Quantum Mode Coupling Theory and Path Integral Monte Carlo

Eran Rabani

School of Chemistry, Tel Aviv University, Tel Aviv 69978, Israel.

Abstract. A theory for dynamical correlations in quantum liquids is presented. The approach is based on augmenting an exact quantum generalized Langevin equation (QGLE) for the Kubo transform of the dynamical correlation of interest, combined with an approximation for the memory kernel obtained within the framework of a quantum mode-coupling theory (QMCT) developed by Rabani and Reichman. The solution to the quantum generalized Langevin equation requires as input static equilibrium information which is generated from a path-integral Monte Carlo method suitable for observables that combine positions and momenta of all particles. The theory is applied to the case of liquid para-hydrogen and liquid ortho-deuterium near their triple points. Good agreement for the intermediate scattering function, for the self-diffusion constant, and for the real time velocity autocorrelation function is obtained in comparison to experimental measurements and to numerical results obtained from a maximum entropy analytic continuation approach.

INTRODUCTION

One of the longstanding problems in chemical physics is the quantum mechanical treatment of dynamical properties in highly quantum liquids. It is well known that the calculation of time correlation functions in these condensed phase systems is an extremely difficult task due to the well known sign problem. This difficulty has led to a variety of different techniques to include the effects of quantum fluctuations on the dynamic response in liquids.

Recently, Rabani and Reichman (RR) have developed a molecular hydrodynamic approach suitable for liquids that are characterized by quantum mechanical fluctuations [1, 2, 3, 4]. Their approach is based on augmenting an exact quantum generalized Langevin equation (QGLE) for the dynamical variable of interest and introducing a suitable approximation to the memory function of the QGLE [5, 6, 7]. A similar approach has been developed for the computation of dynamical correlations in classical liquids, and has been applied successfully to a great number of physically interesting classical problems [8, 9, 10].

The solution of the QGLE requires only static, equilibrium information as input, which can be generated using an appropriate path-integral Monte Carlo (PIMC) scheme [11]. The static input involves thermal averages over operators that combine the 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 proceeding I provide a short overview of the Rabani-Reichman quantum mode-coupling theory (QMCT), and describe the PIMC scheme used to generate the equilibrium input required to solve the QGLE. Examples are given for various dynamical
correlations in liquid hydrogen and liquid deuterium.

**QUANTUM MODE COUPLING THEORY**

The QMCT developed by Rabani and Reichman has many similar feature to its classical counterpart. However, the RR theory has been developed for the time evolution of the **Kubo transform** of the correlation function of interest, and therefore is fully quantum mechanical in nature.

Let assume that we are interested in the time evolution of a general dynamical operator $\hat{A}(t)$. Using the following projection operator, $P^\kappa_A$

$$P^\kappa_A = \frac{\langle \hat{A}, \cdots \rangle}{\langle \hat{A}, \hat{A}^\kappa \rangle} \hat{A}^\kappa,$$

(1)

where

$$\hat{A}^\kappa = \frac{1}{\beta \hbar} \int_0^{\beta \hbar} d\lambda e^{-\lambda \hat{H}} \hat{A} e^{\lambda \hat{H}}$$

(2)

is the Kubo transform [12] of the $\hat{A}(t)$, we can write down an exact QGLE for the Kubo transform of the autocorrelation function of $\hat{A}(t)$:

$$\dot{C}^\kappa_A(t) = i \Omega^\kappa_A C^\kappa_A(t) - \int_0^t dt' K^\kappa_A(t') C^\kappa_A(t - t'),$$

(3)

where $\dot{C}^\kappa_A(t) = \partial C^\kappa_A(t) / \partial t$, and the Kubo transforms of the frequency factor, $\Omega^\kappa_A$, and the memory kernel, $K^\kappa_A(t)$, are given by $\Omega^\kappa_A = \langle \hat{A}, \hat{A}^\kappa \rangle$, and $K^\kappa_A(t) = \frac{1}{\langle \hat{A}, \hat{A}^\kappa \rangle} \langle \hat{A}, e^{i(1 - P^\kappa_A) \wedge \hat{A}} \rangle$, respectively.

The above expression for $K^\kappa_A(t)$ combined with the equation of motion for $C^\kappa_A(t)$ is simply another way for rephrasing the quantum Wigner-Liouville equation for the dynamical variable $\hat{A}(t)$. The difficulty of numerically solving the Wigner-Liouville equation for a many-body system is shifted to the difficulty of evaluating the memory kernel. Even in the classical limit, the solution to the memory kernel is still not possible, since the memory kernel involves projected dynamics.

To circumvent this difficulty Rabani and Reichman made approximation to the memory kernel similar to those made in the classical case. Specifically, the memory kernel was written in terms of a sum of a fast decaying “quantum binary” term, $K^\kappa_{A,f}(t)$, and a slower decaying “quantum mode-coupling” term, $K^\kappa_{A,s}(t)$, $K^\kappa_A(t) = K^\kappa_{A,f}(t) + K^\kappa_{A,s}(q,t)$.

The fast decaying binary term can be obtained from a short-time expansion of the exact Kubo transform of the memory function, and is given by

$$K^\kappa_{A,f}(t) = K^\kappa_A(0) f(t / \tau_A),$$

(4)

where $f(x)$ is taken to be a Gaussian $\exp(-x^2)$ or sech$^2(x)$, and the lifetime in Eq. (4) is given by

$$\tau_A = [-\hat{K}_A^\kappa(0) / 2K_A^\kappa(0)]^{-1/2}.$$

(5)
The above expression for the short time portion of the memory kernel is exact to second order in time. The Kubo transforms of the moments of the memory kernel are given by

\[ K_A^\kappa(0) = \frac{\langle \dot{A}, \dot{A}^\kappa \rangle}{\langle A, \dot{A}^\kappa \rangle}, \]

and

\[ K_A^\kappa(0) = -\frac{\langle \dot{A}, \dot{A}^\kappa \rangle}{\langle A, \dot{A}^\kappa \rangle} + [K_A^\kappa(0)]^2. \]  

To obtain the slow decaying mode-coupling portion of the memory kernel, \( K_{A,m}^\kappa(t) \), Rabani and Reichman introduced another projection operator that projects any variable onto the subspace spanned by the slow set of modes. These modes are typically combinations of the self-density and density modes of the liquid, and are given by:

\[ \hat{b}_q^\kappa = \hat{\rho}_s, q \hat{\rho} - \hat{\rho}_{-q} - 1 = N \sum_{\alpha \neq 1} e^{i q (\hat{r}_1 - \hat{r}_\alpha)}. \]  

In terms of this slow variable, the new projection operator is given by:

\[ \mathcal{S}_{v,m}^\kappa = \sum_q \frac{\hat{b}_q^\kappa \hat{b}_q^\dagger \cdots}{NF_s^\kappa(q,0)S_s^\kappa(q)}. \]  

where \( \hat{b}_q^\kappa = \hat{\rho}_s, q \hat{\rho}_s - 1 \), and \( F_s^\kappa(q,0) \) and \( S_s^\kappa(q) \) are the zero-time value of the self-intermediate and intermediate scattering functions, respectively. Rabani and Reichman then applied two common approximations made by mode-coupling theory, namely, they replaced the projected time evolution operator \( e^{i(1-\beta^\kappa)\mathcal{L}t} \) by its projection onto the subspace spanned by \( \hat{b}_q \), and factorized four-point density correlations into a product of two-point density correlations. Under these two approximations the slow mode-coupling portion of the memory kernel is given by:

\[ K_{A,m}^\kappa(t) = \frac{1}{2\pi^2 n(A,\dot{A}^\kappa)} \int_0^\infty dq dq^2 V_s^\kappa(q) V_s^\kappa(q) \left[ F_s^\kappa(q,0) - F_s^\kappa(q,t) \right] F_s^\kappa(q,t), \]  

where \( n \) is the number density. The vertices in Eq. (10) can be approximated by:

\[ V_s^\kappa(q) V_s^\kappa(q) \approx \left| \frac{\langle \hat{b}_q^\kappa \hat{\rho}_s^\kappa \rangle}{NF_s^\kappa(q,0)F_s^\kappa(q,0)} \right|^2. \]  

To generate \( C_s^\kappa(t) \) one needs to generate the binary and mode-coupling terms of the memory kernel. These require as input the values of the memory function at \( t = 0 \), the second time derivative at \( t = 0 \), and the vertex. These static properties can be obtained from the PIMC method described in below. In addition to these time-independent terms, one requires also the Kubo transforms of the time-dependent intermediate (\( F_s^\kappa(q,t) \)) and self-intermediate (\( F_s^\kappa(q,t) \)) scattering functions, both can be generated from the quantum mode-coupling theory described in Ref. [3].
A PATH-INTEGRAL MONTE CARLO SCHEME

A path-integral Monte Carlo scheme suitable for the calculation of the time-independent terms needed for the memory kernel and the frequency factor is described in this section. These static terms involve thermal averages over operators that combine positions and momenta of all particles, and thus special care must be taken. As noted by Schulman, the calculational rules of such operators can be tricky [13].

For the sake of simplicity and clarity I describe the method for the Kubo transform of a general average of the form

$$\psi^K = \langle \hat{O}_\alpha \hat{O}^\dagger_{\alpha'} \rangle = \frac{1}{\beta \hbar} \int_0^\beta \frac{d\lambda}{\hbar} \psi(\lambda) = \frac{1}{\beta \hbar Q} \int_0^\beta \frac{d\lambda}{\hbar} \text{Tr} \ e^{-(\beta - \lambda)\hat{H}} \hat{O}_\alpha e^{-\lambda\hat{H}} \hat{O}^\dagger_{\alpha'}, \quad (12)$$

where $Q = \text{Texp}(-\beta \hat{H})$ is the partition function, and the operator $\hat{O}_\alpha$ is given by the general form

$$\hat{O}_\alpha = (\hat{p}_\alpha G(\hat{r}) + G(\hat{r}) \hat{p}_\alpha), \quad (13)$$

where $G(\hat{r})$ is an arbitrary well-behaved complex function, and $\hat{r} \equiv \hat{r}_1, \cdots, \hat{r}_N$ is a shorthand notation for the position vectors of all liquid particles. The derivation of the Kubo transform of an average that contains higher powers of momentum can be obtained following similar lines given below [11].

Using the coordinate representation, the trace in Eq. (12) can be written as

$$\psi(\lambda) = \frac{1}{Q} \int d\mathbf{r} d\mathbf{r}' \langle \mathbf{r} | e^{-(\beta-\lambda)\hat{H}} \hat{O}_\alpha^\dagger e^{-\lambda\hat{H}} | \mathbf{r}' \rangle \langle \mathbf{r}' | \hat{O}_{\alpha'} | \mathbf{r} \rangle. \quad (14)$$

The interval $\beta$ can be discretized into $P$ Trotter slices of size $\epsilon = \beta / P$, such that $\lambda \equiv \lambda_j = (j - 1)\epsilon$, where $j$ is the index of the slice. Inserting complete set of states between the short imaginary time propagators it is easy to show that

$$\psi(\lambda_j) = \int d\mathbf{r}_1 \cdots d\mathbf{r}_{P+1} P_j(\mathbf{r}_1, \cdots, \mathbf{r}_{P+1}) \langle \mathbf{r}_{P-j+1} | \hat{O}_\alpha | \mathbf{r}_{P-j+2} \rangle \langle \mathbf{r}_{P+1} | \hat{O}_{\alpha'} | \mathbf{r}_1 \rangle, \quad (15)$$

where the “open chain” probability, $P_j(\mathbf{r}_1, \cdots, \mathbf{r}_{P+1})$, is given by

$$P_j(\mathbf{r}_1, \cdots, \mathbf{r}_{P+1}) = \frac{1}{Q} \prod_{s \neq P-j+1} P_j(\mathbf{r}_s | e^{-\epsilon\hat{H}} | \mathbf{r}_{s+1}), \quad (16)$$

Using the coordinate representation of the matrix element of the operator $\hat{O}_\alpha$

$$\langle \mathbf{r}' | \hat{p}_\alpha G(\hat{r}) + G(\hat{r}) \hat{p}_\alpha | \mathbf{r} \rangle = i \left( G(\mathbf{r}) \nabla_{\mathbf{r}_\alpha} \delta(\mathbf{r} - \mathbf{r}') - G(\mathbf{r}') \nabla_{\mathbf{r}_\alpha} \delta(\mathbf{r} - \mathbf{r}') \right), \quad (17)$$

and the well-known relation

$$\int d\mathbf{r} f(\mathbf{r}) \nabla_{\mathbf{r}_\alpha} \delta(\mathbf{r}) = - \int d\mathbf{r} \delta(\mathbf{r}) \nabla_{\mathbf{r}_\alpha} [f(\mathbf{r})], \quad (18)$$
it is simple to show that

\[
\psi(\lambda_j) = -\int d\mathbf{r}_1 \cdots d\mathbf{r}_{p+1} \delta(\mathbf{r}_1 - \mathbf{r}_{p+1}) \delta(\mathbf{r}_{p-j+2} - \mathbf{r}_{p-j+1}) \times \\
\left( G^\dagger(\mathbf{r}_{p-j+2}) \nabla_{\mathbf{r}_{p-j+1}}^{\alpha} - G^\dagger(\mathbf{r}_{p-j+1}) \nabla_{\mathbf{r}_{p-j+2}}^{\alpha} \right) \times \\
\left( G(\mathbf{r}_1) \nabla^{\alpha}_{\mathbf{r}_{p+1}^\dagger} - G(\mathbf{r}_{p+1}) \nabla^{\alpha}_{\mathbf{r}_{p+1}^\dagger} \right) P_j(\mathbf{r}_1, \cdots, \mathbf{r}_{p+1}),
\]

(19)

Note that the pairs \( G(\mathbf{r}) \) and \( \nabla_{\mathbf{r}_{\alpha}} \) have different arguments in Eq. (17), which is reflected also in the different imaginary time-slice of \( G(\mathbf{r}) \) and \( \nabla_{\mathbf{r}_{\alpha}} \) in Eq. (19). This guarantees that higher derivatives of the function \( G(\mathbf{r}) \) are not required, however, the more important consequence is that this computational scheme is more stable and thus more accurate [11]. The final step involves the differentiation of \( P_j(\mathbf{r}_1, \cdots, \mathbf{r}_{p+1}) \) and the integration over the two delta functions in Eq. (19), which leads to

\[
\psi(\lambda_j) = -\frac{1}{\mathcal{E}} \int d\mathbf{r}_1 \cdots d\mathbf{r}_p P(\mathbf{r}_1, \cdots, \mathbf{r}_p) \\
\times G^\dagger(\mathbf{r}_{p-j+1}) G(\mathbf{r}_1)(\mathbf{r}_{p-j+2}^\alpha - \mathbf{r}_{p-j}^\alpha)(\mathbf{r}_0^\dagger - \mathbf{r}_{p+1}^\dagger),
\]

(20)

for \( j = 2 \cdots P - 1 \). In the above equation a second order Trotter split for the short imaginary time propagators was used. In the above result only the lowest term in \( 1/\mathcal{E} \) was kept, and \( P(\mathbf{r}_1, \cdots, \mathbf{r}_p) \) is the regular sampling function used in the standard cyclic PIMC method (with \( \mathbf{r}_{p+1} = \mathbf{r}_1 \) and \( \mathbf{r}_0 = \mathbf{r}_1 \)).

**SOME RESULTS**

The most natural application of the quantum mode-coupling theory described above is the study of the density fluctuations and self-diffusion in liquid hydrogen and deuterium. These dense liquids are characterized by highly quantum dynamical susceptibilities, and have been studied extensively both experimentally [14, 15, 16, 17, 18] and theoretically [1, 2, 18, 19, 20, 21, 22]. Therefore, these systems are ideal to assess the accuracy of the RR quantum mode-coupling approach.

The self-diffusion of neat liquid hydrogen can be obtained from the Green-Kubo relation. The equation of motion for the velocity autocorrelation function (VACF) is given by Eq. (3), with \( \hat{A} \equiv \hat{v} \), and a vanishing frequency factor \( \Omega_\nu^X = \langle \hat{v}, \hat{v}^X \rangle = 0 \).

To obtain the static input required by the quantum mode-coupling approach outlined above we have performed PIMC simulations of liquid hydrogen and deuterium in the NVT ensemble with 256 particles interacting via the Silvera-Goldman potential [23] with minimum image periodic boundary conditions. The staging algorithm [24] for Monte Carlo chain moves was employed to compute the numerically exact Kubo-transformed static input. The imaginary time interval was discretized into \( P \) Trotter slices of size \( \mathcal{E} = \beta / P \), where \( \beta = 1 / k_\text{B}T \) is the inverse temperature, and \( P = 20 \) to \( P = 50 \) depending on the thermodynamic point. Approximately \( 3 \times 10^6 \) Monte Carlo passes were made, each pass consisted of attempting moves in all atoms and all the beads that were staged.
FIGURE 1. The real-time velocity autocorrelation function (lower panels) and the frequency dependent diffusion constant (upper panels) of liquid para-hydrogen at $T = 14K$, $\rho = 0.0235\text{Å}^{-3}$ (left panels) and $T = 25K$, $\rho = 0.0190\text{Å}^{-3}$ (right panels). The solid lines are the results of the quantum mode-coupling theory and the dashed lines are the results of the maximum entropy analytic continuation approach.

The real-time VACF and the frequency dependent diffusion constant are shown in Fig. 1. The results obtained from the quantum mode coupling theory (solid line) are compared with the results obtained using the maximum entropy (MaxEnt) analytic continuation method (dashed line) [21]. The agreement between the two methods is remarkable. The best agreement for the VACF is obtained at short times. This is expected since the quantum mode-coupling theory is exact to order $t^6$, and the statistical errors in the MaxEnt analytic continuation method are small at short times. The small deviations between the two methods at longer times may result from increasing statistical errors in the MaxEnt method, or from the approximations introduced in the quantum mode-coupling theory. However, the overall good agreement between the two methods is a strong indication for the robustness and accuracy of both approaches.

The self-diffusion constant of liquid hydrogen can be obtained from the zero frequency value of $D(\omega)$. The values of the self-diffusion constants obtained from the quantum mode-coupling theory are $0.30\text{Å}^2\text{ps}^{-1}$ for the lower temperature and $1.69\text{Å}^2\text{ps}^{-1}$ for the higher temperature. These values are in good agreement with the MaxEnt analytic continuation results ($0.28\text{Å}^2\text{ps}^{-1}$ and $1.47\text{Å}^2\text{ps}^{-1}$) and with the experimental results ($0.44\text{Å}^2\text{ps}^{-1}$ and $1.60\text{Å}^2\text{ps}^{-1}$) [25].

The last application presented here is for density fluctuations in liquid ortho-deuterium and liquid para-hydrogen. The correlation function of interest is the Kubo transformed intermediate scattering function $F^K(q,t) = \left\langle \hat{\rho}_q^{\dagger}(t)\hat{\rho}_q^K(t) \right\rangle$, where $\hat{\rho}_q = \sum_{\alpha=1}^{N} e^{iq\cdot\hat{r}_\alpha}$ is the quantum collective density operator. The details of the derivation of the QGLE for this correlation function and the approximation to the memory kernel
FIGURE 2. Plots of the dynamic structure factor for liquid ortho-deuterium (solid lines) and liquid para-hydrogen (dashed lines). Open circles are experimental results from Ref. [16]. The values of $q$ are in units of inverse angstroms.

are given elsewhere [3, 4].

The experimental observable is the Fourier transform of the intermediate scattering function, namely, the dynamic structure factor, $S(q, \omega)$, which is shown in Fig. 2 for three different wavevectors $q$, at $T = 20.7 K$ (the experimental temperature). The results for ortho-deuterium are compared with the single excitation collective dynamics obtained from a fit to the experimental results of Mukherjee et al. [16]. The agreement between the experimental results and the QMCT results is excellent (note that there are no fitting parameters in the QMCT). In particular the theory captures the position of the high intensity peaks and their width for all three wavevectors shown. In other words, the quantum molecular hydrodynamic approach captures the collective coherent excitations as well as the decoherence relaxation time.

CONCLUSIONS

The Rabani-Reichman quantum mode coupling approach has been applied to study transport and density fluctuations in liquid hydrogen and liquid deuterium. The applications discussed above indicate that the Rabani-Reichman theory provides quantitative results for these dynamical susceptibilities in comparison with experiments and other
computational methods. The simplicity of the quantum mode coupling approach and its applicability to the complex many-body quantum systems discussed here, should be useful in many other situations, including system characterized by non-Boltzmann statistics and quantum impurities in condensed phases.

ACKNOWLEDGMENTS

This work was supported by The Israel Science Foundation (grant number 31/02-1).

REFERENCES