A self-consistent mode-coupling theory for dynamical correlations in quantum liquids: Application to liquid para-hydrogen

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The self-consistent quantum mode-coupling theory developed in the preceding paper [J. Chem. Phys. 116, 6271 (2002)] is applied to the study of density fluctuations and transport in liquid para-hydrogen. The method combines exact static input generated by a path-integral Monte Carlo method, and an approximate form of the quantum memory function, for the solution of the exact generalized Langevin equation under consideration. The approach provides exact results for any correlation function at short times, and is expected to provide accurate results at long times. The quantum mode-coupling theory is compared with experimental observations for a variety of dynamical correlations in liquid para-hydrogen. We find that the quantum mode-coupling theory provides quantitative agreement with experiments. Improvement of the methodology and future applications are discussed. © 2002 American Institute of Physics. [DOI: 10.1063/1.1458546]

I. INTRODUCTION

Understanding dynamical phenomena in highly quantum liquids has been at the forefront of theoretical chemistry 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 This work is not only important from the fundamental standpoint, but it may also lead to novel approaches for molecular self-assembly. The study of liquid para-hydrogen has also been of much current interest. Experimental breakthroughs have led to direct measurement of both the incoherent5 and coherent6,7 dynamic structure factors in this system. A recent experimental study has even suggested that para-hydrogen may exhibit superfluid behavior under certain conditions.8

The theoretical calculation of time-correlation function in quantum liquids is an extremely difficult task. In the preceding paper,9 hereafter referred to as Paper I, we have developed a quantum mode-coupling formalism for general time-correlation functions in dense quantum liquids. The approach is based on augmenting an exact closed, quantum generalized Langevin equation (QGLE) for the dynamical variable of interest, and introducing a suitable approximation to the memory kernel of the QGLE. Such an approach has been developed for the computation of dynamical observables in classical liquids,10–12 and has been applied successfully to a great number of physically interesting classical problems, including the study of transport,10–12 density and current fluctuations,10–12 solvation dynamics,13,14 Raman spectroscopy,15 and vibrational relaxation.13 The solution of the QGLE requires as input static, equilibrium information which can be generated using an appropriate path-integral Monte Carlo (PIMC) scheme.9,16 The static input involves thermal averages over operators that combine positions and momenta of all particles. Thus special care must be taken to properly implement a PIMC scheme suitable for such operators in a many-body system.

In this paper we apply the quantum mode-coupling formalism developed in Paper I to a realistic system. We focus on the study of collective density fluctuations and quantum transport in liquid para-hydrogen at two thermodynamic state points: a liquid near the triple point and a high temperature liquid. The reason we chose to apply our approach to liquid para-hydrogen is based on the following two arguments: (a) Liquid para-hydrogen is a dense liquid characterized by quantum dynamical susceptibilities. (b) It has been studied extensively both experimentally5,7,17 and theoretically,7,18–24 and thus is an ideal system to assess the accuracy of our quantum mode-coupling approach. We show that the quantum mode-coupling formalism combined with exact static input generated from the PIMC method provide quantitative results for the density fluctuations and transport in liquid para-hydrogen.

The paper is organized as follows: In Sec. II we describe the model used for liquid para-hydrogen, and provide technical detailed regarding the PIMC simulations. In Sec. III we introduce an approximation to the quantum mode-coupling theory, and apply the method to the case of collective density fluctuations. The study of transport in liquid para-hydrogen is discussed in Sec. IV. Comparison with experimental observations, and other theoretical predictions is made in both sections. Finally, conclusions are given in Sec. V.

II. MODEL AND SIMULATION DETAILS

In this section we describe the model used to study the dynamical properties of liquid para-hydrogen, and provide some technical details of the path-integral Monte Carlo simulations.
The model potential we use to study liquid para-hydrogen is based on the Silvera–Goldman potential where the entire H₂ molecule is described as a spherical particle, so the potential depends only on the radial distance between particles. This potential has been used to study thermodynamic properties and phase equilibrium of fluid hydrogen, and has also been used to study transport and density fluctuations of liquid para-hydrogen. The Silvera–Goldman potential is given by

\[ V(r) = \exp(\alpha - \delta r - \gamma r^2) - \left( \frac{C_6}{r^6} + \frac{C_8}{r^8} + \frac{C_{10}}{r^{10}} \right) f_c(r) + \frac{C_9}{r^9} f_c(r), \]

where the first term on the right-hand side (RHS) accounts for short range repulsion interactions, the second set of terms on the RHS account for long range attractive dispersion interactions, and the last term on the RHS is an effective three body correction. The last two terms are multiplied by a damping function which turns off these interactions at short distances, and is given by

\[ f_c(r) = e^{-(r_c/r)^2} \theta(r_c - r) + \theta(r - r_c), \]

where \( \theta(r) \) is the Heaviside function (step function). The parameters for the potential are given in Table I.

To obtain the static input required by the quantum mode-coupling approach described in Paper I, we have performed PIMC simulations at two thermodynamic state 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 was chosen to be the average density under zero pressure. The PIMC simulations were done using the NVT ensemble with \( 10^8 \) particles interacting via the Silvera–Goldman potential defined in Eq. (1). The staging algorithm for Monte Carlo chain moves was employed to compute the numerically exact Kubo-transformed static input. The imaginary time interval was discretized into 5 Trotter slices of size \( \varepsilon = \beta / P \), where \( \beta = 1/K_B T \) is the inverse temperature, and \( P = 50 \) and \( P = 28 \) for the low and high temperatures, respectively. \( 2 \times 10^7 \) Monte Carlo passes were made, each pass consisted of attempting moves in all atoms and all the beads that were staged. The acceptance ratio was set to be approximately 0.35 for both state points. The PIMC simulations were done on a Pentium III cluster, and took approximately a week using 24 nodes.

The static input obtained from the PIMC simulations was then used to generate the proper memory kernel needed for the solution of the QGLE under consideration. Since the memory kernel can depend on the value of the correlation function itself, the solution must be obtained self-consistently. The initial guess for the memory kernel was taken to be equal to the fast binary portion. The differential equations were integrated using a fifth-order Gear predictor–corrector algorithm. Typically, less than 15 iterations were required to converge the correlation function, with an average error smaller than 10\(^{-8}\) percent.

To motivate the use of the quantum molecular hydrodynamic approach for liquid para-hydrogen we have compared the potential of mean force (PMF) for classical (dashed line) and quantum (solid line) liquid para-hydrogen at \( T = 14 \) (lower panel) and \( T = 25 \) (upper panel). The classical densities are \( \rho = 0.0321 \) Å\(^{-3}\) and \( \rho = 0.0289 \) Å\(^{-3}\) for the lower and higher temperatures, respectively. Note that the quantum fluctuations lead to a significantly softer PMF.

III. COLLECTIVE DENSITY FLUCTUATIONS

In this section we study the collective density fluctuations of liquid para-hydrogen at the two thermodynamic

| Parameters of the Silvera–Goldman model potential for para-hydrogen in atomic units. |
|---|---|---|---|---|---|---|---|
| \( \alpha \) | \( \delta \) | \( \gamma \) | \( C_6 \) | \( C_8 \) | \( C_{10} \) | \( r_c \) |
| 1.713 | 1.5671 | 0.00993 | 12.14 | 215.2 | 143.1 | 4813.9 | 8.321 |

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-hydrogen at \( T = 14 \) (lower panel) and \( T = 25 \) (upper panel). The classical densities are \( \rho = 0.0321 \) Å\(^{-3}\) and \( \rho = 0.0289 \) Å\(^{-3}\) for the lower and higher temperatures, respectively. Note that the quantum fluctuations lead to a significantly softer PMF.
is known to be very accurate for a variety of mode-coupling approach. The fully self-consistent approximation to the memory kernel based on a quantum form of the memory kernel.

liquids. However, it is well known that for systems with the strict hydrodynamic limit. Since liquid quantitative description of simple exponential form for the memory kernel provides a "soft" potentials of mean force, such as liquid metals, a memory kernel is given by Eq. 11,29

\[ F_0(q, t) = \int_0^t dt' K(q, t-t') \frac{dF(q, t')}{dt'} = 0, \]  

where the Kubo transform of the frequency factor, \( \omega_0^2(q) \), is given by Eq. (7) of Paper I, and \( K(q, t) \) is the Kubo transform of the memory kernel.

In Paper I, we have derived a fully self-consistent approximation to the memory kernel based on a quantum mode-coupling approach. The fully self-consistent approach is known to be very accurate for a variety of classical dense liquids. However, it is well known that for systems with "soft" potentials of mean force, such as liquid metals, a simple exponential form for the memory kernel provides a quantitative description of \( F_0(q, t) \) for values of \( q \) at which the structure factor, \( S(q) = F(q, 0) \), reaches its first maximum, and semiquantitative \( F_0(q, t) \) for smaller values of \( q \) outside the strict hydrodynamic limit. Since liquid para-hydrogen has a PMF that resembles that of a liquid metal, we adopt the simpler approach, where the Kubo transform of the memory kernel is given by\(^{11,29}\)

\[ K(q, t) = K(q, 0) \exp(-t/\tau_0(q)). \]  

In the above equation the relaxation time is estimated using the Lovesey approximation\(^{29}\)

\[ \tau_0(q) = \frac{1}{2} \sqrt{\frac{\pi}{K(q, 0)}}. \]  

where the zero time value of the Kubo transform of the memory kernel is given by Eq. (12) in Paper I. Following the classical notation this approximation is referred to as the quantum viscoelastic model (QVM).\(^{23}\)

In Fig. 2 we plot the values for the Kubo transform of the lifetime, the frequency factor and the structure factor obtained from the PIMC simulations. The calculation of the Kubo transform of the lifetime and the frequency factor involves averages over operators that combine positions and momenta of all particles, while that of the structure factor involves only position dependent operators. As clearly can be seen in the figure, the Kubo transform of the structure factor does not reach the plateau value of one at high values of \( q \), however, the positions of its peaks are identical to those of the "non-Kubo" structure factor.\(^{23}\) The Kubo transform of the lifetime and the frequency factor have a very similar overall shape compared to that of a classical liquid metal. The Kubo transform of the lifetime increases with \( q \) showing a very small dip near the first maximum of \( S(q) \), while the frequency factor has a very pronounced minimum at the first peak in \( S(q) \) giving rise to a quantum de Gennes narrowing discussed below.\(^{10}\)

Using the static input generated by the PIMC simulations, we have solved the QGLE for the Kubo transform of the intermediate scattering function given by Eq. (3). The results for several different values of \( q \) are shown in Fig. 3.
At low values of $q$, the Kubo transform of the intermediate scattering function shows a pronounced oscillatory behavior for the lower temperature liquid, signifying the existence of collective coherent excitations in liquid $\text{para}$-hydrogen. This is not the case for the higher temperature liquid, where the Kubo transform of the intermediate scattering function decays monotonically as a function of time. As $q$ approaches the value of the first maximum in $S(q)$ ($q_{\text{max}} \approx 2$) the decay rate of the Kubo transform of the intermediate scattering function decreases, giving rise to a quantum mechanical narrowing of the dynamic structure factor (see below).

In order to compare our results with recent experimental observation, and with recent simulations using the centroid molecular dynamics (CMD) method, we have calculated the dynamic structure factor, $S(q, \omega)$, given by

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

where $S^\ast(q, \omega)$ is the Fourier–Kubo transform of the intermediate scattering function. The calculated dynamic structure factor for liquid $\text{para}$-hydrogen is shown in Fig. 4. The results for the lower temperature liquid near the triple point are quite different as compared to the results for the high temperature liquid, reflecting the collective coherent density fluctuations of liquid $\text{para}$-hydrogen near the triple point. We also find that our calculated results are in semiquantitative agreement with the experimental results of Bermejo et al., although the instrument response was not included in our calculation (but was included in the calculation of Ref. 7). In particular, a high intensity peak at finite frequency is observed, and disappears around $q = 1.4 \text{ Å}^{-1}$ for the low temperature state point, in agreement with the experiment.

The peak positions and widths do show slight differences from the experimental values, as do the CMD simulations presented by Kinugawa. Comparing our results with the earlier calculation that did not account for the instrument response shows that the CMD 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-transform of the dynamical structure factor, $S_\delta(k, \omega)$, the QVM will satisfy the first three even sum rules, while the CMD method with classical operators as used by Kinugawa will not satisfy any sum rule.

### IV. TRANSPORT

In this section we study the quantum transport of liquid $\text{para}$-hydrogen at the two thermodynamic state points described in Sec. II. First, the self-consistent QGLE derived in Paper I is solved for the velocity autocorrelation function (VACF), $C_v(t)$. Next, the Green–Kubo relation is used to calculate the self-diffusion constant of liquid $\text{para}$-hydrogen. Finally, the results obtained using the present approach are compared to the experimental results, and to other theoretical predictions obtained using the CMD simulation method.

The solution of the QGLE for the VACF requires as input the Kubo transform of the corresponding memory kernel. To obtain both the fast binary portion and the slow mode-coupling portion 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 were generated using the PIMC method described in Paper I. To obtain the vertex we have introduced an additional approximation where the double-Kubo transform of $\hat{V}_\kappa(\mathbf{q})$ given by Eq. (43) in Paper I was replaced with the complex conjugate of $V_\kappa(\mathbf{q})$. The results for the imaginary-time data of $\langle \hat{\phi} \hat{\phi}(\lambda) \rangle$, $\langle \hat{\phi} \hat{\phi}(\lambda) \rangle$, and $\langle \hat{\phi} \hat{\phi}(\lambda) \rangle$ which determine the time moments of the memory kernel are shown in Fig. 5. It is important to note that the average $\langle \hat{\phi} \hat{\phi}(\lambda) \rangle$ depends only on momenta of all particles, the average $\langle \hat{\phi} \hat{\phi}(\lambda) \rangle$ depends only on positions of all particles [since $\hat{\phi} = \hat{F}(\mathbf{r})$, $\hat{\phi} = \hat{F}(\mathbf{r})$ is the force], and the average $\langle \hat{\phi} \hat{\phi}(\lambda) \rangle$ combines both positions and momenta of all particles. We find that the statistical error is quite small for all three imaginary-time correlation functions, indicating the accuracy of the PIMC method. It is interesting to note that the initial value of the Kubo transform of the VACF obtained from the PIMC simulation equals exactly $K_\kappa \text{Im}$ for both thermodynamic points, i.e., the initial value is identical to its classical value, yet the non-Kubo average is much higher, as can clearly be seen in the lower panel of Fig. 5.

In addition to the static input, one requires also the Kubo transforms of the time-dependent intermediate and self-intermediate scattering functions to generate the memory kernel for the VACF. The former can be obtained using the QVM described in Sec. III, while for the latter we assume a Gaussian approximation given by
In Fig. 6 we plot the normalized 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) for liquid para-hydrogen at $T=25$ K, $\rho=0.0190$ Å$^{-3}$ (lower panel).

Comparing the results obtained using our quantum mode-coupling approach to the simulation results obtained using the CMD method, we find very small differences for the VACF. This agreement is somewhat surprising, given that the quantum mode-coupling theory and the CMD simulation method are so different. We find that the initial decay of the VACF using the CMD approach is somewhat faster compared to the result shown in Fig. 6. However, the overall good agreement for the VACF between these different methods, suggests that even simple approximations to memory kernel of the QGLE for the VACF provide quantitative results, and implies that the quantum mode-coupling approach developed in Paper I is accurate and robust.

In Fig. 7 we plot the Kubo transform of the memory kernel of the VACF of liquid para-hydrogen. The overall shape of the memory kernel resembles that obtained from a classical mode-coupling theory. The assumption that there is a distinct separation of time scales between the decay of the binary portion and that of the mode-coupling portion of the memory kernel is clearly evident for liquid para-hydrogen. At the lower temperature state point, the contribution of the slower mode-coupling portion of the memory kernel is dramatic. The area under the fast binary portion is comparable to that of the slow mode-coupling portion. Neglecting the latter for the low temperature case results in a self-diffusion which is about twice as large compared to the full mode-coupling result. This is not the case at the higher temperature state point, where 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.

To obtain the self-diffusion constant of liquid para-
sues are governed by quantum-mechanical effects.\textsuperscript{16,34–38} The frequency-dependent friction appears in the framework of the self-consistent quantum mode-coupling theory.\textsuperscript{15} These results are in very good agreement with the experimental results (0.4 and 1.6 Å\(^2\) ps\(^{-1}\))\textsuperscript{17} and with the full CMD results (0.32 and 1.54 Å\(^2\) ps\(^{-1}\)).\textsuperscript{33} It should be emphasized that the mode-coupling portion of the memory kernel is \textit{essential} for obtaining the self-diffusion constant at the lower temperature point that is in quantitative agreement with the experimental value. The classical result for the self-diffusion at \(T = 25\) K, \(\rho = 0.0289\) Å\(^3\) is 0.5 Å\(^2\) ps\(^{-1}\), more than three times smaller compared with the quantum result. Since the initial value of the Kubo transform of the VACF obtained from the PIMC simulations is identical to that of the classical VACF, we conclude that the differences in the self-diffusion constant arise from purely quantum-dynamical effects. These quantum-dynamical processes are well captured by our quantum mode-coupling theory.

Another interesting property that can be obtained within the framework of the self-consistent quantum mode-coupling theory is the frequency-dependent diffusion constant, which is related to the frequency-dependent friction, and is shown in Fig. 8. The frequency-dependent friction appears in the theory of vibrational relaxation, where many dynamical issues are governed by quantum-mechanical effects.\textsuperscript{16,34–38} The shape of the frequency-dependent diffusion constant resembles that of the frequency-dependent rate, recently introduced by Rabani \textit{et al.}\textsuperscript{39} This suggests that the self-diffusion constant of liquid \textit{para}-hydrogen can be obtained using sophisticated numerical analytical continuation of exact imaginary-time PIMC data.\textsuperscript{40}

V. CONCLUSIONS

We have applied the quantum mode-coupling theory developed in Paper I to study density fluctuations and transport in liquid \textit{para}-hydrogen at two thermodynamic state 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 approach taken here is unique in that it does not rely on computing dynamical trajectories of any kind. Rather, the computation of any time-dependent correlation function was accomplished by augmenting an exact (quantum) generalized Langevin equation for the Kubo transform of the corresponding correlation function with exact static structural input generated from an appropriate PIMC simulations method, and a suitable approximation to the memory function.

Motivated by the fact that the inclusion of quantum fluctuations results in a “softening” of the effective potential, we have used a very simple exponential form for the memory function, where the lifetime of the exponential decay of the memory function was obtained from the PIMC simulation method described in Paper I. Following the classical notation, this approximation was referred to as the quantum viscoelastic model. Given the memory kernel, we have solved the QGLE for the intermediate scattering function, and obtained semiquantitative agreement in comparison to the experiment of Bermejo \textit{et al.}\textsuperscript{7} In particular, our method predicts the existence of coherent density fluctuations in liquid \textit{para}-hydrogen near the triple points, in agreement with the experiments. As suggested in Paper I, the QVM can be improved using an approximate closure for the memory function based on a quantum mode-coupling theory.

FIG. 7. A plot of the normalized time-dependent Kubo transform of the memory kernel for the velocity autocorrelation function for liquid \textit{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 \(K_s(t)\), and the slow mode-coupling portion \(K_m(t)\), respectively.

FIG. 8. A plot of the frequency-dependent diffusion constant for liquid \textit{para}-hydrogen at \(T = 14\) K, \(\rho = 0.0235\) Å\(^3\) (solid line), and \(T = 25\) K, \(\rho = 0.0190\) Å\(^3\) (dashed line).
We have also studied the transport properties of liquid para-hydrogen under similar thermodynamic conditions. The static input required to obtain the memory kernel for the VACF was generated within the framework of the PIMC simulation method. In addition, the memory kernel requires as input the intermediate scattering function which was obtained from the QVM, and the self-intermediate scattering function which was obtained from a simple Gaussian approximation. 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. 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. We find that the self-diffusion process of liquid para-hydrogen is strongly determined by a quantum-dynamical process.

The agreement between the results obtained from the quantum mode-coupling theory and the experiments is indeed remarkable. We believe that this level of agreement would be difficult to obtain with other methodologies, such as semiclassical approximations. The success of the quantum mode-coupling approach in the study of collective density fluctuations and transport is in no ways confined to the case of liquid para-hydrogen. This approach should be extremely useful for the difficult problem of the computation of any dynamical correlation functions in other dense quantum liquids, such as superfluid helium. This system has not yet been successfully modeled, as illustrated by the failure of the analytic continuation method.41 This, and other aspects of dynamical phenomena in quantum liquids will be the subject of future study.

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