bath.

- ¹A. Laubereau and W. Kaiser, *Rev. Mod. Phys.* **50**, 607 (1978).
- ²B. Faltermeyer, R. Protz, M. Maier, and E. Werner, *Chem. Phys. Lett.* **74**, 425 (1980).
- ³B. Faltermeyer, R. Protz, and M. Maier, *Chem. Phys.* **62**, 377 (1981).
- ⁴M. Chateau *et al.*, *J. Chem. Phys.* **71**, 4799 (1979).
- ⁵C. Delalande and G. M. Gale, *J. Chem. Phys.* **73**, 1918 (1980).
- ⁶P. Roussignol, C. Delalande, and G. M. Gale, *Chem. Phys.* **70**, 319 (1982).
- ⁷E. J. Heilweil, M. P. Casassa, R. R. Cavanagh, and J. C. Stephenson, *Chem. Phys. Lett.* **117**, 185 (1985).
- ⁸E. J. Heilweil, M. P. Casassa, R. R. Cavanagh, and J. C. Stephenson, *J. Chem. Phys.* **85**, 5004 (1986).
- ⁹E. J. Heilweil, F. E. Doany, R. Moore, and R. M. Hochstrasser, *J. Chem. Phys.* **76**, 5632 (1982).
- ¹⁰A. L. Harris, J. K. Brown, and C. B. Harris, *Annu. Rev. Phys. Chem.* **39**, 341 (1988).
- ¹¹M. E. Paige, D. J. Russell, and C. B. Harris, *J. Chem. Phys.* **85**, 3699 (1986).
- ¹²M. E. Paige and C. B. Harris, *J. Chem. Phys.* **93**, 3712 (1990).
- ¹³M. E. Paige and C. B. Harris, *Chem. Phys.* **149**, 37 (1990).
- ¹⁴A. Moustakas and E. Weitz, *J. Chem. Phys.* **98**, 6947 (1993).
- ¹⁵D. Zimdars *et al.*, *Phys. Rev. Lett.* **70**, 2718 (1993).
- ¹⁶A. Tokmakoff, B. Sauter, and M. D. Fayer, *J. Chem. Phys.* **100**, 9035 (1994).
- ¹⁷N. Pugliano, A. Z. Szarka, S. Gnanakaran, and R. M. Hochstrasser, *J. Chem. Phys.* **103**, 6498 (1995).
- ¹⁸W. F. Calaway and G. E. Ewing, *J. Chem. Phys.* **63**, 2842 (1975).
- ¹⁹S. R. J. Brueck and R. M. Osgood, *Chem. Phys. Lett.* **39**, 568 (1976).
- ²⁰D. A. V. Kliner, J. C. Alfano, and P. F. Barbara, *J. Chem. Phys.* **98**, 5375 (1993).
- ²¹J. C. Owrutsky *et al.*, *Chem. Phys. Lett.* **184**, 368 (1991).
- ²²L. E. Brus and V. E. Bondybey, in *Radiationless Transitions*, edited by S. H. Lin (Academic, New York, 1980).
- ²³H. Dubost, in *Inert Gases*, edited by M. Klein (Springer, Berlin, 1984).
- ²⁴H. Dubost, in *Chemistry and Physics of Matrix Isolated Species*, edited by L. Andrews and M. Moskovits (Elsevier, Amsterdam, 1989).
- ²⁵V. E. Bondybey, *J. Chem. Phys.* **65**, 5138 (1976).
- ²⁶V. E. Bondybey and A. Nitzan, *Phys. Rev. Lett.* **38**, 889 (1977).
- ²⁷J. Goodman and L. E. Brus, *J. Chem. Phys.* **69**, 1853 (1978).
- ²⁸L. Young and C. B. Moore, *J. Chem. Phys.* **81**, 3137 (1984).
- ²⁹D. Kuszner and N. Schwentner, *J. Chem. Phys.* **98**, 6965 (1993).
- ³⁰A. Salloum and H. Dubost, *Chem. Phys.* **189**, 179 (1994).
- ³¹D. Oxtoby, *Adv. Chem. Phys.* **47** (part 2), 487 (1981).
- ³²D. W. Oxtoby, *Annu. Rev. Phys. Chem.* **32**, 77 (1981).
- ³³D. W. Oxtoby, *J. Phys. Chem.* **87**, 3028 (1983).
- ³⁴J. Chesnoy and G. M. Gale, *Ann. Phys. Fr.* **9**, 893 (1984).
- ³⁵J. Chesnoy and G. M. Gale, *Adv. Chem. Phys.* **70** (part 2), 297 (1988).
- ³⁶T. Elsaesser and W. Kaiser, *Annu. Rev. Phys. Chem.* **42**, 803 (1991).
- ³⁷J. C. Owrutsky, D. Raftery, and R. M. Hochstrasser, *Annu. Rev. Phys. Chem.* **45**, 519 (1994).
- ³⁸C. B. Harris, D. E. Smith, and D. J. Russell, *Chem. Rev.* **90**, 481 (1990).
- ³⁹D. W. Miller and S. A. Adelman, *Int. Rev. Phys. Chem.* **13**, 359 (1994).
- ⁴⁰C. Delalande and G. M. Gale, *J. Chem. Phys.* **71**, 4804 (1979).
- ⁴¹W. M. Madigosky and T. A. Litovitz, *J. Chem. Phys.* **34**, 489 (1961).
- ⁴²P. S. Dardi and R. I. Cukier, *J. Chem. Phys.* **89**, 4145 (1988).
- ⁴³P. S. Dardi and R. I. Cukier, *J. Chem. Phys.* **95**, 98 (1991).
- ⁴⁴B. Khalil-Yahyavi and M. Châtelet, *J. Chem. Phys.* **92**, 2598 (1990).
- ⁴⁵B. Oksengorn, *Chem. Phys.* **140**, 233 (1990).
- ⁴⁶D. J. Russell and C. B. Harris, *Chem. Phys.* **183**, 325 (1994).
- ⁴⁷D. J. Nesbitt and J. T. Hynes, *J. Chem. Phys.* **77**, 2130 (1982).
- ⁴⁸A. Nitzan and J. Jortner, *Mol. Phys.* **25**, 713 (1973).
- ⁴⁹A. Nitzan, S. Mukamel, and J. Jortner, *J. Chem. Phys.* **60**, 3929 (1974).
- ⁵⁰A. Nitzan, S. Mukamel, and J. Jortner, *J. Chem. Phys.* **63**, 200 (1975).
- ⁵¹D. J. Diestler, *J. Chem. Phys.* **60**, 2692 (1974).
- ⁵²D. J. Diestler, in *Radiationless Processes in Molecules and Condensed Phases*, edited by F. K. Fong (Springer-Verlag, Berlin, 1976).
- ⁵³S. H. Lin, *J. Chem. Phys.* **61**, 3810 (1974).
- ⁵⁴S. H. Lin, H. P. Lin, and D. Knittel, *J. Chem. Phys.* **64**, 441 (1976).
- ⁵⁵*Radiationless Transitions*, edited by S. H. Lin (Academic, New York, 1980).
- ⁵⁶V. P. Sakun, *Soviet Phys. Solid State* **18**, 1470 (1976).
- ⁵⁷M. Berkowitz and R. B. Gerber, *Chem. Phys.* **37**, 369 (1979).
- ⁵⁸R. Zwanzig, *J. Chem. Phys.* **34**, 1931 (1961).
- ⁵⁹R. M. Whitnell, K. R. Wilson, and J. T. Hynes, *J. Phys. Chem.* **94**, 8625 (1990).
- ⁶⁰R. M. Whitnell, K. R. Wilson, and J. T. Hynes, *J. Chem. Phys.* **96**, 5354 (1992).
- ⁶¹I. Benjamin and R. M. Whitnell, *Chem. Phys. Lett.* **204**, 45 (1993).
- ⁶²B. P. Hills, *Mol. Phys.* **35**, 1471 (1978).
- ⁶³P. S. Dardi and R. I. Cukier, *J. Chem. Phys.* **86**, 2264 (1987).
- ⁶⁴P. S. Dardi and R. I. Cukier, *J. Chem. Phys.* **86**, 6893 (1987).
- ⁶⁵H. Metiu, D. W. Oxtoby, and K. F. Freed, *Phys. Rev. A* **15**, 361 (1977).
- ⁶⁶S. Velsko and D. W. Oxtoby, *J. Chem. Phys.* **72**, 2260 (1980).
- ⁶⁷B. Mishra and B. J. Berne, *J. Chem. Phys.* **103**, 1160 (1995).
- ⁶⁸J. Chesnoy and J. J. Weis, *J. Chem. Phys.* **84**, 5378 (1986).
- ⁶⁹F. E. Figueirido and R. M. Levy, *J. Chem. Phys.* **97**, 703 (1992).
- ⁷⁰P. Moore, A. Tokmakoff, T. Keyes, and M. D. Fayer, *J. Chem. Phys.* **103**, 3325 (1995).
- ⁷¹G. Goodyear, R. E. Larsen, and R. M. Stratt, *Phys. Rev. Lett.* **76**, 243 (1996).
- ⁷²V. M. Kenkre, A. Tokmakoff, and M. D. Fayer, *J. Chem. Phys.* **101**, 10618 (1994).
- ⁷³D. E. Smith and C. B. Harris, *J. Chem. Phys.* **92**, 1312 (1990).
- ⁷⁴M. Tuckerman and B. J. Berne, *J. Chem. Phys.* **98**, 7301 (1993).
- ⁷⁵J. S. Bader, B. J. Berne, E. Pollak, and P. Hänggi, *J. Chem. Phys.* **104**, 1111 (1996).
- ⁷⁶S. A. Adelman and R. H. Stote, *J. Chem. Phys.* **88**, 4397 (1988).
- ⁷⁷R. H. Stote and S. A. Adelman, *J. Chem. Phys.* **88**, 4415 (1988).
- ⁷⁸S. A. Adelman, R. Muralidhar, and R. H. Stote, *J. Chem. Phys.* **95**, 2738 (1991).
- ⁷⁹S. A. Egorov and J. L. Skinner, *J. Chem. Phys.* **106**, 1034 (1996).
- ⁸⁰S. A. Egorov and J. L. Skinner, *J. Chem. Phys.* **105**, 7047 (1996).
- ⁸¹P. Schofield, *Phys. Rev. Lett.* **4**, 39 (1960).
- ⁸²P. A. Egelstaff, *Adv. Phys.* **11**, 203 (1962).
- ⁸³B. J. Berne, J. Jortner, and R. Gordon, *J. Chem. Phys.* **47**, 1600 (1967).
- ⁸⁴Y. Guissani, S. Bratoz, and J.-C. Leicknam, *C. R. Acad. Sc. Paris* **269**, 137 (1969).
- ⁸⁵B. J. Berne, in *Physical Chemistry: An Advanced Treatise*, Vol. 8B, edited by D. Henderson (Academic, New York, 1971).
- ⁸⁶J. Borysow, M. Moraldi, and L. Frommhold, *Mol. Phys.* **56**, 913 (1985).
- ⁸⁷J. A. White, S. Velasco, A. C. Hernandez, and D. Luis, *Phys. Lett. A* **130**, 237 (1988).

- ⁸⁸L. Frommhold, *Collision-Induced Absorption in Gases* (Cambridge University Press, Cambridge, 1993).
- ⁸⁹J. S. Bader and B. J. Berne, *J. Chem. Phys.* **100**, 8359 (1994).
- ⁹⁰D. Rapp and T. Kassal, *Chem. Rev.* **69**, 61 (1969).
- ⁹¹A. G. Basile, C. G. Gray, B. G. Nickel, and J. D. Poll, *Mol. Phys.* **66**, 961 (1989).
- ⁹²S. A. Egorov and J. L. Skinner, *J. Chem. Phys.* **103**, 1533 (1995).
- ⁹³A. Nitzan, S. Mukamel, and J. Jortner, *J. Chem. Phys.* **60**, 3929 (1974).
- ⁹⁴S. A. Egorov and J. L. Skinner, *J. Chem. Phys.* **105**, 10153 (1996).
- ⁹⁵J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids* (Wiley, New York, 1954).
- ⁹⁶D. E. O'Reilly, *J. Chem. Phys.* **55**, 2876 (1971).
- ⁹⁷J. A. Barker, *Lattice Theories of the Liquid State* (Pergamon, New York, 1963).
- ⁹⁸A. A. Maradudin, in *Dynamical Properties of Solids*, Vol. 1, edited by G. K. Horton and A. A. Maradudin (NHPC, Amsterdam, 1974).
- ⁹⁹A. C. Hernandez, S. Velasco, and F. Mauricio, *J. Chem. Phys.* **86**, 4607 (1987).
- ¹⁰⁰K. S. Singwi, K. Skold, and M. P. Tosi, *Phys. Rev. A* **1**, 454 (1970).
- ¹⁰¹G. Herzberg, *Spectra of Diatomic Molecules*, 2nd ed. (Van Nostrand, Toronto, 1950).