

Quantum dynamics in simple fluids

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We use quantum-correction factors to calculate approximately the quantum velocity time-correlation function (TCF) of supercritical Lennard-Jones argon from the classical TCF. We find that for this quite classical system, several different quantum-correction schemes yield essentially identical results for the real and imaginary parts of the quantum TCF, and also agree well with the recent forward-backward semiclassical dynamics (FBSD) results of Wright and Makri [J. Chem. Phys. **119**, 1634 (2003)]. We also consider a more quantum-mechanical fluid of lighter atoms (neon) at a lower temperature. In this case different quantum-correction schemes give different results. FBSD calculations show that the harmonic quantum correction factor works the best for this system.

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The treatment of nuclear quantum-mechanical effects in the dynamics of condensed phase systems is a fundamental problem in physical chemistry. While, in principle, one could calculate these effects through a fully quantum-mechanical simulation for the nuclear degrees of freedom, at this point this is simply not computationally feasible for a large system due to exponential scaling with the number of degrees of freedom. This has led to a significant body of research in what are referred to as semiclassical approaches.¹⁻¹⁷ The idea behind these approaches is to obtain an approximate solution for a quantum-mechanical problem using the results of classical trajectories. These methods are quite appealing in that they are much less demanding numerically, and since the results are derived from classical dynamics, they can be easier to interpret. For example, in the centroid molecular dynamics approach developed by Voth and co-workers, the idea is to determine an effective potential energy surface that includes the effects of nuclear quantum mechanics, such as zero-point energy, and then perform a classical simulation with that surface.⁵⁻⁷ In another scheme developed by Makri and co-workers, forward-backward semiclassical dynamics (FBSD), one is able to calculate a quantum-mechanical time-correlation function (TCF) using input from classical trajectories with weights given by a quantized phase space density.⁸⁻¹³ Recently Wright and Makri¹² have applied these techniques to the calculation of the velocity TCF of neat supercritical argon.

Argon is often described as the quintessential example of a classical atomic fluid. At temperatures near its triple point, the deBroglie wavelength of the atoms is 0.3 Å—about a tenth of the size of the atoms themselves. From the Fourier transform of the velocity TCF one finds that the characteristic frequency of the motion of these atoms is about 30 cm⁻¹,

corresponding (near the triple point) to about $kT/2$. Thus while this system is not completely classical, one would nonetheless expect that any quantum-mechanical effects in dense fluid argon would be small. Wright and Makri¹² found that although the real part of the approximate quantum velocity TCF is very similar to that obtained from a classical molecular dynamics simulation, surprisingly, the TCF has a significant imaginary part as well (which is of course absent in a classical system), with a peak magnitude of nearly 15% of the initial value of the real part.

Defining the quantum TCF of some operator A by

$$G(t) = \langle A(t)A(0) \rangle, \quad (1)$$

the FBSD expression for the TCF has the form

$$G(t) = \int d\mathbf{x}_0 \int d\mathbf{p}_0 P_A(\mathbf{x}_0, \mathbf{p}_0) A(\mathbf{x}_t, \mathbf{p}_t), \quad (2)$$

where P_A is a complex valued function of the system's phase space variables and \mathbf{x}_t , \mathbf{p}_t are the final coordinates of a classical trajectory. Equation (2) is the forward-backward semiclassical approximation of the TCF in a coherent state basis for an exponential derivative representation of the operator A .^{10,11} The FBSD approximation cannot capture quantum interference effects because of its quasiclassical structure. However, such coherence effects are often naturally suppressed in condensed phase environments. The phase space function that determines the weights of the classical trajectories can be fully quantized using path integral techniques, providing an accurate treatment of prominent quantum mechanical effects related to zero point energy and quantum dispersion. There are also other more elaborate (and thus more demanding) versions of FBSD that can account for some quantum interference.¹⁴⁻¹⁶

An alternative approach to calculating quantum-mechanical effects from classical simulations, which is much easier but much less rigorous than other semiclassical approaches, involves quantum correction factors (QCFs). The implementation of a QCF is quite simple. Defining the Fourier transform of $G(t)$ by

$$\hat{G}(\omega) = \int_{-\infty}^{\infty} dt e^{i\omega t} G(t), \quad (3)$$

in most cases one assumes that $\hat{G}(\omega)$ is related to its classical counterpart $\hat{G}_{cl}(\omega)$ by a multiplicative factor, $Q(\omega)$,

$$\hat{G}(\omega) = Q(\omega) \hat{G}_{cl}(\omega). \quad (4)$$

$Q(\omega)$ satisfies symmetry relationships, such as detailed balance, so that

$$\hat{G}(-\omega) = e^{-\beta\hbar\omega} \hat{G}(\omega), \quad (5)$$

where $\beta = 1/kT$. Therefore, from $\hat{G}_{cl}(\omega)$ and a specification of $Q(\omega)$, it is then a simple matter to perform the inverse Fourier transform of their product, yielding the quantum TCF $G(t)$.

A number of QCFs have appeared in the literature.^{1-3,18-25} For the sake of brevity, we will not discuss their origin in detail, but this can be found in Ref. 2. One such factor is often referred to as the “standard” QCF,^{1,21,22}

$$Q(\omega) = \frac{2}{1 + e^{-\beta\hbar\omega}}. \quad (6)$$

The second that we will consider is known as the “harmonic” QCF, as it is exact if the operator A is a linear combination of degrees of freedom described by a harmonic Hamiltonian,¹⁸⁻²⁰

$$Q(\omega) = \frac{\beta\hbar\omega}{1 - e^{-\beta\hbar\omega}}. \quad (7)$$

A third scheme was developed by Schofield,²⁴

$$Q(\omega) = e^{\beta\hbar\omega/2}. \quad (8)$$

For some model problems it was noted^{2,3} that the geometric mean of the harmonic and Schofield QCFs yielded results that agree well with exact solutions. Hence, we will also consider the “harmonic-Schofield” QCF,

$$Q(\omega) = \left(\frac{\beta\hbar\omega}{1 - e^{-\beta\hbar\omega}} \right)^{1/2} e^{\beta\hbar\omega/4}. \quad (9)$$

Finally, Egelstaff suggested an approach that, instead of a multiplicative factor, involves the classical TCF evaluated at a complex time,²³

$$G(t) = G_{cl}([t(t + i\beta\hbar)]^{1/2}), \quad (10)$$

or in the frequency domain, this results in²⁶

$$\hat{G}(\omega) = e^{\beta\hbar\omega/2} \int_{-\infty}^{\infty} dt e^{i\omega t} G_{cl}([t^2 + (\beta\hbar/2)^2]^{1/2}). \quad (11)$$

Functionally, these QCFs are quite different, and at high frequency the Fourier transformed TCFs can vary by several

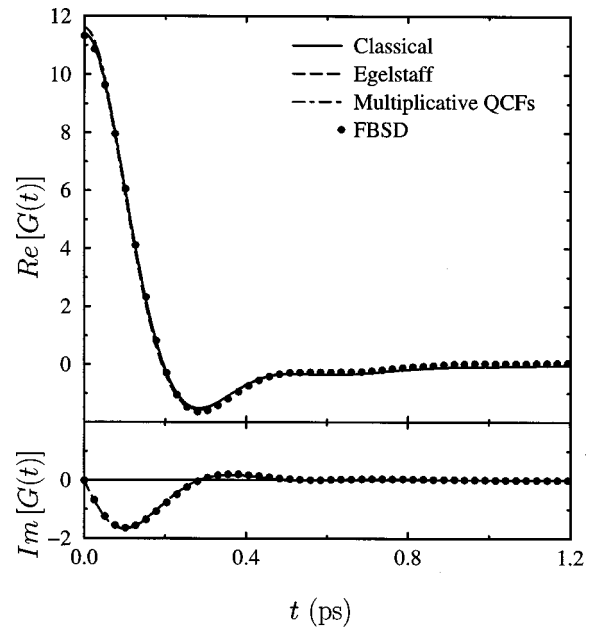


FIG. 1. Real and imaginary parts of the velocity TCF for supercritical argon. The units of the TCF are $\text{\AA}^2/\text{ps}^2$. Note that $\text{Im}[G_{cl}(t)] = 0$.

orders of magnitude.² However, we note that, at least for the multiplicative QCFs all of them are equivalent to first order in $\beta\hbar\omega$.

Below we compare results obtained with this simple QCF approach to the FBSD results of Wright and Makri.¹² To this end we performed a classical simulation of Lennard-Jones argon at $\rho^* = \rho\sigma^3 = 0.95$ and $T^* = kT/\epsilon = 1.50$ (which is in the supercritical region of the phase diagram) to obtain the classical TCF $G(t) = 3\langle v_x(t)v_x(0) \rangle$. The simulation consisted of 500 Lennard-Jones atoms with $\sigma = 3.4 \text{ \AA}$, $\epsilon/k = 122.3 \text{ K}$, and $m = 6.63 \times 10^{-26} \text{ kg}$.¹² After an initial equilibration period, the TCF was obtained from a 300 ps trajectory. In order to apply the multiplicative QCFs, the Fourier transform of the classical TCF, $\hat{G}_{cl}(\omega)$, must be calculated first. After multiplying by the appropriate factor, the inverse transform is performed, yielding the quantum TCF. The application of the Egelstaff correction is not quite as straightforward. First, a shift of the time origin of $G_{cl}(t)$ to $G_{cl}([t^2 + (\beta\hbar/2)^2]^{1/2})$ must be performed through interpolation. Equation (11) can then be used to obtain $\hat{G}(\omega)$, and the inverse transform yields $G(t)$.

In Fig. 1 we show the classical TCF, and also the real and imaginary parts of the various quantum-corrected TCFs. We note that for the real part, the results for three of the different multiplicative QCFs (harmonic, harmonic-Schofield, and Schofield) are virtually indistinguishable (and simply labeled multiplicative QCFs), and the result for the standard QCF is identical to the classical result. For the imaginary part, of course the classical result is zero, and the results for all four multiplicative QCFs are indistinguishable. In Fig. 1 we also show the results obtained from the FBSD approach.¹² We find that for this system *all* methods (QCF and FBSD approaches) give very nearly identical results for the real and imaginary parts of the TCF! The corresponding frequency-domain results are shown in Fig. 2. In the fre-

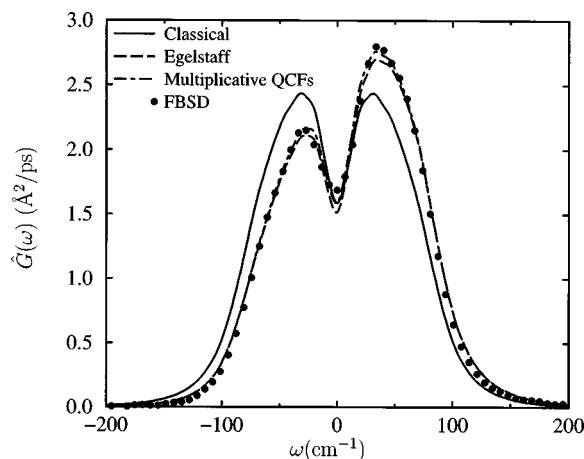
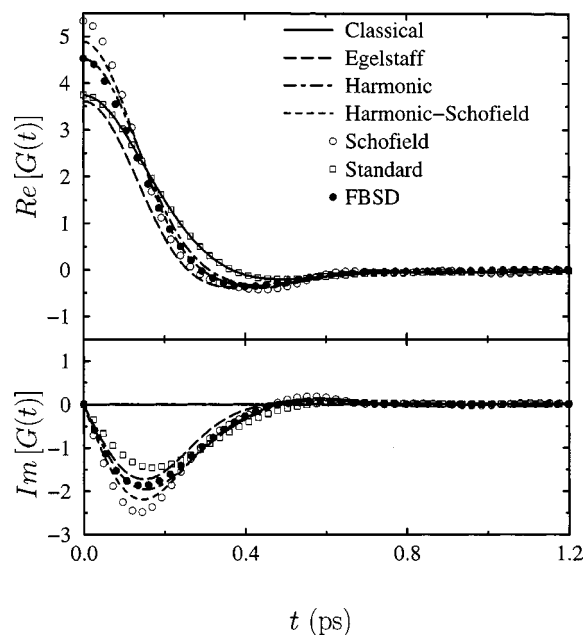


FIG. 2. Fourier transform of the velocity TCF for supercritical argon.

quency domain the similarity of the different QCF schemes is easy to understand, since at this high temperature kT is about four times the characteristic vibrational frequency in the fluid, and as discussed above all multiplicative QCFs give the same results for small $\beta\hbar\omega$. We note that all of the multiplicative QCF schemes result in the same value of $\hat{G}(0)$ (which is proportional to the diffusion constant) as the classical TCF, while FBSD yields $\hat{G}(0)$ that is slightly larger than that of the classical result, and the Egelstaff correction yields one that is slightly smaller. In summary, given that all of the QCF results are essentially the same, it seems likely that they are correct, and indeed they agree well with the more rigorous (but still approximate) FBSD results.

Because supercritical argon is really quite classical, the various schemes all give essentially the same result. In order to provide a more discriminating test of the various models, it is of interest to consider a dense fluid of lighter atoms at lower temperatures. To this end we consider neat neon [treated as a Lennard-Jones fluid with parameters $\sigma=2.749$ Å, $\epsilon/k=35.6$ K, and $m=3.35\times 10^{-26}$ kg (Ref. 27)] at $\rho^*=0.78$ and $T^*=0.84$. This state point is chosen so as to be in the liquid region of both the Lennard-Jones and experimental neon phase diagrams,^{28,29} and is at a fairly low temperature, maximizing quantum effects. The simulation results for the classical and quantum-corrected velocity TCFs are shown in Fig. 3. As expected, the magnitude of the quantum effects are considerably greater than for argon, and all of the quantum-correction schemes are distinguishable from one another. To determine which (if any) of these approaches is accurate, we performed FBSD calculations for the above system. Details of the computational methods can be found in Ref. 13, and the results, for a system of 108 particles, are shown in Fig. 3. We find that of all the different QCFs, the harmonic QCF is in the best agreement with the FBSD results. The initial value (of the real part) is essentially perfect, and the subsequent time dependencies of both the real and imaginary parts are quite good. The Fourier transforms are shown in Fig. 4, and one finds that here too the harmonic QCF provides the best correspondence with the FBSD results. The harmonic QCF gives exact results if the system is harmonic; that is, if the operator A (see above) is a linear

FIG. 3. Real and imaginary parts of the velocity TCF for neon near its triple point. The units of the TCF are Å²/ps².

combination of degrees of freedom described by a harmonic Hamiltonian. And indeed, it is not unreasonable that, at least much of the time, atoms in a Lennard-Jones fluid near the triple point execute relatively small quasiharmonic displacements around instantaneous minima,³⁰ and so in this sense it is perhaps not surprising that the harmonic QCF works quite well.

This problem involving the velocity TCF should be distinguished from other TCFs in simple liquids, like the force-force TCF, since the force is a nonlinear function of atomic displacements. Moreover, in problems like vibrational relaxation of high-frequency modes, the Fourier transform of the force-force TCF is evaluated at high frequencies (higher than the characteristic collective frequencies of the liquid), which leads to a certain multiphonon aspect to the relaxation process.^{2,31} For these types of problems the harmonic-Schofield QCF appears to be more appropriate than the har-

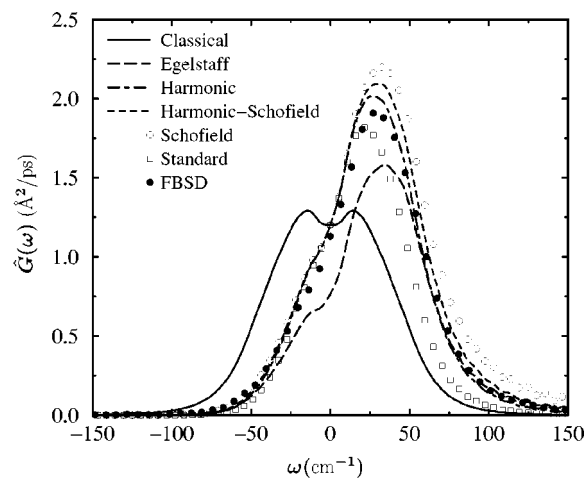


FIG. 4. Fourier transform of the velocity TCF for neon near its triple point.

monic QCF.^{2,3} Thus it seems that different QCFs are indicated for different physical problems.³ Comparisons such as that presented herein of QCFs with accurate numerical results for nontrivial problems helps develop our intuition about which QCF is most appropriate for a given circumstance.

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