Self-Consistent Mode-Coupling Theory for Self-Diffusion in Quantum Liquids

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(Received 12 July 2001; published 10 December 2001)

A closed, self-consistent equation for the velocity autocorrelation function of a quantum liquid within the framework of a quantum mode-coupling theory is derived. The solution of the quantum generalized Langevin equation requires static input which is generated by an appropriate path-integral Monte Carlo scheme. In order to assess the accuracy of our approach we have studied the self-diffusion process of liquid *para*-hydrogen at two thermodynamic state points. Quantitative agreement for the self-diffusion constant is obtained in comparison to experimental measurements and other theoretical predictions.

DOI: 10.1103/PhysRevLett.87.265702 PACS numbers: 67.20.+k

One of the long-standing problems in physics is the quantum mechanical treatment of dynamical properties in highly quantum liquids. The direct calculation of time correlation functions in these condensed phase systems is an extremely difficult task. This has led to a variety of different techniques to include the effects of quantum fluctuations on the dynamic response in liquids. At the present time, one of the viable alternatives to the exact quantum mechanical solution is the use of techniques that are "semiclassical" in nature, namely, the dynamic response is obtained with the aid of *classical* trajectories [1]. While such techniques appear promising, technical issues 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 involves sophisticated numerical analytical continuation of exact imaginary-time path-integral Monte Carlo (PIMC) data [2]. The application of these methods to the understanding of dynamical properties in quantum liquids has so far not been completely successful [3,4].

In this Letter we develop a new approach to study dynamical correlations in quantum liquids within the framework of a quantum mode-coupling theory [5], and focus on the study of transport properties in these systems. Our approach draws upon the pioneering work of Götze and Lücke [6,7], and Sjögren and Sjölander [8–10]. We first derive a closed, self-consistent nonlinear integro-differential equation for the velocity autocorrelation function. The solution to this equation requires static input which is generated by an appropriate path-integral Monte Carlo scheme [11]. The method is then applied to study the self-diffusion process of liquid *para*-hydrogen at two thermodynamic state points, and comparison is made with experimental measurements [12] and other theoretical predictions [13].

The derivation of the quantum generalized Langevin equation (QGLE) for the velocity autocorrelation function (VACF) follows from the work of Zwanzig [14] and Mori [15,16]. We begin with the definition of the projection operator, P_κ [17]:

$$P_\kappa = \frac{\langle v, \cdots \rangle}{\langle v, v_\kappa \rangle} v_\kappa , \tag{1}$$

where

$$v_\kappa = \frac{1}{\beta \hbar} \int_0^{\beta \hbar} d\lambda \, e^{-\lambda H} v e^{\lambda H} \tag{2}$$

is the Kubo transform [18] of the velocity operator $v = p/m$ of a representative liquid particle along a chosen Cartesian direction, H is the Hamiltonian of the system, $\beta = \frac{1}{K_B T}$, and $\langle \cdots \rangle$ denote an ensemble average. In the above equations the notation κ implies that the quantity under consideration involves the Kubo transform given by Eq. (2). Using the above definitions and following the standard procedure [19] it is straightforward to show that the QGLE for the Kubo transform of the VACF, $C_v^\kappa(t) = \langle v v_\kappa(t) \rangle$, is given by the *exact* equation

$$C_v^\kappa(t) = - \int_0^t dt' \, K^\kappa(t') \dot{C}_v^\kappa(t - t') , \tag{3}$$

where $\dot{C}_v^\kappa(t) = \partial C_v^\kappa(t)/\partial t$, and the Kubo transform of the memory kernel, $K_\kappa(t)$, is given by the *exact* equation

$$K^\kappa(t) = \frac{1}{\langle v, v_\kappa \rangle} \langle \dot{v}, e^{i(1-P_\kappa)\mathcal{L} t} \dot{v}_\kappa \rangle . \tag{4}$$

In the above equation, $\mathcal{L} = \frac{1}{\hbar}[H,]$ is the quantum Liouville operator.

The above expression for the memory function combined with Eq. (3) is simply another way of rephrasing the quantum Wigner-Liouville equation for the VACF. The difficulty of numerically solving the Wigner-Liouville equation for the positions and velocities in a many-body system is shifted to the difficulty of evaluating the memory kernel. To circumvent this difficulty we use an approximate closure for the memory kernel of the form $K^\kappa(t) = K_f^\kappa(t) + K_s^\kappa(t)$. This form of mode-coupling theory [20] has been used successfully in the study of a certain class of classical dense fluids with remarkable success in predicting various dynamical correlations in these systems [19,21,22]. Its quantum generalization has been suggested for the application of density fluctuations in superfluid liquid helium [6,7] and in liquid *para*-hydrogen [5]. We note that the above formal expression for the

QGLE of the VACF is very similar to its classical counterpart [19]. However, Eq. (3) describes the time evolution of the *Kubo transform* of the VACF and therefore is a fully quantum mechanical description. The classical limit of Eq. (3) is recovered when $\hbar \to 0$.

To obtain the "quantum binary" portion, $K_f^\kappa(t)$, and the quantum mode-coupling portion, $K_s^\kappa(t)$, of the memory kernel we follow the standard classical procedure, with the projection operator and memory kernel given by Eqs. (1) and (4), respectively. The fast decaying binary term is obtained from a short-time expansion of the exact Kubo transform of the memory function, and is given by

$$K_f^\kappa(t) = K_0^\kappa f(t/\tau), \tag{5}$$

where the lifetime $\tau = [-\ddot{K}^\kappa(0)/2K^\kappa(0)]^{-1/2}$, $K_0^\kappa = \langle \dot{v}, \dot{v}_\kappa \rangle / \langle v, v_\kappa \rangle$, and $\ddot{K}_0^\kappa = -\langle \ddot{v}, \ddot{v}_\kappa \rangle / \langle v, v_\kappa \rangle + [K^\kappa(0)]^2$. The shape of the function $f(x)$ is taken to be a Gaussian $\exp(-x^2)$ or $\operatorname{sech}^2(x)$. Both forms have been used in the study of classical liquids [19], and are exact to second order in time. We have found that both forms give nearly identical results, signifying that the theory presented here is robust.

The slow decaying mode-coupling term is approximated by

$$K_s^\kappa(t) \approx \frac{1}{2\pi^2 n \langle v, v_\kappa \rangle} \int_0^\infty dq\, q^2 |V^\kappa(\mathbf{q})|^2 \times [F_s^\kappa(q,t) - F_{s,b}^\kappa(q,t)] F^\kappa(q,t). \tag{6}$$

In the above equation, n is the number density, $F^\kappa(q,t)$ is the Kubo transform of the intermediate scattering function [5], and $F_s^\kappa(q,t)$ is the Kubo transform of the self-intermediate scattering function. The binary term of the Kubo transform of the self-intermediate scattering function, $F_{s,b}^\kappa(q,t)$, is obtained from a short-time expansion of $F_s^\kappa(q,t)$ similar to the expansion used for the binary term of $K^\kappa(t)$. The vertex in Eq. (6) is given by

$$V^\kappa(\mathbf{q}) = \frac{\langle b(\mathbf{q}) \dot{v}_\kappa \rangle}{N F_s^\kappa(q,0) F^\kappa(q,0)}, \tag{7}$$

where N is the number of particles, and $b(\mathbf{q}) = \sum_{j \neq 1}^N e^{i\mathbf{q}\cdot(\mathbf{r}_1 - \mathbf{r}_j)}$ is related to the single-particle and number-variable density operators.

To obtain both portions of the memory kernel, one requires as input the values of the memory function at $t = 0$, its second time derivative at $t = 0$, and the vertex. These properties can be obtained from *static* equilibrium input; however, they involve thermal averages over operators that combine positions and momenta of all particles. The approach we adopt in this paper to calculate these averages is based on a recent method that we have developed which uses a path-integral Monte Carlo technique and is suitable for thermal averages of such operators for a many-body system [11].

In addition to these static properties, one also requires the Kubo transforms of the *time-dependent* intermediate and self-intermediate scattering functions. The Kubo transform of the intermediate scattering function, $F^\kappa(q,t)$, can be obtained from a similar approach, namely, from a quantum mode-coupling theory combined with the PIMC method [5]. However, in a recent paper [5] we have shown that a simpler approach, the quantum viscoelastic model (QVM), provides semiquantitative results for $F^\kappa(q,t)$, and therefore the QVM is the approach we adopt here. The self-intermediate scattering function cannot be obtained from the viscoelastic model, since this approach is known to fail even for classical liquids. We therefore assume a Gaussian approximation for the Kubo transform of the self-intermediate scattering function [23] given by

$$F_s^\kappa(q,t) = F_s^\kappa(q,0) \exp\left\{-q^2 \int_0^t dt'\, C_v^\kappa(t')(t - t')\right\}, \tag{8}$$

where the Kubo transform $F_s^\kappa(q,0)$ can be obtained from a static equilibrium PIMC method.

To assess the accuracy of the above outlined approach we have studied the self-diffusion of liquid *para*-hydrogen at two thermodynamic points: a liquid near the triple point at $T = 14$ K and $\rho = 0.0235$ Å^{-3}, and a high temperature liquid at $T = 25$ K and $\rho = 0.0190$ Å^{-3} (the density for both state points is the average density at zero pressure [24]). This system has been studied both experimentally [12] and theoretically using the path-integral centroid molecular dynamics (PICMD) method [13], and thus comparison with the present approach can be made.

In order to obtain the static input required by the quantum mode-coupling theory we have performed PIMC simulations of liquid *para*-hydrogen, where the entire H_2 molecule is described as a spherical particle, so the potential depends only on the radial distance between particles. The simulations were done using a *NVT* ensemble with 108 particles interacting via the Silvera-Goldman potential [25]. The staging algorithm [26] for Monte Carlo chain moves was employed to compute the numerically exact Kubo-transformed static input. 2×10^7 Monte Carlo moves were made, with an acceptance ratio of approximately 0.35. The static input generated from the PIMC simulations combined with the Kubo transform of the intermediate scattering function obtained from the QVM [5] was then used to obtain the memory kernel for the VACF. Using $F_{s,b}^\kappa(q,t)$ as an initial guess for the Kubo transform of the self-intermediate scattering function, we have solved Eqs. (3), (5), (6), and (8) self-consistently to obtain the Kubo transform of the VACF. Typically, less than ten iterations were required to converge the self-consistent cycles.

In Fig. 1 we plot the normalized Kubo transform of the VACF and the VACF itself for liquid *para*-hydrogen at the two thermodynamic points considered in this work. The time-dependent VACF was generated from the frequency-dependent diffusion contestant, $D(\omega)$, which was obtained using the standard relation in frequency space:

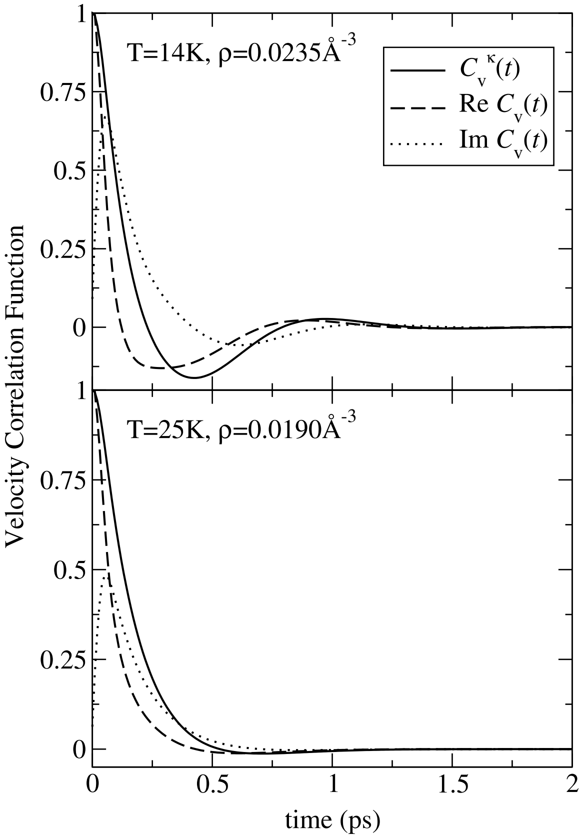

FIG. 1. A plot of the normalized time-dependent Kubo transform of the velocity autocorrelation function (solid line) and the real and imaginary parts of the normalized velocity autocorrelation function (dashed and dotted lines, respectively) for liquid *para*-hydrogen at $T = 14$ K, $\rho = 0.0235$ Å^{-3} (upper panel) and $T = 25$ K, $\rho = 0.0190$ Å^{-3} (lower panel).

$$D(\omega) = \frac{\beta\hbar\omega}{2}\left[\coth\left(\frac{\beta\hbar\omega}{2}\right) + 1\right]D^\kappa(\omega), \qquad (9)$$

where $D^\kappa(\omega)$ is the Kubo transform of the frequency-dependent diffusion constant given by the Fourier transform of $C_v^\kappa(t)$. The time scale for the initial relaxation of the VACF is approximately 0.2–0.25 ps for both thermodynamic points, while the classical result (not shown) predicts a decay on a much faster time scale [27].

While it is beyond the scope of this Letter to give a detailed comparison between the quantum mode-coupling approach and other methods [28,29], it should be noted that the agreement between the quantum mode-coupling approach and the analytic continuation method is remarkable [28], while there are very small differences between the VACF obtained using our approach and the PICMD method [13]. The good agreement between these different methods obtained for the VACF is a strong support for the robustness and accuracy of this theory.

In Fig. 2 we plot the Kubo transform of the memory kernel of the VACF for the two thermodynamic points studied in this work. At the higher temperature point the contribution of the mode-coupling portion to the memory kernel is negligible, and the VACF can be computed using only the fast binary part. This is not the case for the lower temperature studied, and the slower mode-coupling portion of the memory kernel significantly influences the decay of the VACF. Note that the area under the fast binary portion is comparable to that of the slow mode-coupling portion for the lower temperature case.

The frequency-dependent diffusion constant given by Eq. (9) is shown in Fig. 3. The values of the self-diffusion constants which were obtained from the Green-Kubo relation are 0.30 Å^2 ps^{-1} and 1.69 Å^2 ps^{-1} for $T = 14$ K, $\rho = 0.0235$ Å^{-3} and $T = 25$ K, $\rho = 0.0190$ Å^{-3}, respectively. These results are in good agreement with the experimental results (0.4 Å^2 ps^{-1} and 1.6 Å^2 ps^{-1}) [12] and with the full PICMD results (0.32 Å^2 ps^{-1} and 1.54 Å^2 ps^{-1}) [13]. It should be emphasized that the mode-coupling portion of the memory kernel is *essential* for obtaining the self-diffusion constant at the lower temperature point that is in quantitative agreement with the experimental value.

In conclusion, we have developed a quantum mode-coupling approach to study the self-diffusion process in

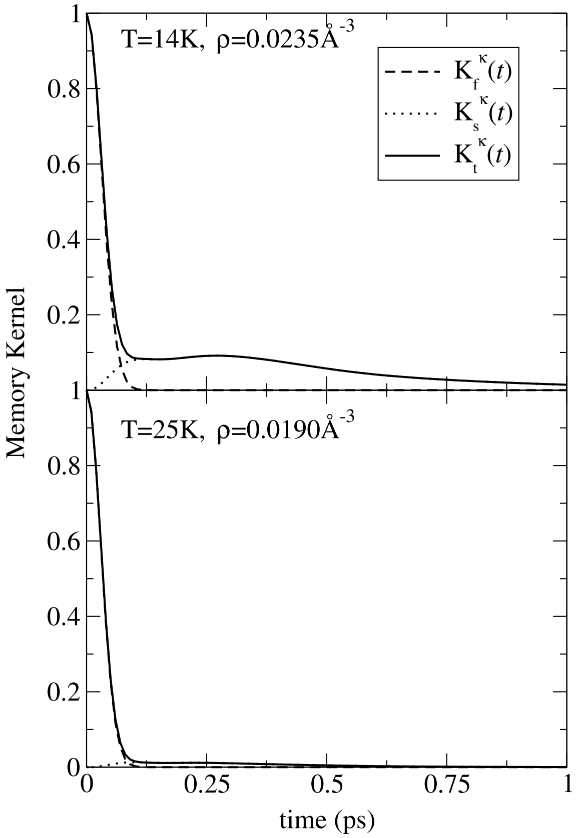

FIG. 2. A plot of the normalized time-dependent Kubo transform of the memory kernel for the velocity autocorrelation function for liquid *para*-hydrogen at $T = 14$ K, $\rho = 0.0235$ Å^{-3} (upper panel) and $T = 25$ K, $\rho = 0.0190$ Å^{-3} (lower panel). The solid, dashed, and dotted curves are for the total memory kernel, the fast binary portion $K_f^\kappa(t)$, and the slow mode-coupling portion $K_s^\kappa(t)$, respectively.

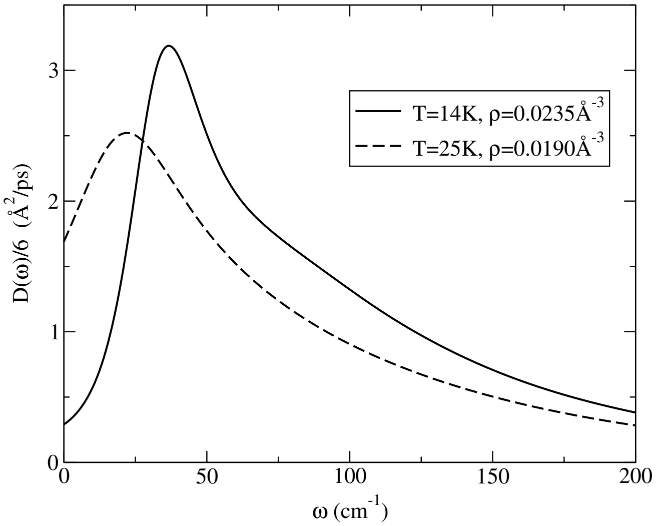

FIG. 3. A plot of the frequency-dependent diffusion constant for liquid *para*-hydrogen at $T = 14$ K, $\rho = 0.0235$ Å^{-3} (solid line) and $T = 25$ K, $\rho = 0.0190$ Å^{-3} (dashed line).

quantum liquids. Our approach does not rely on computing dynamical trajectories of any kind. The computation of the velocity time correlation function is accomplished by augmenting the exact (quantum) generalized Langevin equation for the Kubo transform of this correlation function with the exact static structural input generated from PIMC simulations, and a suitable approximation to the memory function. We applied our approach to study the self-diffusion of liquid *para*-hydrogen at two different thermodynamic state points. We find that, at the higher temperature–lower density, the memory function is well approximated by the binary portion, while, at the lower temperature–higher density, the mode-coupling portion of the memory kernel is very important. By using the Green-Kubo relation, we have obtained the values of the self-diffusion constant, and the results are in very good agreement with the experimental observations and with other theoretical predictions. We find that the self-diffusion process of liquid *para*-hydrogen is strongly determined by a *quantum-dynamical* process.

The method developed here is in no way confined to the case of *para*-hydrogen, and should be extremely useful in general for the difficult problem of computation of dynamical observables in quantum liquids.

This work was supported by The Israel Science Foundation founded by the Israel Academy of Sciences and Humanities (Grants No. 9060/99 and No. 34/00) and by the Research Corporation Inovation. E. R. acknowledges financial support from the Israeli Council of Higher Education, and also thanks the Department of Chemistry at Harvard University for its warm hospitality. D. R. R. thanks Tel Aviv University for its support.

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