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Molecular hydrodynamic approach to dynamical correlations in quantum liquids

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A quantum molecular hydrodynamic formalism is developed for the study of dynamics in quantum liquids. The method combines exact static input, generated by path-integral Monte Carlo, and an approximate form of the quantum memory function for the solution of the exact quantum generalized Langevin equation under consideration. This methodology is applied to the study of the spectrum of density fluctuations in liquid para-H_2. Using a physically motivated approximation for the memory function, semiquantitative agreement is obtained for $S(k,\omega)$ in comparison to the recent experiments of Bermejo *et al.* [Phys. Rev. Lett. **84**, 5359 (2000)]. Improvement of the methodology and future applications are discussed.

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Understanding dynamical phenomena in highly quantum liquids has been at the forefront of theoretical physics for decades. New experimental techniques continue to uncover fascinating behavior in such systems. For example, much experimental and theoretical effort has been focused on characterizing the dynamics of impurity molecules embedded in superfluid liquid nanodroplets [1–4]. These papers are only important from the fundamental standpoint, but it may also lead to different approaches for molecular self-assembly. The study of liquid para-H_2 has also been of much current interest. Experimental breakthroughs have led to direct measurement of both the incoherent [5] and coherent [6,7] dynamic structure factors in this system. A recent experimental study has even suggested that para-H_2 may exhibit superfluid behavior under certain conditions [8].

The theoretical calculation of time correlation functions in quantum liquids is an extremely difficult task. This has led to a variety of different techniques to include the effect of quantum fluctuations on the dynamic response in liquids. Most of these techniques are ‘‘semiclassical’’ in the sense that the dynamic response is calculated with the aid of *classical* trajectories of some kind [9]. While such techniques appear promising, technical issues associated with most semiclassical methodologies have prevented their use in describing dynamics in realistic quantum liquids. Another class of methods that has been used with success in a variety of problems and does not make use of real-time trajectories involves sophisticated numerical analytical continuation of exact imaginary-time path-integral Monte Carlo data (PIMCD) [10]. The application of this method to the understanding of dynamical fluctuations in quantum liquids has so far not been completely successful due to numerical instabilities involved in such methods that smooth out the distinct spectral features of various frequency dependent susceptibilities [11].

In view of the above, it is highly important to develop and implement flexible and accurate approaches for the study of dynamical fluctuations in quantum liquids. For classical liquids, a sophisticated framework called ‘‘molecular hydrodynamics’’ has been developed for the computation of dynamical observables [12–14]. This approach involves formulating an *exact* generalized Langevin equation (GLE) for the dynamical variable of interest and making approximations to the memory function of the GLE. This approach has been applied successfully to a great number of physically interesting classical problems, including the study of transport [12–14], density and momentum fluctuations [12–14], solvation dynamics [15], Raman spectroscopy [16], and vibrational relaxation [15]. An appealing feature of classical molecular hydrodynamics is that dynamics may be approximated from *static, equilibrium* input alone. While only static input is required and, therefore, only short-time behavior may be rigorously captured, often very reasonable, nearly quantitative, *long-time* behavior is generated within this approach.

The method developed here to obtain time correlation functions in quantum liquids is based on augmenting the *exact* quantum generalized Langevin equation (QGLE) for the dynamical variable with *exact* static structural input and a suitable approximation to the memory function of the QGLE. The power of our method will be demonstrated by showing that even simple approximations to the memory function may produce accurate results for the time correlation functions in quantum liquids. Furthermore, we suggest that a powerful framework for the calculation of the dynamics in finite temperature quantum liquids may be built upon the techniques discussed here, and may be used to compute a plethora of important observable dynamical quantities in quantum liquids. A similar ‘‘quantum molecular hydrodynamics’’ approach has been suggested in the past [17–19], however, it has never been combined with numerically *exact* means of calculating all of the structural input necessary for a proper implementation and solution of the QGLE.

For simplicity we focus on a particular model system, namely, on liquid para-H_2, and derive the QGLE for the intermediate scattering function $F(k,t)$ that describes the correlation of density fluctuations. Well-defined collective density excitations were recently observed experimentally in this system [6,7], even though classically such excitations are not expected to survive in liquids of this class, except at extremely low wave-vector values. This strongly suggests that quantum fluctuations have a large influence on the collective dynamics in this low-temperature liquid. While only density fluctuations in liquid para-H_2 is studied here, the methods developed hold the promise of general utility, even under superfluid conditions where previous path-integral related techniques have dramatically failed to properly reproduce experimentally observed dynamical phenomena [11].

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The derivation of the QGLE for the intermediate scattering function $F(k,t)$ follows from the work of Zwanzig [20] and Mori [21,22]. We begin with the definition of two dynamical variables—the quantum density operator $\hat{\rho}_{\mathbf{k}} = \Sigma_{\alpha=1}^{N} \mathrm{e}^{i\mathbf{k}\cdot\hat{\mathbf{r}}_\alpha}$ and the longitudinal current operator $\hat{j}_{\mathbf{k}} = (1/2m)(1/k)\Sigma_{\alpha=1}^{N}[(\mathbf{k}\cdot\dot{\hat{\mathbf{p}}}_\alpha)\mathrm{e}^{i\mathbf{k}\mathbf{r}_\alpha} + \mathrm{e}^{i\mathbf{k}\mathbf{r}_\alpha}(\dot{\hat{\mathbf{p}}}_\alpha\cdot\mathbf{k})]$. These two operators satisfy the continuity equation $\dot{\hat{\rho}}_{\mathbf{k}} = ik\hat{j}_{\mathbf{k}}$, where the dot denotes a time derivative. Next we define the projector $P^{\boldsymbol{\kappa}} = (\langle \underline{A}^\dagger, \cdots\rangle / \langle \underline{A}^\dagger, \underline{A}^{\boldsymbol{\kappa}}\rangle)\underline{A}^{\boldsymbol{\kappa}}$, where $\underline{A}^{\boldsymbol{\kappa}} = 1/\beta\hbar\int_0^{\beta\hbar}\mathrm{e}^{-\lambda H}\underline{A}\mathrm{e}^{\lambda H}$ is the Kubo transform [23] of $\underline{A}$, and the vector operator $\underline{A}$ combines the two dynamical variables $\hat{\rho}_{\mathbf{k}}$ and $\hat{j}_{\mathbf{k}}$ to form a row vector $\underline{A} = [\hat{\rho}_{\mathbf{k}}, \hat{j}_{\mathbf{k}}]$. Using the projection operator defined above the time evolution of the Kubo transform of the intermediate scattering function, $F_\kappa(k,t) = (1/N)\langle \hat{\rho}_{\mathbf{k}}^\dagger, \hat{\rho}_{\mathbf{k}}^\kappa(t)\rangle$, is given by

$$\frac{d^2F^\kappa(k,t)}{dt^2} + \omega_\kappa^2(k)F^\kappa(k,t) + \int_0^t d\tau K^\kappa(k,t-\tau)\frac{dF^\kappa(k,\tau)}{d\tau} = 0. \tag{1}$$

Equations *similar* to Eq. (1) have been derived before [18,19]. In the present paper this equation is augmented with exact input from path-integral Monte Carlo, and solved with an appropriate approximation for the memory function for a *realistic* system. This will lead to the important conclusion that even simple approximations to $K^\kappa(k,t)$ may yield frequency dependent susceptibilities in agreement with the nontrivial features that are experimentally exposed. Note that the above formal expression is very similar to the classical equation of motion for the intermediate scattering function [12]. However, Eq. (1) describes the time evolution of the *Kubo transform* of the intermediate scattering function and, therefore, is a fully quantum mechanical description. The classical limit of Eq. (1) is recovered when $\hbar \to 0$.

To obtain $F^\kappa(k,t)$ from Eq. (1) one requires as input the frequency factor $\omega_\kappa^2(k)$ and the memory function $K^\kappa(k,t)$. Within the framework of the molecular hydrodynamics approach developed below, both quantities can be obtained from static equilibrium input, i.e., from an appropriate path-integral Monte Carlo scheme, and thus are also described quantum mechanically. The frequency factor is given by $\omega_\kappa^2(k) = k^2J^\kappa(k)/S^\kappa(k)$, where $S^\kappa(k) = F^\kappa(k,0) = (1/N) \times\langle \hat{\rho}_{\mathbf{k}}^\dagger, \hat{\rho}_{\mathbf{k}}^\kappa(0)\rangle$ is the Kubo transform of the static structure factor and $J^\kappa(k) = (1/N)\langle \hat{j}_{\mathbf{k}}^\dagger, \hat{j}_{\mathbf{k}}^\kappa(0)\rangle$ is the Kubo transform of the zero time longitudinal current correlation function. The memory function is related to the Kubo transform of the random force, $\hat{R}_k = d\hat{j}_{\mathbf{k}}/dt - ik[J^\kappa(k)/S^\kappa(k)]\hat{\rho}_{\mathbf{k}}$, and is given formally by $K^\kappa(k,t) = \langle \hat{R}_k^\dagger, \hat{R}_k^\kappa(t)\rangle / [NJ^\kappa(k)]$.

The above expression for the memory function combined with Eq. (1) is simply another way for rephrasing the quantum Wigner-Liouville equation for the dynamical variable $F^\kappa(k,t)$. The difficulty of numerically solving the Wigner-Liouville equation for a many-body system is shifted to the difficulty of evaluating the memory kernel. For a certain class of classical dense fluids, a simple *exponential* approximation to the memory function is known to provide a semiquantitative description of $S(k,\omega) = \int_{-\infty}^{\infty} dt F(k,t)e^{i\omega t}$. It is well known that for systems with "soft" potentials of mean force (PMF), such as liquid metals, this approximation provides a quantitative description of $S(k,\omega)$ for values of k near that for which $S(k)$ reaches its first maximum, and a semiquantitative $S(k,\omega)$ for smaller values of k outside the strict hydrodynamic limit [12–14]. In Fig. (1) we compare the PMF for quantum liquid para-H_2 in the temperature and density range of the experiment of Bermejo *et al.* [6] to the PMF for classical para-H_2 under dense liquid conditions. An examination of the classical PMF would lead one to the expectation that this system is not in the "soft" limit. It should be noted, however, that quantum fluctuations greatly soften the PMF between two particles. As clearly can be seen in the figure, the quantum PMF shows a lower frequency of oscillation about its first minimum and a softer repulsive wall than the classical PMF does. In fact, the quantum PMF resembles that of a classical liquid metal, for which the aforementioned exponential approximation for the memory function produces quantitative results for $S(k,\omega)$. These facts motivate the use of the simple exponential form for the memory function in quantum liquid para-H_2.

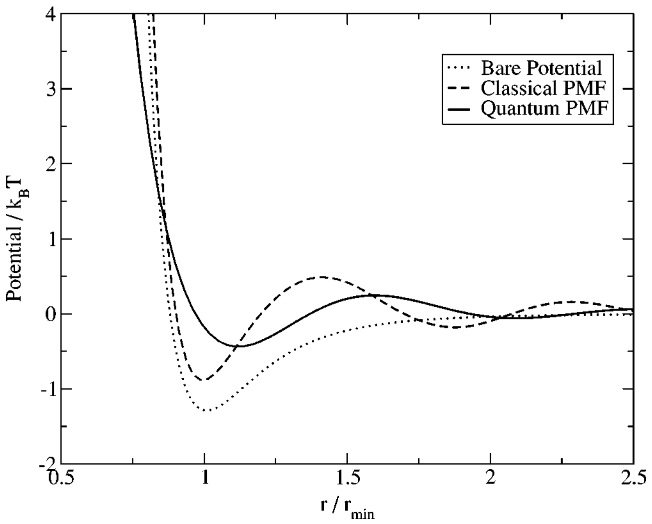

FIG. 1. A plot of the potential (dotted line) and the potential of mean force (PMF) for classical (dashed line) and quantum (solid line) liquid para-H_2. The thermodynamic point is $T = 25$ K, $\rho = 0.0289$ Å^{-3} for the classical result, and $T = 14$ K, $\rho = 0.0235$ Å^{-3} for the quantum result. Note that the quantum fluctuations lead to a significantly softer PMF.

In view of the above discussion, we assume that the time dependence of the longitudinal memory function $K^\kappa(k,t)$ follows an exponential decay law [13,24]

$$K^\kappa(k,t) = K^\kappa(k,0)\exp(-t/\tau_k)$$

where the relaxation time

$$\tau_k = \frac{1}{2}\sqrt{\pi/K^\kappa(k,0)}$$

is estimated using the Lovesey approximation [24] and

$$K^{\kappa}(k,0)=\frac{\langle\omega^4(k)\rangle^{\kappa}}{\langle\omega^2(k)\rangle^{\kappa}}-\frac{\langle\omega^2(k)\rangle^{\kappa}}{S^{\kappa}(k)},$$

where

$$\langle\omega^n(k)\rangle^{\kappa}=(-1)^{n/2}\frac{d^n}{dt^n}F^{\kappa}(k,t)\big|_{t=0}/S^{\kappa}(k)$$

are the normalized frequency moments of $S(k,\omega)$. Following the classical notation this approximation is referred to as the *quantum viscoelastic model* (QVM).

The short-time moments of the Kubo transform of the intermediate scattering function that determine the longitudinal memory kernel involve thermal averages over an operator that combines positions and momenta of all particles. The term for $\omega_{\kappa}^4(k)$ (not given explicitly here) is more complicated and involves higher powers of momenta operators. The approach we adopt in the present study to calculate these moments is based on a recent method that we have developed that uses path-integral Monte Carlo (PIMC) technique and is suitable for thermal averages of such operators for a many-body system [25]. We note that the required averages could be obtained from a standard "primitive" path-integral Monte Carlo algorithm for the ensemble average of operators involving momentum and position [26], however, more Monte Carlo passes would be required to reach convergence.

To obtain the dynamic structure factor given by

$$S(k,\omega)=\frac{\beta\hbar\omega}{2}\left[\coth\left(\frac{\beta\hbar\omega}{2}\right)+1\right]S^{\kappa}(k,\omega),$$

we solve Eq. (1) with the approximate memory function given by the exponential decay law. The PIMC simulations were performed with 108 particles interacting via the Silvera-Goldman potential [27] at $T=14$ K and $\rho=0.0235$ Å^{-3}. The staging algorithm [28] for Monte Carlo chain moves was employed to compute the numerically exact Kubo-transformed static moments. 2×10^7 Monte Carlo moves were made, with an acceptance ratio of approximately 0.35.

In Fig. (2), we show the calculated dynamic structure factor for para-H_2 at a thermodynamic state point very similar to the one studied experimentally by Bermejo *et al.* [7]. Although the instrument response is *not* included in our calculation (but *has* been included in the calculation of Ref. [7]), the results are clearly in semiquantitative agreement with the experimental results. In particular, a high intensity peak at finite frequency is observed, and disappears around $k=1.4$ Å^{-1}, in agreement with the experiment [7]. The peak positions and widths do show slight differences from the experimental results, as do the simulations presented by Bermejo *et al.* [7]. Comparing our results with the earlier path-integral centroid molecular dynamics (PICMD) calculation that did not account for the instrument response [29] shows that the PICMD results are nearly identical to our simple QVM results. This agreement is somewhat surprising, given that the two approaches are so different. It should be noted that for the approximate Kubo-transformed $S^{\kappa}(k,\omega)$, the QVM will satisfy the first three even sum rules, while the PICMD result will not.

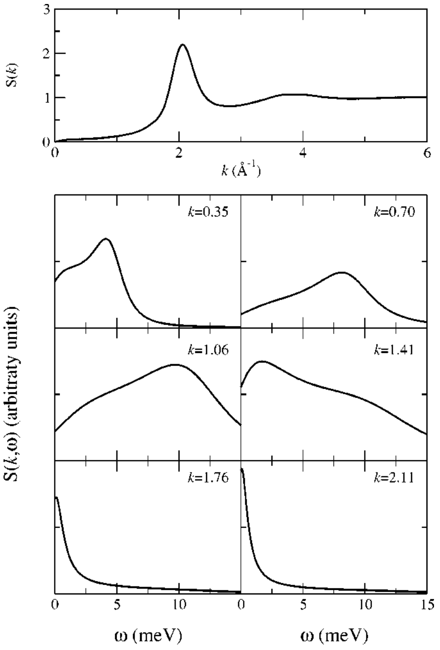

FIG. 2. The dynamics structure factor for para-H_2 at $T=14$ K and $\rho=0.0253$ Å^{-3} calculated from the quantum viscoelastic model. The upper panel shows the static structure factor obtained from a PIMC simulation. The k values are in units of Å^{-1}.

While it is beyond the scope of the present paper to give a detailed comparison of the relative merits of other methods to the approach taken here, it should be noted that the present technique has some very attractive advantages. First, the method requires no computation of semiclassical trajectories, thus offering a more efficient numerical scheme to approximate quantum mechanical correlation functions. Second, as is well known in the classical case, the approach taken here may be applied to *general* liquid state correlation functions, as long as a reasonable approximation to the memory function of interest is used. Furthermore, situations where the static distribution is not described by Boltzmann statistics can easily be handled within the framework of the quantum hydrodynamic approach developed here, since the additional complication of proper particle statistics may be absorbed into the PIMC calculation of the static input. Lastly, since the starting point of the methods used in this work is the *exact* QGLE given by Eq. (1), improvements upon simple approaches such as the QVM may be made with more sophisticated approximations to the memory function.

What is most remarkable about the present calculation is the fact that very good agreement with experiment in a nontrivial system may be obtained via a simple approach that *makes no use of dynamical trajectories*. This is significant, since the method proposed is flexible and *improvable*. It is known, for example, that the classical viscoelastic approximation can underestimate the intensity of the low frequency behavior of $S(k,\omega)$ for small values of k [12]. A means of improvement here would be through the use of a quantum mode-coupling theory (QMCT) for the construction of the memory function. For example, an approximate closure of the form $K^{\kappa}(k,t)\approx K_{\kappa,QB}(k,t)+K_{\kappa,QMCT}(k,t)$ where the "quantum binary" portion $[K_{\kappa,QB}(k,t)]$ is determined from a short-time expansion of the exact Kubo-transformed memory function, while the quantum mode-coupling portion $[K_{\kappa,QMCT}(k,t)]$ is obtained with a generalization of the standard expression [12] for classical liquids,

$$K^{\kappa}_{QMCT}(k,t)=\frac{1}{N}\sum_{q}\Phi_{k,q}[F^{\kappa}(q,t)F^{\kappa}(|k-q|,t)-F^{\kappa}_{B}(q,t)F^{\kappa}_{B}(|k-q|,t)], \tag{2}$$

where $\Phi_{k,q}\approx[2/J^{\kappa}(q)]|V_{k,q}|^2$ and

$$V_{k,q}=\frac{1}{2N}\left(\frac{\left\langle \hat{\rho}_{-\mathbf{q}}\hat{\rho}_{\mathbf{q}-\mathbf{k}},\frac{d}{dt}\hat{j}^{\kappa}_{\mathbf{k}}\right\rangle}{S^{\kappa}(q)S^{\kappa}(|\mathbf{k}-\mathbf{q}|)}-i|k|\frac{J^{\kappa}(k)}{S^{\kappa}(k)}\frac{\langle\hat{\rho}_{-\mathbf{q}}\hat{\rho}_{\mathbf{q}-\mathbf{k}},\hat{\rho}^{\kappa}_{\mathbf{k}}\rangle}{S^{\kappa}(q)S^{\kappa}(|\mathbf{k}-\mathbf{q}|)}\right). \tag{3}$$

In the above equation $F_{B,\kappa}(k,t)$ refers to the short-time binary scattering function, which can be obtained from a simple quantum generalization of the classical version of this function $F^{\kappa}_{B}(k,t)=F^{\kappa}_{B}(k,0)\exp(-\omega^{2}_{\kappa}(k)t^{2}/2)$. All quantum input may again be obtained from path-integral quantum Monte Carlo techniques [25]. Interestingly, a simplified version of this approach (without exactly determined static information) was suggested for application to the problem of density fluctuations in superfluid liquid helium [18,19]. Given the recent experimental interest in superfluid helium clusters and the failure of previous path-integral-based approaches to density fluctuation in bulk superfluid helium [11], the development of this approach is of obvious importance. Results for $S(k,\omega)$ in ^{4}He near and below T_{λ} computed by the quantum mode-coupling approach will be presented in a future work.

In conclusion we have developed a simple quantum molecular hydrodynamic formalism to study dynamical phenomena in quantum liquids. Our approach does not rely on computing dynamical trajectories of any kind. The computation of any time correlation function is accomplished by augmenting the exact (quantum) generalized Langevin equation for the Kubo transform of the correlation function with exact static structural input and a suitable approximation to the memory function. We have applied our approach to study collective density fluctuations in liquid para-H_2 near the triple point. Motivated by the fact that the inclusion of quantum fluctuations results in a "softening" of the effective potential, we have used a very simple form for the memory function (QVM), where the lifetime of the exponential decay of the memory function was obtained from path-integral Monte Carlo simulations. Semiquantitative agreement was obtained in comparison to the experiment of Bermejo *et al.* [7]. We have suggested that the QVM can be improved using an approximate closure for the memory function based on the mode-coupling theory. The method developed here is in no way confined to the case of para-H_2, and should be extremely useful in general for the difficult problem of computation of dynamical observables in quantum liquids.

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