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Quantum Dynamics and Vibrational Relaxation

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The accurate numerical calculation of general quantum time correlation functions for many-body systems is not possible at present. We discuss several schemes for obtaining approximate quantum time correlation functions using as input only the corresponding classical results, and assess the merits of each scheme by considering three exactly solvable model problems. We then turn to the problem of the vibrational energy relaxation of a high-frequency oscillator in a liquid, where the relaxation rate constant can be related to a certain quantum force−force time correlation function. Focusing specifically on the case of liquid oxygen, we calculate the classical force−force time correlation function using a molecular dynamics simulation and then determine various approximations to the relaxation rate constant by applying the schemes considered earlier. The Egelstaff scheme is found to lead to reasonable agreement with experiment.

I. Introduction

It is well-known that for condensed phase systems many experimental observables can be related theoretically to time correlation functions (TCFs) of appropriate dynamical variables. And in many cases it is essential that these TCFs be calculated quantum mechanically, since thermal energies can be small compared to the relevant energy splittings. While there is much interest, and has been much progress, in the numerical calculation of quantum TCFs for many-body interacting systems, a general, tractable, and reliable method is not yet at our disposal.

On the other hand, the calculation of classical TCFs for many-body interacting systems is commonplace, either by analytic methods or by molecular dynamics simulation. It would be very useful, therefore, if there was some reliable method by which one could obtain an approximate quantum TCF from its classical analogue. While a general solution to this problem seems unlikely, to say the least, several such approximation schemes have been discussed over the last 40 years.[1,2] One of the purposes of this paper is to examine critically these approximation schemes by considering three exactly solvable model problems.

The other purpose of this paper is to apply these various approximation schemes to a problem of current theoretical and experimental interest, namely, condensed phase vibrational energy relaxation.[3−6] A simple golden rule calculation shows that the state-to-state relaxation rate constant is related to the Fourier transform, at the oscillator frequency, of a certain quantum force−force TCF.[7] If $\hbar$ times the oscillator frequency is smaller than thermal energies, then it may be possible to approximate the quantum TCF simply by its classical analogue. If, however, the oscillator energy is much higher than thermal energies, the classical approximation is quite poor, and it becomes essential to use better approximations. As an example of this latter situation, we consider specifically the vibrational relaxation of neat liquid oxygen at 70 K.[8,9]

II. Exact and Approximate Quantum Dynamics

Consider the quantum TCF for a general non-Hermitian operator A:

$$G(t) = (\langle A(t)\, A^{\dagger}(0)\rangle + \langle A^{\dagger}(t)\mathrm{A}(0)\rangle)/2, \tag{1}$$

where the time dependence of any operator O is given by the Heisenberg expression

$$O(t) = \mathrm{e}^{iHt/\hbar} O \mathrm{e}^{-iHt/\hbar}, \tag{2}$$

H is the Hamiltonian of the system, and the ensemble average of operator O is

$$\langle O\rangle = \mathrm{Tr}[\mathrm{e}^{-\beta H} O]/\mathrm{Tr}[\mathrm{e}^{-\beta H}], \tag{3}$$

with $\beta = 1/kT$. This TCF is a complex function of t, but it is easy to show that it has the following time symmetries:[10]

$$G(-t) = G(t)^* = G(t - i\beta\hbar). \tag{4}$$

We will also be interested in the Fourier transform of the quantum TCF, defined by

$$\hat{G}(\omega) = \int_{-\infty}^{\infty} \mathrm{d}t\, \mathrm{e}^{i\omega t} G(t). \tag{5}$$

From the first of the time symmetries it follows that $\hat{G}(\omega)$ is real. It is also straightforward to show that $\hat{G}(\omega) \geq 0$. From the second time symmetry follows the detailed balance condition:[10]

$$\hat{G}(-\omega) = \mathrm{e}^{-\beta\hbar\omega}\, \hat{G}(\omega). \tag{6}$$

Decomposing $G(t)$ into its real and imaginary parts:

$$G(t) = G_{\mathrm{R}}(t) + i\, G_{\mathrm{I}}(t), \tag{7}$$

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one can define the Fourier transforms

$$\hat{G}_S(\omega) = \int_{-\infty}^{\infty} dt\, e^{i\omega t}\, G_R(t), \tag{8}$$

$$\hat{G}_A(\omega) = i \int_{-\infty}^{\infty} dt\, e^{i\omega t} G_I(t), \tag{9}$$

so that of course

$$\hat{G}(\omega) = \hat{G}_S(\omega) + \hat{G}_A(\omega). \tag{10}$$

Since $G_R(t)$ and $G_I(t)$ are both real and are symmetric and antisymmetric functions of t, respectively, it is straightforward to show that $\hat{G}_S(\omega)$ and $\hat{G}_A(\omega)$ are both real and are symmetric and antisymmetric functions of ω, respectively.

The detailed balance condition shows that $\hat{G}_S(\omega)$ and $\hat{G}_A(\omega)$ are not independent, but in fact are related by[1]

$$\hat{G}_A(\omega) = \hat{G}_S(\omega) \tanh(\beta\hbar\omega/2). \tag{11}$$

That means that $\hat{G}(\omega)$ can be related to either $\hat{G}_S(\omega)$ by

$$\hat{G}(\omega) = \frac{2}{1 + e^{-\beta\hbar\omega}}\, \hat{G}_S(\omega), \tag{12}$$

or to $\hat{G}_A(\omega)$ by

$$\hat{G}(\omega) = \frac{2}{1 - e^{-\beta\hbar\omega}}\, \hat{G}_A(\omega). \tag{13}$$

It is also clear that $G_R(t)$ and $G_I(t)$ are not independent; by expanding the hyperbolic tangent in eq 11 in powers of ω, performing the inverse Fourier transform term by term, and resumming, one sees that[11]

$$G_I(t) = \tan\left(\frac{\beta\hbar}{2}\frac{d}{dt}\right) G_R(t). \tag{14}$$

The classical limit is defined by $\hbar \to 0$, and so we can define $G_{cl}(t)$ by $G_{cl}(t) = \lim_{\hbar\to 0} G(t)$. From eq 14 it is clear that in the classical limit $G_I(t) \to 0$, and since $G_R(t)$ is a symmetric function of time, so is $G_{cl}(t)$ (as is well-known). Furthermore, one sees from taking the classical limit of eq 6 that $\hat{G}_{cl}(\omega) = \hat{G}_{cl}(-\omega)$. Of particular interest is some sort of semiclassical approximation to $G(t)$, which will be approximately valid when $\hbar \neq 0$, and which does satisfy detailed balance. Below we will discuss four such schemes; for an excellent general discussion of these schemes the reader is referred to the book by Frommhold.[1]

The first scheme, associated with the names of Litovitz,[12] Berne,[10] and Oxtoby,[7] which has also been discussed by Frommhold[1] (and probably by many others), and which we denote as the "standard" approximation, comes about as follows. In the classical limit by definition $G_R(t) = G_{cl}(t)$, and one can in fact expand $G_R(t)$ in powers of $\hbar^2$,[13] $G_{cl}(t)$ being the zeroth-order term. The standard approximation is equivalent to simply taking $G_R(t) \simeq G_{cl}(t)$, even when $\hbar \neq 0$, which at least ensures that $G_R(t)$ is a symmetric function of time. Defining

$$\hat{G}_{cl}(\omega) = \int_{-\infty}^{\infty} dt\, e^{i\omega t} G_{cl}(t), \tag{15}$$

eq 8 shows that within this approximation $\hat{G}_S(\omega) = \hat{G}_{cl}(\omega)$, and then one uses the exact equation 12 to determine $\hat{G}(\omega)$:

$$\hat{G}(\omega) = \frac{2}{1 + e^{-\beta\hbar\omega}}\, \hat{G}_{cl}(\omega). \tag{16}$$

As a result, $\hat{G}(\omega)$ does indeed satisfy detailed balance, and from it $G(t)$ can be obtained by inverse Fourier transformation.

The second approximation scheme, associated with the names of Wilson,[14] Frommhold,[1] and Berne,[15] which for reasons to become clear below we denote the "harmonic" approximation, can be obtained by expanding the tangent in eq 14 to lowest order in $\hbar$:

$$G_I(t) \simeq \frac{\beta\hbar}{2}\frac{d}{dt} G_R(t). \tag{17}$$

Next, expanding (as above) $G_R(t)$ in powers of $\hbar^2$ and keeping only the zeroth-order term yields

$$G_I(t) \simeq \frac{\beta\hbar}{2}\frac{d}{dt} G_{cl}(t). \tag{18}$$

Upon Fourier transformation we then obtain

$$\hat{G}_A(\omega) \simeq \frac{\beta\hbar\omega}{2}\, \hat{G}_{cl}(\omega). \tag{19}$$

Finally, one then uses the exact eq 13 to obtain the approximation

$$\hat{G}(\omega) = \frac{\beta\hbar\omega}{1 - e^{-\beta\hbar\omega}}\, \hat{G}_{cl}(\omega). \tag{20}$$

Note that within this approximation $\hat{G}(\omega)$ also satisfies detailed balance, but, for example, is distinctly different from the standard approximation in eq 16.

The third approximation scheme, originally due to Schofield,[16] can be obtained by combining ideas from the first two schemes (that is, to expand $G_R(t)$ to zeroth order in $\hbar$, and $G_I(t)$ to first order in $\hbar$), to arrive at the exact equation

$$G(t) = G_{cl}(t) + \frac{i\beta\hbar}{2}\frac{d}{dt} G_{cl}(t) + O(\hbar^2). \tag{21}$$

Now suppose that in fact $G(t) = G_{cl}(t + i\beta\hbar/2)$. Expansion to first order in $\hbar$ gives precisely the above equation, and furthermore this approximation satisfies the required time symmetries for $G(t)$, which means, for example, that detailed balance is obeyed. In the frequency domain one obtains

$$\hat{G}(\omega) = e^{\beta\hbar\omega/2}\hat{G}_{cl}(\omega). \tag{22}$$

This simple and seemingly attractive approximation, again distinctly different from the first two, is called the "Schofield" approximation.

The fourth scheme, first discussed by Egelstaff,[17] is closely related to the Schofield approximation. There is another form for $G(t)$ that also yields eq 21 when expanded to first order in $\hbar$, and also satisfies the required time symmetries, which is $G(t) = G_{cl}((t(t + i\beta\hbar))^{1/2})$. This, the "Egelstaff" approximation, in the frequency domain gives[18]

$$\hat{G}(\omega) = e^{\beta\hbar\omega/2} \int_{-\infty}^{\infty} dt\, e^{i\omega t}\, G_{cl}(\sqrt{t^2 + (\beta\hbar/2)^2}). \tag{23}$$

One feature common to the first three schemes is that $\hat{G}(0) = \hat{G}_{cl}(0)$ (see eqs 16, 20, and 22), a result that is sometimes, but not generally, correct. The Egelstaff scheme, on the other hand, does not lead to this equality. The first three schemes also all give $\hat{G}(\omega) \geq 0$ (which, as discussed earlier, is always true for the exact quantum TCF), since $\hat{G}_{cl}(\omega) \geq 0$ (for example, from the Wiener−Khintchine theorem) and the multiplicative correction factors in eqs 16, 20, and 22 are all positive. The

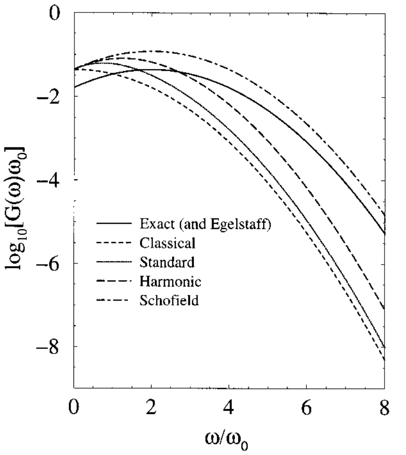

Figure 1. Exact and approximate $\hat{G}(\omega)$ for the free particle dynamic structure factor. $kT/\hbar\omega_0 = 1/2$.

Egelstaff scheme does not share this felicitous feature and can in fact sometimes lead to a negative $\hat{G}(\omega)$ (see below).

In summary, then, we have described four different semiclassical schemes for obtaining an approximation to the quantum TCF, each of which satisfies detailed balance, and each of which requires only the classical TCF as input. Our next step is to evaluate the merits and demerits of these four schemes by comparing results for three exactly solvable model problems.

III. Results for Exactly Solvable Model Problems

The first model involves the dynamic structure factor for a free particle in three dimensions. Thus $H = \vec{p}\cdot\vec{p}/2m$, where $\vec{p}$ is the momentum and m is the mass of the particle, and $A = e^{i\vec{k}\cdot\vec{r}}$, where $\vec{r}$ is the particle's position and $\vec{k}$ is a wave vector. $G(t)$ as defined in eq 1 is then

$$G(t) = (F_s(\vec{k},t) + F_s(-\vec{k},t))/2, \tag{24}$$

where $F_s(\vec{k},t)$ (the dynamic structure factor) is given by

$$F_s(\vec{k},t) = \langle e^{i\vec{k}\cdot\vec{r}(t)}\, e^{-i\vec{k}\cdot\vec{r}(0)}\rangle. \tag{25}$$

$G(t)$ can be calculated exactly, with the result that[19]

$$G(t) = e^{-\omega_0^2 t(t + i\beta\hbar)}, \tag{26}$$

where $\omega_0^2 = k^2/2\beta m$. The classical limit is of course $G_{cl}(t) = e^{-\omega_0^2 t^2}$. One notices immediately that since in this case $G(t) = G_{cl}((t(t + i\beta\hbar))^{1/2})$ the Egelstaff scheme is exact! (This fact has been appreciated for some time.[1])

In this work we will be particularly interested in the frequency-domain comparison of the various approximation schemes. To this end we note that for this free-particle problem one can obtain simple analytic results for both $\hat{G}(\omega)$ and $\hat{G}_{cl}(\omega)$.

In Figure 1 we compare the exact results for $\hat{G}(\omega)$, with the various approximations to $\hat{G}(\omega)$ discussed earlier, as well as with $\hat{G}_{cl}(\omega)$, for $kT/\hbar\omega_0 = 1/2$. One sees that in this case the Schofield scheme provides the best approximation to the exact result, differing from it by a constant factor. (Recall again that the Egelstaff scheme is exact in this case.) The harmonic and standard approximations (as well as the classical result) all fall off significantly too fast as frequency increases.

The next exactly solvable problem involves a collection of harmonic oscillators with Hamiltonian $H = \sum_k \hbar\omega_k(b_k^\dagger b_k + 1/2)$, where ω_k are the mode frequencies and $b_k^\dagger$ and b_k are the creation and annihilation operators. We next define a collective coordinate by $q = \sum_k c_k(b_k^\dagger + b_k)$ (c_k are real expansion coefficients), and the TCF $C(t)$ by $C(t) = \langle q(t)q(0)\rangle$. Now taking A in eq 1 to be q, in this case we have $G(t) = C(t)$. (In the third model problem, discussed below, $C(t)$ will be defined as above but $G(t)$ will be different.)

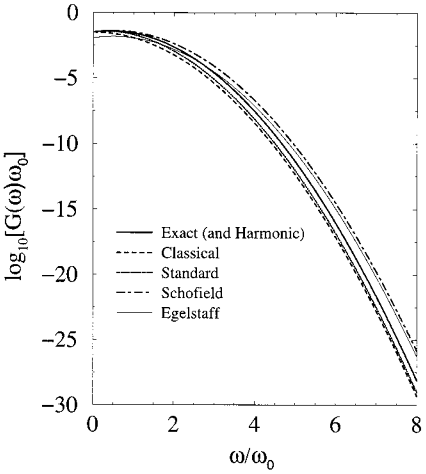

Figure 2. Exact and approximate $\hat{G}(\omega)$ for the harmonic/linear model. $kT/\hbar\omega_0 = 1/2$, $\lambda = 0.2$, and $\alpha = 1$.

The exact solution for $C(t)$ can be represented conveniently in terms of the spectral density $\Gamma(\omega) = \sum_k c_k^2\delta(\omega - \omega_k)$ and thermal occupation number $n(\omega) = (e^{\beta\hbar\omega} - 1)^{-1}$ by[2]

$$C(t) = \int_0^\infty d\omega\, \Gamma(\omega)([n(\omega) + 1]\, e^{-i\omega t} + n(\omega)\, e^{i\omega t}). \tag{27}$$

Note that the classical limit can be obtained easily from this expression to give

$$C_{cl}(t) = \frac{2}{\beta\hbar}\int_0^\infty d\omega\, \frac{\Gamma(\omega)}{\omega}\cos(\omega t). \tag{28}$$

(c_k are implicitly proportional to $\hbar^{1/2}$, and so $\Gamma(\omega)$ is implicitly proportional to $\hbar$.[2]) Note also that in this case these two equations lead to the exact equality

$$G_I(t) = \frac{\beta\hbar}{2}\frac{d}{dt}G_{cl}(t). \tag{29}$$

Recall that for a general TCF this equation is only correct to first order in $\hbar$, and so the previously discussed "harmonic" scheme derived from this equation is (in general) only an approximation. But since for this harmonic model this equation is exact, it means that the "harmonic" approximation scheme is exact for this model, hence the name.

To present explicit calculations for this model we must specify the form of the spectral density, for which we choose (see also Egorov and Berne[20]):

$$\Gamma(\omega) = 2\lambda\, \frac{\omega^\alpha}{\omega_0^{\alpha+1}}\, e^{-\omega^2/\omega_0^2}, \tag{30}$$

with α equal to 1 or 3. For either value of α, $\Gamma(\omega)$ is normalized according to

$$\int_0^\infty d\omega\, \Gamma(\omega) = \lambda. \tag{31}$$

In Figure 2 we show our calculations for $\hat{G}(\omega)$ for this model, taking $\alpha = 1$ ("Ohmic dissipation"), $\lambda = 0.2$, and $kT/\hbar\omega_0 = 1/2$. As in the previous case all results can be obtained

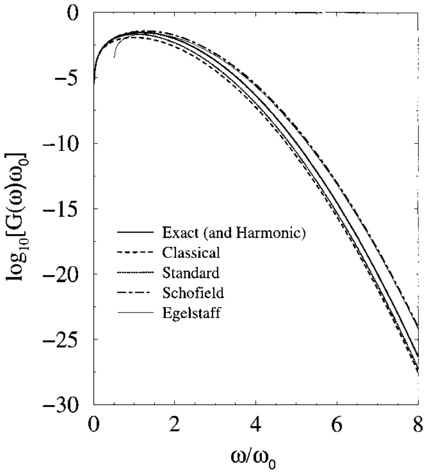

Figure 3. Exact and approximate $\hat{G}(\omega)$for the harmonic/linear model. $kT/\hbar\omega_0 = 1/2$, $\lambda = 0.2$, and $\alpha = 3$.

analytically. One sees that (except for small frequencies) both Schofield and Egelstaff overestimate the value of $\hat{G}(\omega)$, while the standard approximation (and the purely classical result) are underestimates. (Recall again that in this case the harmonic approximation is exact.) Note the scale on the ordinate! Even when the value of $\hat{G}(\omega)$ has decreased by 20 orders of magnitude, the worst approximation scheme is only off by 2 orders of magnitude.

In Figure 3 we show results for the same parameters except now $\alpha = 3$. As in the case for $\alpha = 1$ all approximate and exact results can be obtained analytically. The Egelstaff scheme actually goes negative for $\omega/\omega_0 < 1/2$! For higher frequencies the Schofield and Egelstaff approximations overestimate, and the standard and classical approximations underestimate, the exact (and harmonic) result. Note again, however, that none of the approximation schemes is too bad at high frequency, even when the value of $\hat{G}(\omega)$ has dropped dramatically.

Our final exactly solvable model is closely related to the above.[2] The Hamiltonian is harmonic (as above), and q is defined identically as above, but now $A = e^{q} - \langle e^{q}\rangle$. In this case the TCF is

$$G(t) = \langle e^{q(t)}\, e^{q(0)}\rangle - \langle e^{q}\rangle^2. \tag{32}$$

The exact solution to this TCF is given by[21]

$$G(t) = e^{C(0)}\, (e^{C(t)} - 1), \tag{33}$$

where $C(t)$ is given by eq 27. As before, the time domain results can all be obtained analytically, but now the Fourier transforms must be performed numerically.

Our numerical results for the same parameters as in Figure 2 are shown in Figure 4. One sees that for this model at high frequencies the different approximations are quite different. The Egelstaff result, while clearly an overestimate, is the closest to the exact result. Results for the same parameters as in Figure 3 are shown in Figure 5. In this case the Egelstaff result again becomes negative for low frequencies, while at high frequencies it is the best approximation.

To summarize this section, for the dynamic structure factor for the free particle the Egelstaff result is exact, and the Schofield result is off by a constant factor. The harmonic result can easily be off by several orders of magnitude, especially at high frequencies and low temperatures. For the harmonic model the harmonic result is exact, and the Egelstaff and other

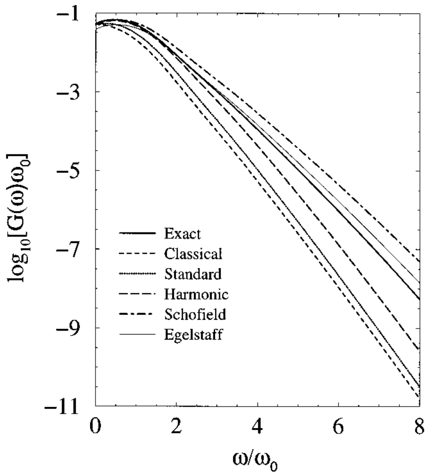

Figure 4. Exact and approximate $\hat{G}(\omega)$ for the harmonic/exponential model. $kT/\hbar\omega_0 = 1/2$, $\lambda = 0.2$, and $\alpha = 1$.

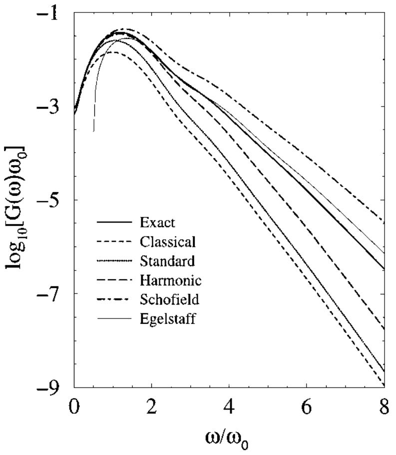

Figure 5. Exact and approximate $\hat{G}(\omega)$ for the harmonic/exponential model. $kT/\hbar\omega_0 = 1/2$, $\lambda = 0.2$, and $\alpha = 3$.

approximations can be off by several orders of magnitude. For the model involving an exponential function of harmonic coordinates, none of the approximation schemes is exact, but the Egelstaff approximation generally performs significantly better than the other schemes. The Egelstaff scheme does, however, suffer from the unfortunate drawback that it can lead to negative (unphysical) results at low frequencies.

So we clearly do not yet have a satisfactory solution to this problem. Indeed, it would not be reasonable to expect one of these simple schemes, involving only the classical TCF, to be able to reproduce the quantum TCF for all physical situations. Nonetheless, under certain circumstances, one or more of these schemes may provide reasonable approximations to the quantum TCF.

IV. Applications to Vibrational Relaxation in Liquid Oxygen

In this section we apply the ideas discussed above to the physical problem of vibrational energy relaxation (VER) in liquids. To be specific, consider the VER of neat liquid oxygen, for which experimental measurements of the vibrational state-to-state ($v = 1$ to $v = 0$) relaxation rate constant have been performed.[8] While vibration−vibration (excitonic) energy transfer is surely rampant in liquid oxygen, the experiments measure only the total population of the $v = 1$ state, independent of whether it has transferred from molecule to molecule during the course of the experiment. The relaxation mechanism must therefore be due solely to vibration−translation and vibration−rotation channels.[9]

The simplest way to approach this problem divides the Hamiltonian into system, bath, and interaction components. The system is the harmonic oscillator for a single oxygen molecule, the bath consists of the translations and rotations of all the oxygen molecules (including the "tagged" one), and the interaction involves the force exerted by the neighboring molecules on the bond of the tagged one. Within this picture the VER state-to-state rate constant can be calculated using Fermi's golden rule. Translated into the TCF language one finds that[9,22]

$$k_{1\to 0} = \frac{\hat{G}(\omega_0)}{2\mu\hbar\omega_0}, \tag{34}$$

where $G(t) = \langle \delta F(t)\delta F(0)\rangle$ is the quantum TCF of the force fluctuations on the tagged molecule's bond, and μ and ω_0 are the reduced mass and frequency of the oscillator. Such a quantum TCF, for say 500 interacting oxygen molecules, is not possible to calculate at present. And so in order to proceed one is forced to consider the approximation schemes discussed herein.

Of course, the big question is which (if any) of the approximation schemes is appropriate for this problem? There are several issues to consider. The first involves simply the ratio of the oscillator frequency (1552.5 cm^{-1} for oxygen) compared to kT (about 50 cm^{-1}) at 70 K. The large size of this ratio indicates that quantum effects are likely to be important (that is, the purely classical approximation to calculating $\hat{G}(\omega)$ will fail).

One way to think about the VER process in this system is similar to multiphonon relaxation in crystals.[23,24] That is, one considers the translations and rotations of the oxygen molecules in the liquid to be more or less harmonic, with characteristic frequencies on the order of 50 or 100 cm^{-1} (above which, for example, the Fourier transforms of the velocity or angular velocity TCFs decay considerably). Since the energy gap of the system is much larger than that, to emit one quantum of oxygen vibration one must create many quanta of translations and rotations.[9,20,22,25,26] This is possible since the force is a strongly nonlinear function of the (nearly) harmonic coordinates. This picture is reminiscent of the third model discussed in the previous section—that of a harmonic bath, but the TCF involves an exponential function of the coordinates. In that case for the high-frequency Fourier transform of the TCF we found that the Egelstaff approximation was the best, implying to us that it might also be the most appropriate approximation scheme for the oxygen problem.

An alternative picture is that, presumably because of central limit theorem arguments, the (classical) force on a given molecule describes a Gaussian random process. As such, this force can be thought of as a "coordinate" of an effective harmonic bath, which because of nonlinear couplings within the bath has a spectral density that extends well past the characteristic frequencies described in the preceding paragraph. In this view, then, the VER process corresponds to the creation of only one quantum of a very high frequency effective "mode" of the bath. This picture is equivalent to the purely harmonic model discussed in the previous section (the bath is harmonic and the TCF involves a linear function of the coordinates). To the extent that this scenario is valid, then, the harmonic approximation discussed above might be the most appropriate scheme for the oxygen problem. To assess the validity of this picture, one can consider, for example, a special case of the four-point TCF: $G^4_{\text{cl}}(t) = \langle \delta F(t)^2 \delta F(0)^2\rangle_{\text{cl}}$, which if the force is "Gaussian" should be equal to $\langle \delta F^2\rangle_{\text{cl}}{}^2 + 2G_{\text{cl}}(t)^2$.

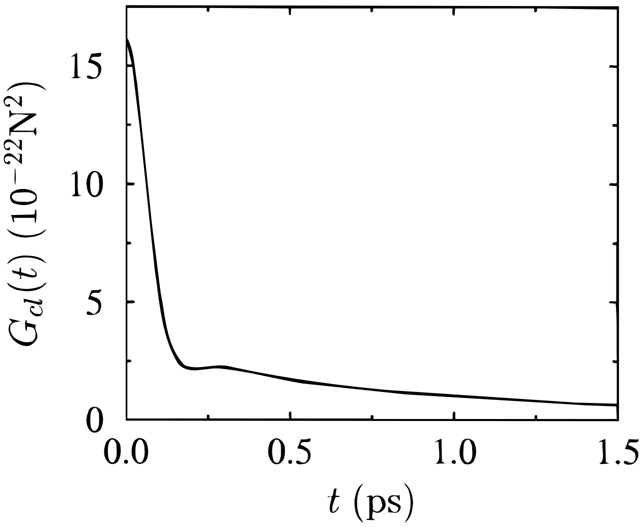

Figure 6. Classical force−force TCF for liquid oxygen at 70 K.

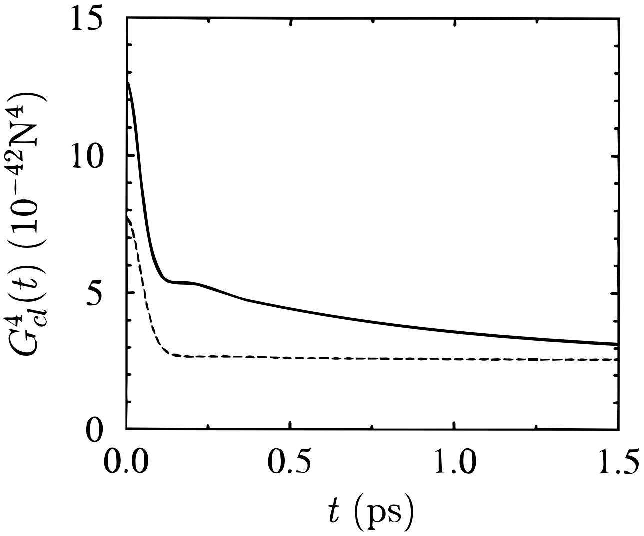

Figure 7. Comparison of $\langle \delta F(t)^2 \delta F(0)^2\rangle_{\text{cl}}$ (solid line) and $\langle \delta F^2\rangle_{\text{cl}}{}^2 + 2G_{\text{cl}}(t)^2$ (dashed line).

We have performed a classical molecular dynamics simulation of neat rigid oxygen at 70 K,[9,27] and from the simulation we have obtained the fluctuating force on the bond of a tagged oxygen molecule. Our result for $G_{\text{cl}}(t)$ is shown in Figure 6. In Figure 7 we show the comparison of the four-point TCF discussed above and its Gaussian decomposition. We see in fact that the force does not appear to be very Gaussian. This is really not surprising: since the intermolecular force is such a quickly varying function of distance, essentially only a few neighboring molecules contribute to the total force on a given molecule at any given time,[26] whereas for the central limit theorem to apply one needs many independent and roughly equal magnitude contributions. This observed non-Gaussian behavior of the fluctuating force would seem to indicate that the harmonic approximation scheme would not be appropriate for oxygen.

The Fourier transform of $G_{\text{cl}}(t)$ is shown in Figure 8. Also shown is the Egelstaff approximation to $\hat{G}(\omega)$, obtained from eq 23 numerically. It is seen that the Fourier transforms are only reliable up to about 500 or 600 cm^{-1}, whereas according to eq 34 they need to be evaluated at 1552.5 cm^{-1}. We have discussed several approaches toward extending the frequency

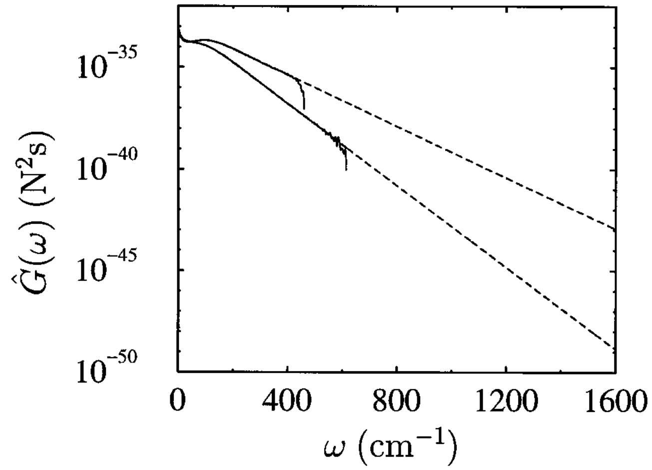

Figure 8. Classical (lower) and Egelstaff (upper) approximations to $\hat{G}(\omega)$ for liquid oxygen. The solid lines are directly calculated from $G_{cl}(t)$, while the dashed lines are their extrapolations to high frequency.

TABLE 1: $k_{1\to0}$ at 70 K for Liquid Oxygen, Theory and Experiment[a]

experiment[8]	360	harmonic	0.015
classical	0.00047	Egelstaff	270
standard	0.00095	Schofield	4030

[a] All numbers in units of s^{-1}.

range, using the Wiener–Khintchine theorem, or using an analytical ansatz for $G_{cl}(t)$ whose parameters can be determined from a short-time expansion.[9] Here we simply perform a linear (on a log plot) extrapolation of the displayed Fourier transforms, which is essentially equivalent to assuming that the VER rate exhibits an exponential energy gap law.[22,28]

Using these results, eq 34, and the expressions in section II, we can then compare the predictions of the various approximation schemes to the VER rate for the oxygen problem. The different results, together with the experimental rate, are shown in Table 1. One sees that the different approximation schemes give wildly different results, that the classical result is off by orders of magnitude (as anticipated), that the harmonic approximation is not in good agreement with experiment (also as anticipated), and that the Egelstaff approximation is in surprisingly good agreement with experiment.

Of course the success of the Egelstaff result could be fortuitous, arising from a cancellation of errors due to (1) the approximation scheme, (2) the extrapolation to high frequencies, and (3) the intermolecular potential. While we cannot rule out any of these possibilities, regarding the third one we do note that this same system has been studied using a potential function with quite different parameters, and the result for the VER rate is similar (differing by about a factor of 5).[29]

V. Conclusion

The accurate numerical calculation of quantum time correlation functions for many-body systems is not yet at hand. We have discussed several schemes for obtaining approximate quantum TCFs using as input only the corresponding classical TCFs and have tried to assess the merits of each scheme by comparing the results for exactly solvable model problems. It is clear that no scheme will work well for all physical problems. We then considered the difficult theoretical problem of the energy relaxation of a high-frequency vibration in a simple liquid. Our calculations indicate that for liquid oxygen at 70 K the Egelstaff scheme may provide a reasonable approximation to the required quantum force–force TCF.

Note Added in Proof. From Figures 4 and 5 one can see that for the harmonic/exponential model the logarithmic average of the harmonic and Schofield approximations would agree quite well with the exact results. Such an average produces the approximation

$$\hat{G}(\omega) = e^{\beta\hbar\omega/4}\left(\frac{\beta\hbar\omega}{1 - e^{-\beta\hbar\omega}}\right)^{1/2}\hat{G}_{cl}(\omega).$$

This new suggestion does not have strong theoretical justification, and may or may not be a good approximation for specific systems (for example, for the liquid oxygen problem at 70 K it gives $k_{1\to0} \simeq 8$ s^{-1}). But it does satisfy the basic symmetry requirements of a quantum TCF, and does not suffer from the low-frequency problems of the Egelstaff approximation.

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