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Frequency-Dependent Diffusion Constant of Quantum Fluids from Path Integral Monte Carlo and Tikhonov's Regularizing Functional

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Abstract: We present a novel implementation of the analytic continuation of the velocity autocorrelation function method that has been developed to study the transport properties of quantum liquids at finite temperatures. To invert the ill-posed linear Fredholm integral equation of the first kind, we combine Tikhonov's first-order regularizing functional with several methods used for automatic selection of the regularization parameter. Taking into account our results, we recommend two methods for automatic selection of the regularization parameter, namely: L-curve and quasi-optimality criterion. We found that the frequency-dependent diffusion power spectrum of normal liquid ^{4}He at $T = 4$ K and $\rho = 0.01873$ Å^{-3} ($\rho = 31.1$ mmol cm^{-3}) is characterized by a single asymmetric peak. The predicted self-diffusion coefficient of ^{4}He at this state point of $0.57-0.58$ Å^2/ps is in excellent agreement with previous works. We demonstrate that, within proposed mathematical treatment of the quantum transport at finite temperatures, the entire real-time frequency-dependent diffusion power spectrum of liquid normal ^{4}He, can be successfully reconstructed from the limited number of Trotter slices and without the knowledge of covariance matrix. Moreover, the small values of regularization parameters (i.e., order of 10^{-7}) indicate that the information about quantum dynamics of normal liquid ^{4}He can be easily withdrawn from the high quality imaginary-time correlation function collected in the standard path integral Monte Carlo simulation.

Introduction

The understanding of dynamics of light particles (such as proton, electron, molecular hydrogen, helium, and others) at finite temperatures is essential for the designing of enzymatic reactions, solar cells, proton conducting membranes, quantum sieves, membranes for hydrogen purification, etc.[1-7] Thus, the fundamental works for well-defined quantum systems at finite temperatures are necessary to validate the methods of quantum dynamics, where a satisfactory solution has not been found yet. Of all quantum liquids,

^{4}He is the most common and characteristic one.[8] It is, therefore, an ideal system for investigating the microscopic origin of quantum effects and doing comparisons between experiments and theory.[9-14]

Rabani et al.[14] published the paper where they compared several techniques used for estimating the frequency-dependent diffusion constant in normal liquid helium above the λ transition. The techniques studied were the quantum version of mode-coupling theory (QMCT),[15-18] the numerical analytic continuation method (NAC),[14,19] the centroid molecular dynamics (CMD),[20-24] and the Nakayama–Makri semiclassical approach (SC).[25,26] Their study showed that all aforementioned methods yielded similar self-diffusion constants (i.e., zero time value of the velocity autocorrelation)

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for normal liquid ^{4}He at $T = 4$ K and $\rho = 0.01873$ Å^{-3} ($\rho = 31.1$ mmol cm^{-3}). Moreover, all mentioned methods predicted asymmetric power spectrum of the quantum velocity autocorrelation function characterized by a single frequency peak. However, the power spectrum, over the entire frequency range, obtained with QMCT and NAC was quite different comparing to the results obtained using other methods. In other words, the diffusion of normal liquid ^{4}He at finite frequency (i.e., collective dynamics of quantum particles) depends on the method used for the study of dynamics. Hone et al.[27] investigated the same state point for ^{4}He using Feynman−Kleinert linearized path integral (FK-LPI) molecular dynamics,[28,29] ring polymer molecular dynamics (RPMD),[30−35] and CMD. They also observed significant differences among the results obtained for the quantum correction functions with these three methods over the short time and intermediate regions of the frequency spectrum. They concluded that it was not possible to assert which method was more accurate, owing to the lack of a benchmark result to compare with.

The analytic continuation of the velocity autocorrelation function is, in principle, an exact method that has been successfully used to study the transport properties of 'realistic' liquids.[14−19,36] The imaginary-time correlation function that can be easily computed from the standard path integral Monte Carlo (PIMC) method yields a real frequency-dependent diffusion constant from an inversion of the integral equation. This problem is ill-posed (i.e., ill-conditioned) because the imaginary-time correlation function is defined over a finite range of imaginary time as well as it contains statistical noise.[14−19,36−41] The Bayesian-based maximum entropy (ME) combined with the correlation matrix have been successfully used for inversion of the ill-posed integral equation. On the other hand, the limitations of ME have been reported.[38−41] Numerous studies have shown that, in general, ME solutions tend to be too broad and smooth and often lack clarity defined peaks.[38−41] In 1963, Tikhonov introduced a new method for approximate solution of ill-posed problems, known as a *regularizing algorithm*.[42] Nowadays, Tikhonov's regularizing functional, supported with several algorithms for automatic selection of the regularization parameter, is a very convenient method used for the approximate solution of board classes of ill-posed problems, including Fredholm and Volterra integral equations.[43−46] It is worth nothing that stochastic regularization[47] (SR) as well as singular value decomposition[39] (SVD) have been used for study of the quantum many-body systems. However, these approaches have not met with much general success.

In the current paper, we implement the first-order Tikhonov's regularizing functional for determination of the frequency-dependent diffusion constant at finite temperatures from the imaginary-time correlation function. Throughout numerical calculations, we show that the frequency-dependent diffusion constant can be successfully reconstructed from the limited number of Trotter slices and without the knowledge of covariance matrix. Moreover, for this particular integral equation, we recommended two methods for automatic selection of the regularization parameter, namely: L-curve and quasi-optimality criterion.[43] Finally, we com-

puted the frequency-dependent diffusion constant for liquid ^{4}He at 4 K and a density of 31.1 mmol cm^{-3}. As for numerical calculations, we found that the power spectrum of the normal liquid ^{4}He velocity autocorrelation function reconstructed from 64, 100, and 120 Trotter slices are almost identical. The predicted self-diffusion coefficient of helium at this state point of 0.57−0.58 Å^2/ps is in excellent agreement with previous works.[14,27] The shape and the position of the frequency-dependent diffusion power spectrum agree well with the results of NAC and QMCT published by Rabani et al.[14]

Theory

A. Inversion of Frequency-Dependent Diffusion Constant from Tikhonov's First-Order Regularizing Functional. Following Rabani et al.,[14−19] the frequency-dependent diffusion constant, $D(\omega)$, can be computed from the following integral equation (from now on, we set $\hbar = 1$, $e = 1$, $M_e = 1$):

$$G_v(\tau) = \frac{1}{2\pi} \int_0^\infty [e^{-\omega\tau} + e^{-(\tau-\beta)\omega}] D(\omega) d\omega \qquad (1)$$

where $G_v(\tau)$ denotes the imaginary-time correlation function, $\beta = (k_b T)^{-1}$ is the inverse temperature, $0 < \tau < \beta$ is the imaginary time, and P is the number of Trotter slices.

The imaginary-time correlation function can be computed in straightforward fashion using an appropriate PMIC simulation,[14−19]

$$G_v(\tau_j) = \delta_{j1}\frac{1}{3m\varepsilon} -$$
$$\frac{1}{N\varepsilon^2} \sum_{\alpha=1}^N \int d\mathbf{r}_1, ..., d\mathbf{r}_P P(\mathbf{r}_1, ..., \mathbf{r}_P)(\mathbf{r}_\alpha^j - \mathbf{r}_\alpha^{j-1})(\mathbf{r}_\alpha^2 - \mathbf{r}_\alpha^1)$$
$$(2)$$

where $\varepsilon = \beta/P$, N is the total number of liquid particles, $\mathbf{r}_j$ is a shorthand notation for the position vectors of all liquid particles assisted with bead j, $\mathbf{r}_\alpha^i$ is the position vector of liquid particle α of bead j, and $P(\mathbf{r}_1, ..., \mathbf{r}_P)$ is the regular sampling function used in standard *cyclic* PIMC method (with $\mathbf{r}_0 = \mathbf{r}_P$).

Equation 1 is the *linear Fredholm integral equation of the first kind* with Laplace-type kernel, which is known to be ill-posed.[42,43] We rewrite eq 1 in generic form:

$$Az = \int_0^b K(\tau, \omega)z(\omega)d\omega = G(\tau), \qquad c \leq \tau \leq d$$
$$(3)$$

$K(\tau,\omega)$ is a real-valued function defined and continuous on the rectangle $\Pi = \{0 \leq \omega \leq b, c \leq \tau \leq d\}$.

We introduce the smoothing functional $M^\gamma[z]$ (i.e., first-order Tikhonov's regularizing functional):[42,43]

$$M^\gamma[z] = \left\|Az - G\right\|^2 + \gamma\left\|z\right\|^2 =$$

$$\int_c^d \left[\int_0^b K(\tau, \omega)z(\omega)\mathrm{d}\omega - G(\tau)\right]^2 \mathrm{d}\tau + \gamma\int_0^b \{z^2(\omega) +$$

$$[z'(\omega)]^2\}\mathrm{d}\omega \quad (4)$$

where $\gamma > 0$ denotes the *regularization parameter.*[42,43]

We choose grids $\{\omega_j\}_{j=1}^n$ and $\{\tau_i\}_{i=1}^m$ on the intervals $[0,b]$ and $[c,d]$, respectively. For simplicity, it is assumed that the grids are uniform with steps h_ω and h_τ. Then, using trapezium quadrature we approximate eq 4 by finite-difference analog:

$$M^\gamma[z] = \sum_{i=1}^m \left[\sum_{j=1}^n a_{ij}z_jh_\omega - G_i\right]^2 h_\tau + \gamma\sum_{j=1}^n z_j^2 h_\omega +$$

$$\gamma\sum_{j=2}^n \frac{(z_j - z_{j-1})^2}{h_\omega} \quad (5)$$

where

$$\begin{matrix} z_j = z(\omega_j), & j = 1, 2, ..., n \\ G_i = G(\tau_i), & i = 1, 2, ..., m \end{matrix} \quad (6)$$

$$\left.\begin{matrix} a_{ij} = K(\tau_i, \omega_j), & j = 2, 3, ..., n - 1 \\ a_{ij} = \dfrac{K(\tau_i, \omega_j)}{2}, & j = 1, n \end{matrix}\right\} i = 1, 2, ..., m \quad (7)$$

Note that for $\gamma > 0$, eqs 5−7 can be easily solved by any method of linear algebra because the resulting matrix is well-defined. However, the sole of the regularizing functional is a correct selection of the regularization parameter, γ, that controls the smoothness of the unknown function, $z(\omega)$. An increase in γ smoothes $z(\omega)$, but simultaneously the agreement between the $G_v(\tau)$ computed from PIMC and the theoretical one becomes worse. However, if γ is chosen to be small, then eq 5 would not be well-conditioned. Simply, the resulting matrix is still singular. The regularization parameter can be selected manually (i.e., through a series of trials by an interactive judgment of the solution) or automatically (i.e., applying some criteria). In the current work, we used three criteria for automatic selection of the regularization parameter, namely: the L-curve, the quasi-optimality criterion, and the generalized cross-validation method. However, we found that for considered regularizing functional, only L-curve and quasi-optimality criterion generate stable solutions.

Both L-curve and quasi-optimality criterion select the regularization parameter in inverse problems without taking into account the noise level. As mentioned by Hansen,[43] the most convenient graphical tool for analysis of discrete ill-posed problems is the so-called L-curve, which is a plot for all valid regularization parameters of the discrete smoothing norm $M^\gamma[z]$, e.g., the (semi)norm $\|z\|^2$ of the regularized solution versus the corresponding residual norm $\|Az - G\|^2$. The L-curve clearly displays the compromise between minimization of these two quantities, which is the heart of any regularization method. For discrete ill-posed problems, it turns out that the L-curve, when plotted in the log−log scale, very often has a characteristic L-shaped appearance (hence its name) with a distinct corner separating the vertical

and horizontal parts of the curve.[43] This corner corresponds to the optimal value of the regularization parameter. Following Tikhonov et al.,[42] the optimal regularization parameter is determined from the minimization of the following norm,

$$\min_{\gamma\in\mathscr{R}^+}\left\|\gamma\frac{\mathrm{d}z^\gamma}{\mathrm{d}\gamma}\right\|^2$$

where z^γ denotes the solution of the discrete smoothing norm $M^\gamma[z]$ for $\gamma > 0$. This rule known as quasi-optimality criterion works remarkably well in practice.

B. Theoretical Study. To investigate the limitations and accuracy of the Tikhonov's regularizing algorithm with automatic selection of γ, we performed an inversion of eq 5 using theoretical imaginary-time correlation data (see eq 1). Since the reported $D(\omega)$ power spectrum for normal liquid ^{4}He is characterized by a single asymmetric peak,[14,27] we model this function by a linear combination of two Gaussian functions:

$$D(\omega) = \zeta f_1 + (1 - \zeta)f_2 \quad (8)$$

$$f_i = \frac{1}{\sqrt{2\pi\delta_i^2}}\exp\left[-\frac{(\omega - \omega_i)^2}{2\delta_i^2}\right] \quad (9)$$

where $0\le \zeta \le 1$, ω_i and δ_i denote the mean and standard deviation of i-th Gaussian function, respectively. We computed $G_v(\tau)$ from eq 1 with parameters corresponding to normal ^{4}He at 4 K. The Feynman path integral representation of quantum particle at finite temperature is an exact for infinite number of Trotter slices.[48,49] Thus, we address the following question: *how the finite number of Trotter slices in isomorphic cyclic polymer impacts the reconstruction of the frequency-dependent diffusion power spectrum?* To answer this question we computed $G_v(\tau)$ for a different number of Trotter slices, i.e., 500, 100, and 50. Next we reconstructed those $D(\omega)$ power spectra from eq 5 using the singular-value decomposition method (SVD) and automatically selected γ from L-curve and quasi-optimality criterion.

C. Normal Liquid Helium. Dynamic properties of low-temperature quantum liquids have been always difficult to measure or to calculate. The dynamic properties of helium at 4 K have been extensively studied by different approximate methods of quantum dynamics.[14,27] That is why we focus on the computation of the frequency-dependent diffusion constant for ^{4}He at 4 K and a density of 31.1 mmol cm^{-3}. In order to obtain the imaginary-time correlation function, that is the input required for the inversion of eq 5, we have performed a series of PIMC simulations in a NVT ensemble at the mentioned above state point. In our simulations, we used 256 helium atoms interacting via HFD-B2 He(4) potential due to Aziz et al.[50] We investigated a different number of Trotter slices, i.e., 1, 4, 8, 16, 32, 64, 100, and 128. For each studied system, we performed 2×10^6 Monte Carlo steps using the staging algorithm. The kinetic energy was computed from thermodynamic estimator.

Results and Discussion

In figure 1, we present the reconstruction of the theoretical $D(\omega)$ power spectra for normal liquid ^{4}He at 4 K. Note that
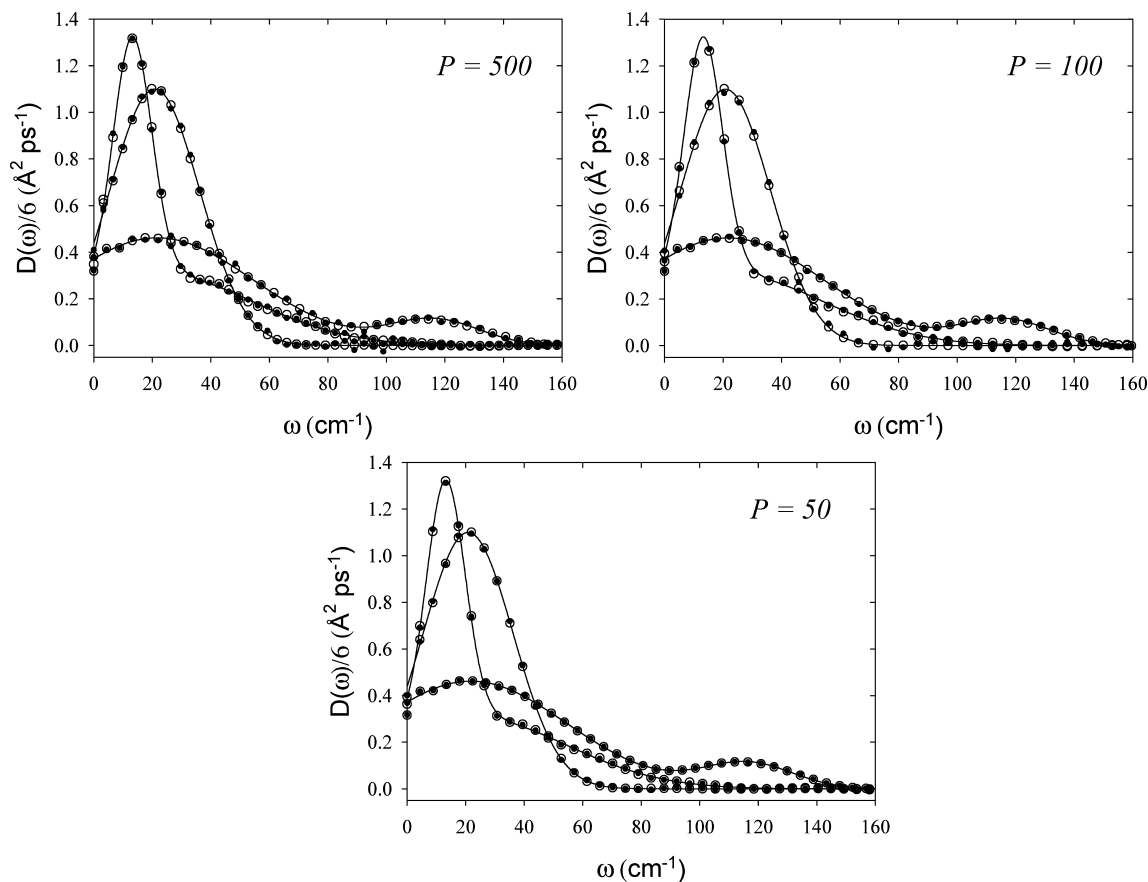
Figure 1. Reconstruction of the theoretical frequency-dependent diffusion power spectra (solid lines) from the first-order Tikhonov's regularizing functional using L-curve (open circles) and quasi-optimality criterion (close circles) for automatic selection of the regularization parameter. Theoretical curves are generated from eqs 1, 8, and 9 using parameters for normal liquid ^{4}He at 4 K and different numbers of Trotter slices, i.e., 500, 100, and 50.

we did not attach the random noise to numerical $G_v(\tau)$ generated from eqs 1, 8, and 9. This is because the high quality $G_v(\tau)$ can be computed from the PIMC simulation. Since $G_v(\tau)$ is always collected for the finite number of Trotter slices, we want to shed more light on the problem of incomplete imaginary-time correlation function. It is commonly known that the static properties of quantum fluids can be easily computed from the finite number of Trotter slices, once the kinetic energy estimator has been converged. However, as far as the dynamics of quantum fluids at finite temperatures is concerned, the same statement has not been reached yet. Throughout numerical experiments, we found that different positions as well as shapes of theoretical $D(\omega)$ power spectra are correctly reproduced using two methods for automatic selection of the regularization parameter, namely: L-curve and quasi-optimality criterion, as is presented in figure 1. Moreover, the first-order Tikhonov's regularizing functional implemented via eqs 5−7, is able to recover original entire $D(\omega)$ power spectra using different numbers of Trotter slices. An important conclusion of our theoretical calculations is that the $D(\omega)$ power spectrum can be successfully reconstructed from a limited number of Trotter slices and without the knowledge of covariance matrix. Let us now focus on the calculation of $D(\omega)$ power spectrum for normal liquid ^{4}He at 4 K and a density of 31.1 mmol cm^{-3}. First, we performed a series of PIMC simulations of ^{4}He at 4 K (31.1 mmol cm^{-3}) to investigate

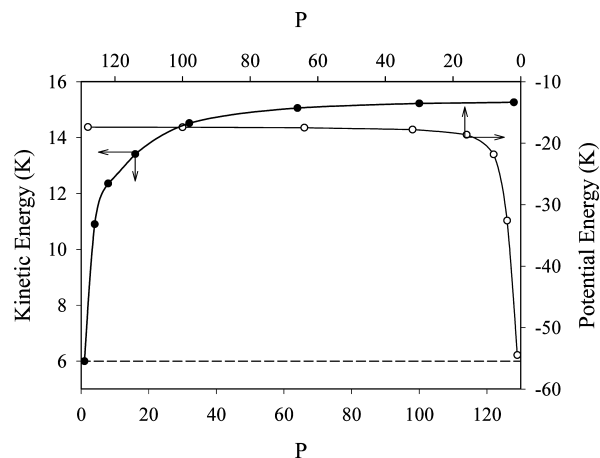**Figure 2.** Kinetic and potential energy of normal liquid ^{4}He (4 K and density of 31.1 mmol cm^{-3}) as a function of the number of Trotter slices. Dashed line corresponds to the classical kinetic energy of ^{4}He at 6 K.

convergence of the kinetic and potential energy estimators (see figure 2). It is clear that convergence of kinetic and potential energy estimators have been achieved for the number of Trotter slices of 100. The kinetic energy of normal liquid ^{4}He at this state point of 15.3 K is close to 15.36 K reported by Hone et al.[27] In figure 3 we present $G_v(\tau)$ collected in PIMC simulation, where the helium atoms were quantized by 128 Trotter slices. Similarly to previous
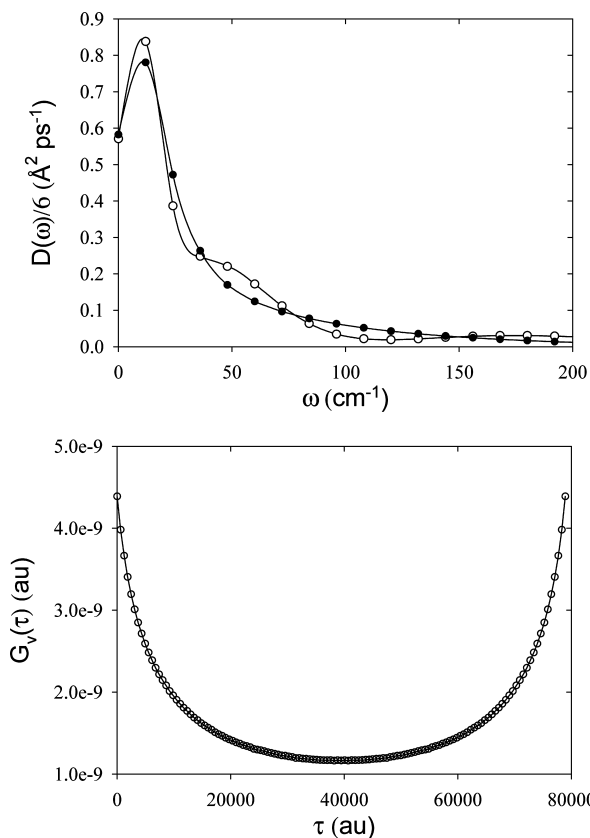
Figure 3. A plot of frequency-dependent diffusion constant for normal liquid ^{4}He at 4 K and density of 31.1 mmol cm^{-3} computed from the first-order Tikhonov's regularizing functional using L-curve (open circles) and quasi-optimality criterion (close circles) for the automatic selection of regularization parameter. Bottom panel shows the imaginary-time correlation function computed from PIMC (open circles) and eq 1 (solid line).

Figure 4. Regularization parameters computed from L-curve (top panel) and quasi-optimality criterion (bottom panel) for normal liquid ^{4}He (4 K and density of 31.1 mmol cm^{-3}) and the number of Trotter slices of 128.

reports,[14,27] we found that the frequency-dependent diffusion power spectrum is characterized by a single asymmetric peak. Note, that both the L-curve and quasi-optimality criterion predict a similar value of the regularization parameter, as displayed in figure 4. The L-curve is characterized by a sharp well-defined corner with the optimum regularization parameter of 1.29×10^{-7}. The quasi-optimal criterion predicts a slightly higher value of the regularization parameter. That is why $D(\omega)$ computed from eq 5, using the second value of the regularization parameter, is smoother. This observation does not depend on the number of Trotter slices used in PIMC simulations (see figure 5). The small values of regularization parameters computed from the both criteria confirmed the high quality of $G_v(\tau)$ collected in our PIMC simulations. Strictly speaking, the final matrix given by eq 5 is singular for $\gamma = 0$; however, its singularity is easily removed by adding a small regularization penalty, i.e. $\gamma \approx 10^{-7}-10^{-6}$. Predicted self-diffusion coefficient of liquid normal ^{4}He for this state point of 0.57−0.58 Å^2/ps is in excellent agreement with previous works.[14,27] Let us now focus on the results presented in Figure 5. As for numerical experiments, we observe that $D(\omega)$ power spectrum can be successfully extracted from a limited number of Trotter slices (i.e., incomplete data of imaginary-time fluctuations). Indeed, for $P = 64$, 100, and 128, the computed $D(\omega)$ power spectra
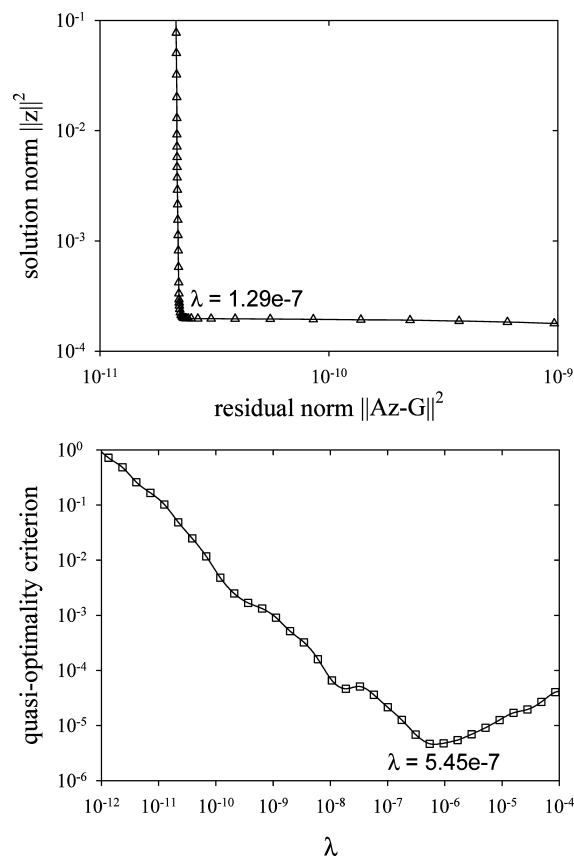
are almost identical. Because the quasi-optimality criterion predicts higher values of regularization parameters in comparison to the L-curve, $D(\omega)$ power spectra inverted using these regularization parameters are smoother. However, both high and decay of the peaks are very similar for both regularization parameters. Surprisingly, even for $P = 32$ and regularization parameter selected from quasi-optimality criterion, the computed $D(\omega)$ power spectrum is very similar to those computed from higher number of Trotter slices.

Although, PIMC simulation generates incomplete data of imaginary-time correlation function (i.e., the number of Trotter slices quantizing quantum particle is in principle finite), our computational results indicate that real time $D(\omega)$ power spectrum of liquid normal ^{4}He at 4 K (in deep quantum region) can be reconstructed from this incomplete information. Furthermore, we show that within proposed mathematical treatment, the covariance matrix is not needed for the reconstruction of $D(\omega)$. Finally, small values of regularization parameters automatically selected from L-curve and quasi-optimality criterion indicate that the singularity of the final matrix given by eq 5 can be easily removed. Thus, it is not surprising that the unique $D(\omega)$ power spectrum of normal liquid helium is reconstructed from a limited number of Trotter slices and without the knowledge of covariance matrix. The extension of the proposed implementation of the analytic continuation of the velocity
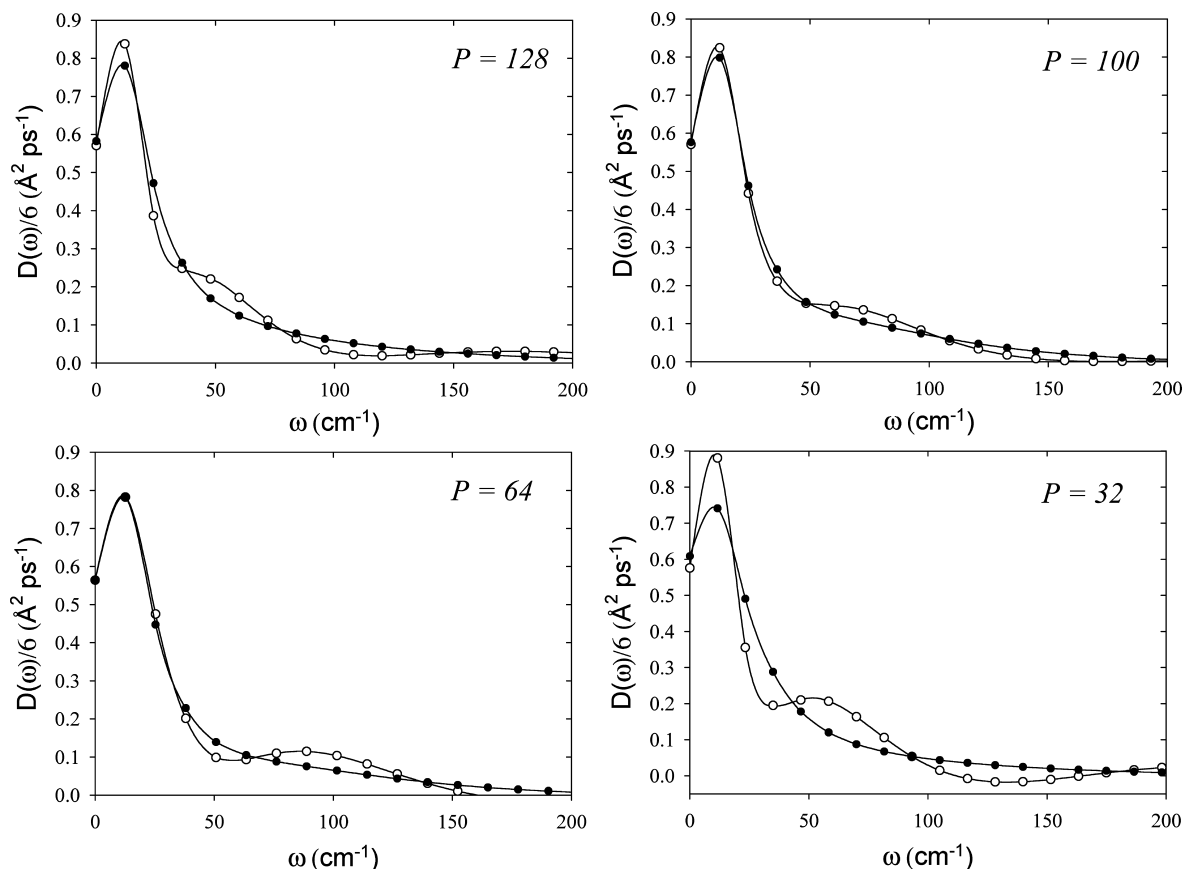
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Figure 5. Plots of frequency-dependent diffusion power spectrum for normal liquid ^{4}He at 4 K and density of 31.1 mmol cm^{-3} computed from the first-order Tikhonov's regularizing functional using L-curve (open circles) and quasi-optimality criterion (close circles) for automatic selection of the regularisation parameter. For PIMC simulations we used different number of Trotter slices, i.e., 128, 100, 64, and 32.

autocorrelation function to the other quantum systems will be the subject of our future works.

Conclusions

In the current work we present a novel implementation of the analytic continuation of the velocity autocorrelation function. This method allows computing a real-time frequency-dependent diffusion power spectrum of quantum fluid from the imaginary-time fluctuations collected in standard PIMC simulation. To solve the ill-posed Fredholm-type integral equation, we combine Tikhonov's first-order regularizing functional with several methods used for automatic selection of the regularization parameter. From our computational results we concluded that two methods used for automatic selection of regularization parameter, namely: the L-curve and quasi-optimality criterion predict reliable frequency-dependent power spectrum of liquid normal ^{4}He. An important conclusion of this study is that, within proposed mathematical treatment of quantum dynamics at finite temperatures, a frequency-dependent diffusion constant can be successfully reconstructed from the limited number of Trotter slices and without the knowledge of covariance matrix. This remark seems to be important for study of transport of other light particles, such as an electron or proton near ambient temperatures.

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