Analytic continuation average spectrum method for transport in quantum liquids

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ABSTRACT

Recently, we have applied the analytic continuation averaged spectrum method (ASM) to calculate collective density fluctuations in quantum liquid [27]. Unlike the maximum entropy (MaxEnt) method, the ASM approach is capable of revealing resolved modes in the dynamic structure factor in agreement with experiments. In this work we further develop the ASM to study single-particle dynamics in quantum liquids with dynamical susceptibilities that are characterized by a smooth spectrum. Surprisingly, we find that for the power spectrum of the velocity autocorrelation function there are pronounced differences in comparison with the MaxEnt approach, even for this simple case of smooth unimodal dynamic response. We show that for liquid para-hydrogen the ASM is closer to the centroid molecular dynamics (CMD) result while for normal liquid helium it agrees better with the quantum mode coupling theory (QMCT) and with the MaxEnt approach.

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1. Introduction

The description of the dynamics of quantum liquids is an important and challenging problem. Phenomena ranging from the rich collective dynamics of superfluid helium [1] to electron transport in liquids [2,3] have long gained the attention of physical scientists. The recent experimental and theoretical attention focus on new questions, such as the interplay between the glass transition and superfluidity [4–6], illustrates the enduring interest in the dynamics of quantum liquids.

In principle simulating the dynamics of quantum liquid should be simple. Essentially any imaginary-time quantum correlation function may be computed [7,8] and then a well-defined analytical continuation to the real-time domain may be carried out [9]. The difficulty with this procedure is that the continuation is numerically unstable, making the results unreliable [9]. While there are several different numerical protocols for performing analytical continuation, the most commonly use method is the maximum entropy (MaxEnt) approach [9–24]. MaxEnt is generally assumed to be accurate in describing spectral functions that have one dominant feature, but is known to have difficulty in resolving fine structure [25–27].

Recently, several related analytical continuation approaches have been developed. The averaged spectrum method (ASM) [28–31], the Genetic Inversion via Falsification of Theories (GIFT) method of Vitali et al. [32], and the Generalized Doetsch formula [33] are examples of such approaches. These methods have been argued to be superior to MaxEnt at least in their ability to resolve sharp spectral features [27,32]. In a recent paper we applied the ASM to the problem of density fluctuations in liquid para-hydrogen and ortho-deuterium [27]. We found that the ASM gave a reasonable description of the coherent scattering function $S(q, \omega)$ and was superior to MaxEnt in describing the sharp quasi-particle peaks revealed in experiments [34–38] and predicted by computational techniques such as the centroid molecular dynamics (CMD) approach [39], and theoretical approaches such as the quantum mode-coupling theory (QMCT) [40].

In this work we investigate single-particle diffusive dynamics as exhibited by the frequency dependent diffusion constant $D(\omega)$ via the ASM approach. The systems we consider are liquid para-hydrogen and normal liquid helium above the lambda transition. These systems have been extensively studied by a variety of techniques [19,21–23,38,41–52]. Such studies have all consistently found that $D(\omega)$ in these systems exhibits only one main broad maximum [19]. In this regard it is expected that MaxEnt should be accurate in its description of $D(\omega)$. Rather surprisingly, we find that while the ASM yields diffusion coefficients consistent with MaxEnt, the spectral features are noticeably different. We demonstrate that for liquid helium the ASM yields a spectrum in close agreement with MaxEnt and QMCT [21], while for para-hydrogen the ASM result is closer to that described by CMD [51,24] and possibly experiments [38].

The paper is organized as follows: In Section 2 we describe the average spectrum method and its implementation to the transport problem. In Section 3 we describe the model for liquid para-hydrogen and normal liquid helium and the computational details, and discuss the results for self-diffusion in these systems. Comparisons
are made between the ASM, MaxEnt, QMCT and CMD. In Section 4 we conclude.

Quantum dynamics in condensed phases has been one of Eli Pollak favorite topics where his contributions span work of several decades [53–57]. It is a great pleasure for us to dedicate this work to him on the occasion of his 60th birthday.

2. Analytic continuation average spectrum method

The analytic continuation of the velocity autocorrelation function and the self-diffusion constant are based on the well-known Green–Kubo relation [19,45,21,40]. For the analytic continuation it is convenient to define a frequency dependent diffusion constant, \( D(\omega) \), which is given in terms of the power spectrum of \( C_v(t) \)

\[
D(\omega) = \int_{-\infty}^{\infty} dt e^{i\omega t} C_v(t),
\]

where the velocity autocorrelation function is given by (from now on we set \( h = 1 \))

\[
C_v(t) = \frac{1}{Z} \text{Tr} \left[ e^{-\beta H} v e^{-\beta H} \cdot \dot{v} \right],
\]

where \( Z = \text{Tr} \left[ e^{-\beta H} \right] \) is the partition function, \( \beta = 1/k_B T \) is the inverse temperature, and \( v \) is the velocity vector of a tagged particle in the liquid. The frequency dependent diffusion constant is analogous to the spectral density used in the analytic continuation of spectral line shapes [58] and to the frequency dependent rate constant used in analytic continuation of the flux-flux correlation function [16,20]. By performing the replacement \( t \to -it \), and using the detailed balance relation \( D(-\omega) = e^{\beta \omega} D(\omega) \) we obtain a relation between the frequency dependent diffusion constant and the imaginary time velocity autocorrelation function, \( G(\tau) \):

\[
G(\tau) = \frac{1}{2\pi} \int_0^\infty d\omega \left[ e^{-\beta \omega} + e^{i \tau \beta \omega} \right] D(\omega),
\]

where \( \tau, \tau \geq 0 \), and

\[
G(\tau) = \frac{1}{Z} \text{Tr} \left[ e^{i\beta \tau H} v e^{-i\beta \tau H} \right]
\]

is the imaginary time velocity autocorrelation function, which, unlike its real time counterpart, is straightforward to numerically obtain by an appropriate path-integral Monte Carlo simulation technique [59,60].

The approach we adopt here to obtain \( G(\tau) \) is based on the method developed in Refs. [61,19]. The result to lowest order in \( \epsilon = \beta/N_c \), where \( N_c \) is the number of Trotter slices, is

\[
G(\tau) = \frac{1}{m \epsilon} \frac{1}{N_c} \sum_{n=1}^{N_c} \int dr_1, \ldots, dr_N,
\]

where \( m \) is the mass, \( N \) is the total number of liquid particles, \( r_i \) is a shorthand notation for the position vector of all liquid particles associated with bead \( j \), \( r_{ij} \) is the position vector of liquid particle \( x \) of bead \( j \), and \( P(r_1, \ldots, r_N) \) is the regular sampling function used in the standard cyclic PICM method (with \( r_0 = r_{N_1} \)).

In the present study we apply the recently developed averaged spectrum method [30,27], related to earlier stochastic continuation approaches [28,31,29], to invert the integral in Eq. (4) to get \( D(\omega) \).

Following our previous notation we will refer to \( G(\tau) \) as the data (input data generated from the PIMC approach), \( K(\tau, \omega) = e^{-\beta \tau} + e^{i \tau \beta \omega} \) as the singular kernel, and \( D(\omega) \) as the solution. Furthermore, we will assume that both the imaginary time axis and the frequency axis are discretized such that \( \tau = j_\tau \delta \tau, (j_\tau = 1, \ldots, N_t) \) and \( \omega = j_\omega \delta \omega, (j_\omega = 1, \ldots, N_\omega) \). Hence, Eq. (4) in its discrete form is given by

\[
G_{\omega} = \sum_{j_\tau=1}^{N_t} \delta \omega K_{\omega_j_\tau,\omega} D_{\omega_j_\tau},
\]

where the vectors \( G \) and \( D \) describe the data and the solution in discrete space, with values given by \( G_\omega \) and \( D_{\omega_j_\tau} \), respectively [27].

In the ASM one picks the final solution for \( D \) as the average spectral function obtained by averaging over a posterior distribution [27]:

\[
\overline{D} = \frac{\int d\mathbf{D} \mathcal{D} \mathbf{D} (\mathbf{D}, \mathbf{G})}{\int d\mathbf{D} \mathcal{D} \mathbf{D}}
\]

where \( \mathbf{D} \) is a solution to Eq. (6) for a given input \( \mathbf{G} \), and the posterior distribution can be expressed using Bayes theorem as [62,9]:

\[
P(\mathbf{D} | \mathbf{G}) = P(\mathbf{G} | \mathbf{D}) P(\mathbf{D}).
\]

In the above, \( P(\mathbf{D}) \) is the prior probability distribution and \( P(\mathbf{G} | \mathbf{D}) \) is the likelihood function. As for the case of density fluctuations, we assume a uniform prior for all positive spectral functions with a zero moment that obeys the sum rule [27] \( \sum_j K_{0j_\omega} D_{\omega_j_\tau} \delta \omega = G_\omega \). Thus, we can write \( P(\mathbf{D}) \) as [27]:

\[
P(\mathbf{D}) \propto \delta \left( \sum_j K_{0j_\omega} D_{\omega_j_\tau} \delta \omega - G_\omega \right) \prod_j \mathbb{I} \Theta(D_{\omega_j_\tau}),
\]

where \( \delta(x) \) is Dirac’s delta function and \( \Theta(x) \) is the Heaviside step function. The likelihood function appearing in Eq. (8) describing the fluctuations of the imaginary time data. In our previous work we assumed a Gaussian form for the likelihood function [27]:

\[
P(\mathbf{G} | \mathbf{D}) \propto \exp \left\{ -\frac{1}{2} \mathbf{E} \mathbf{G} \right\}
\]

with the “energy” function \( \mathbf{E}(\mathbf{D}) \) given by:

\[
\mathbf{E}(\mathbf{D}) = \text{Tr} (\mathbf{G} - \mathbf{G}_0^p)^T \Sigma^{-1} (\mathbf{G} - \mathbf{G}_0^p),
\]

where we have partitioned the PIMC data into \( n \) bins each contains \( m \) measurements, the vector \( \mathbf{G} \) is the average result for bin \( i \), and \( \mathbf{G}_0^p \) is the data vector corresponding to a specific solution \( \mathbf{D} \). The width of the Gaussian distribution is taken from the covariance matrix \( \Sigma \) with elements of \( \Sigma \) given by:

\[
\Sigma_{\omega_j_\tau,\omega_k_\tau} = \frac{1}{n-1} \sum_i (G_{\omega_j_\tau} - \bar{G}_{\omega_j_\tau}) (G_{\omega_k_\tau} - \bar{G}_{\omega_k_\tau}).
\]

3. Model and results

The imaginary time velocity autocorrelations functions required for the analytic continuation approaches were generated by PIMC simulations using the staging algorithm [63] at \( T = 14 \) K and \( \rho = 0.0235 \, \text{A}^{-3} \) for liquid para-hydrogen [64] and \( T = 4 \) K and \( \rho = 0.01873 \, \text{A}^{-3} \) for liquid helium [21]. The imaginary time interval was discretized into \( N_t \) Trotter slices of size \( \epsilon = \beta/N_c \), with \( N_t = 50 \) and \( N_t = 100 \) for liquid para-hydrogen and liquid helium, respectively. Approximately \( 6 \times 10^6 \) Monte Carlo passes were made, each pass consisted of attempting moves in all atoms (total of \( N = 108 \) atoms) and all the beads that were staged. We used the Silvera–Goldman potential for para-hydrogen where the entire molecule is described as a spherical particle [65,66] and the Aziz potential for helium [67].

In Fig. 1 we show the imaginary time data generated for liquid para-hydrogen (lower panel) and liquid helium (upper panel) along with the corresponding ASM results. The solution for \( D(\omega) \) (cf., Eq. (6)) was generated following the recipe of Refs. [30,27]. As pointed above, the frequency access was discretized and two randomly pair of neighboring frequency points, \( j_\omega \) and \( j_\omega + 1 \), were chosen. We then select a random number \( \xi = [-2, 2] \) where
\( x = D_{i,0} K_{0,i} + D_{i,1} K_{0,i+1} \), and make a trial move that preserve the sum rule \( \sum \Delta_i D_i \Delta \theta = \Delta \theta \).

\[
\begin{align*}
D_{i,0}^{\text{new}} &= D_{i,0} + \zeta \frac{K_{i,i+1}}{K_{i,i+1}^* K_{i,i+1}} D_{i,1}^{\text{old}} \\
D_{i,1}^{\text{new}} &= D_{i,1} - \zeta \frac{K_{i,i+1}}{K_{i,i+1}^* K_{i,i+1}} D_{i,0}^{\text{old}}.
\end{align*}
\]

The trial move is accepted only if \( D_{i,1}^{\text{new}} \geq 0 \), i.e., only if the spectrum obeys positivity, with the Metropolis probability given by:

\[
P(D \rightarrow D^{\text{new}}) = P(D^{\text{new}}) \min \left\{ 1, \exp \left[ -\frac{1}{2} \left( E(D^{\text{new}}) - E(D) \right) \right] \right\},
\]

where \( E(D) \) is given by Eq. (11). The ASM results shown in Fig. 1 where averaged over \( \approx 10^8 \) Monte Carlo sweeps, each consists of an attempt to change \( N_{\text{step}} = 1024 \) solution points. As expected, the agreement between the imaginary data generated by the PIMC simulations and imaginary data obtained by the inversion of Eq. (4) is excellent. As is well understood, only disagreement at this level can be used to draw decisive conclusion about the inversion process. However, it is quite satisfactory that the Monte Carlo procedure in the ASM leads to an excellent agreement for the imaginary time data at the same level as the MaxEnt approach.

In Fig. 2 we plot the results for power spectrum of the velocity autocorrelation function, \( D(\omega) \), for both liquids. The ASM results are compared with the MaxEnt [19,21], QMCT [44,21], and CMD methods [43,68,24,51]. Common to all methods is that the power spectrum is asymmetric and is characterized by a single frequency peak. This is precisely the limit in which the different analytic continuation approaches should provide accurate results [45,26].

Indeed, for liquid helium (upper panel of Fig. 2) we find that ASM agrees quite well with the MaxEnt result. In this case, both analytic continuation methods also agree with the QMCT over the entire frequency range. The position of the frequency peak and its width are comparable in all three cases, albeit the fact that the ASM shows a small "bump" at values of \( \omega \) just above the peak in \( D(\omega) \). The bump could certainly result from over-fitting the noise in the imaginary time data. In comparison, the overall shape \( D(\omega) \) calculated from the CMD method is qualitatively similar to that obtained from the QMCT and the analytic continuation methods, however, the position of the peak is somewhat higher and the decay of \( D(\omega) \) at large \( \omega \) is slightly faster for the CMD result. We note in passing, that the ring polymer molecular dynamics (RPMD) [69] approach and the Feynman–Kleinert linearized path-integral molecular dynamics (FK-LPI) [47] method also produces a slower decay of \( D(\omega) \) at large \( \omega \) [51], which implies that this feature is most likely realistic since several different methods predict its presence. However, so far no direct proof of the large frequency behavior of \( D(\omega) \) is known.

In the lower panel of Fig. 2 we plot \( D(\omega) \) for the ASM, MaxEnt, QMCT, and CMD methods for liquid para-hydrogen. In addition, we include the experimental results of Celli et al. [38] based on a Sing-wi–Tosi [70] fit to the experimental data (similar results are obtained using the Berne–Boon–Rice fit [71]). Similar to the case of liquid helium, all methods yield a power spectrum that is asym-

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**Fig. 1.** The imaginary time velocity autocorrelation function calculated from the PIMC technique for liquid helium (upper panel) and liquid para-hydrogen (lower panel). The solid lines are the fits generated by the ASM approach.

**Fig. 2.** The power spectrum \( D(\omega) \) obtained by ASM (green/magenta), MaxEnt approach (red), QMCT (black), and CMD method (blue) for liquid helium (upper panel) and liquid para-hydrogen (lower panel). CMD results are taken from Refs. [51,24] for liquid helium and para-hydrogen, respectively. Experimental results (black solid circles) are taken from Ref. [38]. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
metric and is characterized by a single frequency peak. However, there are pronounced differences between the different methods and in particular between the ASM and MaxEnt results. In this case, the MaxEnt and QMCT show very similar trends both for the position of the peak in \( D(\omega) \), its width and the asymmetric high frequency decay of the spectrum. The ASM approach yields a results that is quantitatively different from the MaxEnt. Specifically, the position of the peak is shifted to higher frequencies and decays quite faster at high frequencies.

To eliminate possible errors in the ASM fitting procedure we include two different scenarios. The first assumes that the input data for the imaginary time velocity autocorrelation function is not correlated, i.e., the covariance matrix \( \Sigma \) (cf., Eq. (12)) is diagonal and the off-diagonal elements are ignored. This recipe is the one that is stable for liquid helium, both for ASM and MaxEnt approaches. In the lower panel of Fig. 2 we also show the result when one takes into account the full covariance matrix (this result is labeled “ASM-corr”). As can be seen the differences between the two recipes is quite small and certainly does not bring the ASM closer to the MaxEnt result.

This disagreement between the ASM and MaxEnt results is unexpected for several reasons. First, the ASM and MaxEnt agree quite well for liquid helium which is characterized by a similar quantumness parameter, \( \epsilon = \sqrt{\frac{E_m}{\sigma}} \) where \( m \) is the mass \( \beta \) the inverse temperature, and \( \sigma \) the inter-particle distance (\( \epsilon_{\text{helium}} = 0.656 \) and \( \epsilon_{\text{para-hydrogen}} = 0.385 \)). Second, the power spectrum of the velocity autocorrelation function is quite smooth and is characterized by a unimodal dynamic response. Thus, this inconsistency between these two approach makes para-hydrogen a challenging case for assessing the different quantum dynamical methods.

To add more confusion to the case of liquid para-hydrogen, in the lower panel of Fig. 2 we also show the experimental results of Celli et al. [38] based on a Singwi–Tosi [70] fit to the experimental data. This fit assumes a Gaussian relation between the real-time velocity autocorrelation function, \( C_v(t) \) and the self-intermediate scattering function, \( F_i(q, t) \):

\[
F_i(q, t) = \exp \left\{ -q^2 \int_0^t dt' C_v(t') |t - t'| \right\}. \tag{15}
\]

This form has been used successfully in the study of self-diffusion in classical dense liquids [72]. As can clearly be seen in the figure, none of the computational/theoretical approaches discussed in this work yields a result that agrees with the experimental observation. In particular, the position of the peak in \( D(\omega) \) is shifted to high frequencies and the sum rule \( \sum K_{ij} D_{ij} \delta \omega = C_0 \) is not preserved. This can result from the nature of the Gaussian relation of Eq. (15), from the approximate procedure of Singwi–Tosi [70], or from errors common to all approaches, for example the usage of the Silvera–Goldman potential which was fitted to crystalline properties only [65,66]. These issues will be the subject of future study.

Before we conclude and for completeness, we show the results for the velocity autocorrelation in real time. As can be seen in Fig. 3 a similar picture emerges, where we show the normalized velocity autocorrelation functions obtained from the ASM, MaxEnt, QMCT, and CMD. For liquid helium, the CMD result differs markedly from the ASM, MaxEnt, and QMCT. In fact, even at short time, where CMD should be exact (for the Kubo transform of the velocity autocorrelation function) it deviates from the other approaches. Comparing the ASM and MaxEnt (which is essentially similar to the QMCT) we find that the two approaches agree well at short times. At longer times there are small deviation where the ASM shows a more oscillatory behavior that is certainly a reflection of the aforementioned “bump” in the corresponding \( D(\omega) \).

4. Conclusions

The calculation of dynamical response in quantum liquids is an extremely challenging task. Often, a Wick rotation may be used to recover real time information and excitation spectra from imaginary time data. In most cases of interest the imaginary time correlation function required as input must be determined numerically via a quantum Monte Carlo technique. The real time response is then obtained by an analytic continuation procedure which is numerically unstable and highly sensitive to statistical error in the imaginary time data. Thus, different analytic continuation schemes may lead to qualitative different result for the dynamic response. Indeed, we have recently shown that this is the case for the dynamic structure factor in liquid para-hydrogen and ortho-deuterium, where two different analytic continuation schemes (ASM and MaxEnt) provide qualitatively different spectra. The difference between the ASM and MaxEnt was attributed to the inability of MaxEnt to resolve well-defined peaks in the spectra and in general, MaxEnt leads to solutions that tend to be too broad and smooth.

The success of the ASM to reveal distinct features in the dynamic structure factor is significant only if the approach is robust and can be used to extract dynamical information for other classes of problems as well. In particular, its accuracy must be tested also for spectral function that are smooth. In such cases, one would expect the ASM and MaxEnt approaches to agree, since the latter is considered accurate for systems characterized by an unimodal dynamic response. This was the major goal of the present study. We have revisited the problem of calculating the velocity autocorrelation function and its smooth power spectrum for liquid para-hydrogen and liquid helium above the lambda transition. Detailed comparison was made between the ASM, MaxEnt, QMCT and CMD methods.

Surprisingly, we find that there are pronounced differences between the ASM and MaxEnt approaches for the power spectrum of the velocity autocorrelation function for liquid para-hydrogen (despite the fact that both predict very similar self-diffusion constants) while the two analytic continuation approaches agree quite well for normal liquid helium. We showed that for liquid para-hydrogen the ASM is closer to the CMD result while for nor-
mal liquid helium it agrees better with the QMCT and with the MaxEnt approach.

The differences between the ASM and MaxEnt methods, attributed in the past to the lack of MaxEnt to reveal fine spectral features, seem to persist even for an unimodal smooth spectral function. The differences between the ASM and MaxEnt approach were attributed to the fact that MaxEnt approach seeks for the single most likely spectrum while the ASM approach averages over many likely candidates [28–31]. In both cases, a different posterior distribution is also used. Revealing the origin of the difference between the two methods is a goal left open for future study.

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