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Binary and multiparticle contributions to the velocity autocorrelation function

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A method for including the contribution of many-body correlation effects to the microscopically obtained results of the two-body contribution to the velocity autocorrelation function has been proposed. A significant improvement over the results obtained through only binary contribution has been found, as can be judged by comparing the results for force and velocity autocorrelation functions of Lennard Jones fluids with that of molecular dynamic simulations. The agreement of results of self-diffusion coefficient is also quite good with simulation data over a wide range of densities and temperatures.

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I. INTRODUCTION

Considerable progress in our theoretical understanding of atomic dynamics at wavelengths and frequencies on the molecular scale of liquids and dense gases has been made during the last three decades [1–3]. Time autocorrelation functions, such as the ones associated with velocity and density, contain information about the dynamics of atomic motions of a system. Computer simulation techniques and neutron scattering experiments have given an invaluable information about the various time correlation functions (TCFs). Theoretically, Mori's memory function (MF) technique has played a key role in the calculations of these time correlation functions.

The microscopic calculations of the memory function in a specific problem can be initiated in two different ways. One of the approaches is based on the investigations of a generalized phase-space kinetic equation for arbitrary frequency and wavelength. The use of phase-space coordinates enables one to analyze the microscopic details of molecular collisions and thus to perform a direct calculation of the time correlation function in terms of a given potential function and equilibrium distribution function. Due to mathematical complexity of solving the kinetic equation for continuous potentials, these equations have been applied mostly to hard sphere fluids [4]. The difficulty of extending hard sphere kinetic theory to continuous potential systems lies in the fact that the collisions are no longer instantaneous and many-particle dynamics cannot be decomposed into sequences of two-particle collisions. There is yet no tractable kinetic equation which can be readily solved to predict time correlation functions and transport coefficients of fluids, particles of which are interacting via continuous potential.

The alternative theoretical approach for the study of time correlation functions is based on the space-time memory functions. The memory function appearing in the Mori-Zwanzig continued fraction representation of the time correlation function can be so chosen that they preserve a number of properties of the TCFs, regardless of the explicit form of the MF [1,5]. The MF can be written as a sum of two terms [6–8], one reflecting two-particle dynamics, while the second is generally thought of as due to the correlated multiparticle collisions which are important at longer times and at high density. In the space-time description, it has been recently possible [9–12] to evaluate binary contribution (BC) to a system of particles interacting via continuous potential. In these calculations, only two-particle contributions have been included. The results of such microscopic calculations are sufficient to explain the properties of a system at low densities. On the other hand, for dense systems, it is known that multiparticle effects are necessary to predict the dynamical and transport properties. But it has not been possible till now to combine the microscopic calculation of binary contribution with that of multiparticle contribution. This, in fact, is one of the motivation behind the present work.

In this paper, first of all, we have numerically calculated the binary contribution to the force autocorrelation function \( \phi_f(t) \). The force autocorrelation function \( \phi_f(t) \) is the autocorrelation function of the forces at two different times acting on a tagged particle, and is directly related to the calculation of velocity autocorrelation function. The expression for \( \phi_f(t) \) involves the six-dimensional integral over function of potential, pair distribution function, and the time dependent position and momentum. We have used Monte Carlo method to evaluate multiple integrals involved in the expression of \( \phi_f(t) \) for Lennard Jones (LJ) fluids over various densities and temperatures. Having the microscopic information about the binary contribution, we propose here a method for combining it with many-body correlation contribution. Many-body correlation effects are included in the present work by using a phenomenological function. The two parameters of the many-body correlation function are so obtained to satisfy two exact conditions for \( \phi_f(t) \). One of the parameters obtained has a value which is of the order of the three-body contribution to the fourth-sum rule obtained using the superposition approximation.

The velocity autocorrelation function (VACF) has been calculated from the knowledge of the force autocorrelation function \( \phi_f(t) \). The results thus obtained are compared with simulation results at few temperatures and densities, and one observes a significant improvement over binary contribution results. We have also calculated self-diffusion coefficients...
from the time evolution of the force autocorrelation function \( \phi(t) \). Our results for the self-diffusion coefficient are much closer to the simulation results of Heyes [13] and also show a significant improvement over the binary contribution's results. Thus, we are able to add multiparticle contribution and estimate separately the many-body correlation effects to the microscopically obtained binary contribution to the force autocorrelation function \( \phi(t) \).

The layout of the paper is as follows. In Sec. II, we have presented the proposed theory. Results and discussion are given in Sec. III. Conclusion is given in Sec. IV.

II. THEORY

The normalized velocity autocorrelation function

\[
\psi(t) = \langle v_{1x}(0)v_{1x}(t) \rangle / \langle v_{1x}^2(0) \rangle,
\]

is related to the self-diffusion coefficient through the Green Kubo expression [1,2], given as

\[
D = \frac{k_B T}{m} \int_0^\infty \psi(t) dt,
\]

where \( v_{1x}(t) \) is the x-component of the velocity of particle 1 at time \( t \), \( k_B \), \( T \), and \( m \) are the Boltzmann constant, temperature, and atomic mass of the particle, respectively. Using Mori's projection operator procedure, the time evolution of \( \psi(t) \) (VACF) can be written as

\[
\frac{d\psi(t)}{dt} = -\int_0^t K(t-\tau) \psi(\tau) d\tau.
\]

Taking Fourier-Laplace transform of Eq. (3), we get

\[
\tilde{\phi}(\omega) = -\frac{\phi(0)}{\omega + \tilde{K}(\omega)},
\]

where the expression for the first-order memory function is given by

\[
\tilde{K}(\omega) = \left( \frac{\omega \psi_{1x}(0)}{\omega - \psi_{1x}(0)} \right) \left( \int \right) \langle v_{1x}^2(0) \rangle.
\]

In the above equation, \( L \) is the Liouville operator defined by

\[
L = \sum_{j<k} L_{jk} = \sum_j \left( \frac{\partial}{\partial \mathbf{p}_j} - \sum_i F_{ji} \frac{\partial}{\partial \mathbf{q}_i} \right)
\]

where \( F_{jk} = -\partial u(r_{jk}) / \partial r_{jk} \) is the force, \( \mathbf{p} \) is momentum, and \( r_{jk} = |\mathbf{r}_j - \mathbf{r}_k| \). \( Q = 1 - P \) is an operator orthogonal to projection operator \( P = \langle \psi_{1x}^2(0) \rangle^{-1} \langle \psi_{1x}(0) \rangle \langle \psi_{1x}(0) \rangle \). The time evolution of \( \psi(t) \) can be expressed in terms of a conventional correlation function whose time evolution is governed by the original Liouville operator \( L \) rather than the projected one, \( \mathcal{L} \), which appears in Eq. (5). A simple way of doing this is by applying the identity

\[
\frac{\omega}{\mathcal{L} - \omega} = -1 + \frac{\mathcal{L}}{\mathcal{L} - \omega}
\]

to the Fourier-Laplace transform of \( \phi(t) \), given by

\[
\tilde{\phi}(\omega) = \int_0^\infty dt e^{\omega t} \phi(t) = \left\{ \begin{array}{l} v_{1x}(0) \frac{1}{\omega - \mathcal{L}} u_{1x}(0) \\ \end{array} \right.,
\]

twice. This yields

\[
\omega^2 \tilde{\phi}(\omega) = \phi(0) [\omega + \tilde{\phi}(\omega)],
\]

where

\[
\tilde{\phi}(\omega) = \left( \mathcal{L} u_{1x}(0) \right) \left( \int \right) \langle v_{1x}^2(0) \rangle
\]

is the Fourier-Laplace transform of the force autocorrelation function. The comparison of Eqs. (4) and (9) gives the following relation:

\[
\tilde{K}(\omega) = \frac{\omega \tilde{\phi}(\omega)}{\omega - \tilde{\phi}(\omega)}.
\]

Writing

\[
\tilde{\phi}(\omega) = \phi'(\omega) + i \phi''(\omega),
\]

where \( \phi'(\omega) \) and \( \phi''(\omega) \) are the real and imaginary parts, respectively, of \( \tilde{\phi}(\omega) \), we obtain expression for the real and imaginary parts of \( K(\omega) \), respectively, given by

\[
K'(\omega) = \frac{\omega \phi'(\omega) - \omega (\phi''(\omega) + \phi''(\omega))}{[\omega - \phi'(\omega)]^2 + \phi''(\omega)^2},
\]

and

\[
K''(\omega) = \frac{\omega^2 \phi''(\omega)}{[\omega - \phi'(\omega)]^2 + \phi''(\omega)^2}.
\]

Defining the frequency spectrum \( f(\omega) \) of the VACF as

\[
f(\omega) = 2 \phi''(\omega) = 2 \int_0^\infty \cos(\omega t) \phi(t) dt,
\]

where \( \phi''(\omega) \) is the imaginary part of \( \tilde{\phi}(\omega) \), given by

\[
\phi''(\omega) = \left( \frac{\omega + K'(\omega)}{[\omega + K'(\omega)]^2 + [K''(\omega)]^2} \right) \tilde{K}(\omega)
\]

where

\[
\tilde{K}(\omega) = K'(\omega) + i K''(\omega).
\]

Therefore, the time evolution of \( \psi(t) \) can be obtained from...
In order to include the multiparticle contribution to $\phi(t)$, we examine its short-time expansion, which is given as

$$
\phi(t) = V_2 - \frac{t^2}{2!} + \frac{t^4}{4!} + \ldots
$$

where

$$
V_2 = \int \frac{d^6p}{(2\pi)^3} \frac{d^6v}{(2\pi)^3} \left( \frac{k_BT}{m} \right) \left( f_{A}(t) - f_{B}(t) \right)
$$

are essentially 2nd sum rules of the velocity autocorrelation function. The expressions for these sum rules are already known [15] up to sixth order. Here, it is important to note that $V_2$, $V_4$, and $V_6$ involve static correlation up to two, three, and four particles respectively. On the other hand, binary part $\phi_B(t)$ involves only two-particle correlations and has a short-time expansion given as

$$
\phi_B(t) = V_2 - \frac{t^2}{2!} + \frac{t^4}{4!} + \ldots
$$

where $V_{nm}$ represents $n$-body contribution to the $m$th sum rule. From the two expansions (25) and (27), one finds that

$$
\phi(t) = \phi_B(t) - \frac{t^2}{2} V_{A_4} \left( 1 - \frac{V_{6_4} + V_{6_2} t^2 + \ldots}{6 V_{4_3}} \right) \phi_B(t) - A t^2 \phi_B(t)
$$

where $F(s)$ is a multiparticle correlation function even in $s$, and $A$ and $B$ are two parameters. In the present work, we take $F(s)$ as hyperbolic secant form. Parameters $A$ and $B$ can be calculated exactly using two exact relations given by Eq. (20) and the expressions for these parameters are obtained to be

$$
A = \frac{C_2}{C_1} \phi_B(0), \quad B = \frac{C_2}{C_1} \phi_B(0)
$$

where

$$
\phi_B(t) = \int \frac{d^6p}{(2\pi)^3} \frac{d^6v}{(2\pi)^3} \left( f_{A}(t) - f_{B}(t) \right),
$$

$$
C_1 = \int \frac{dx}{\sqrt{2\pi}} \frac{d^6p}{\sqrt{2\pi}} \exp \left[ -\frac{1}{2} \left( \frac{p^2}{m^2} + \frac{x^2}{2} \right) \right] \int \frac{dx}{\sqrt{2\pi}} \frac{d^6p}{\sqrt{2\pi}} \exp \left[ -\frac{1}{2} \left( \frac{p^2}{m^2} + \frac{x^2}{2} \right) \right] = 11.8673.
$$

III. RESULTS AND DISCUSSION

The expression for binary contribution to the force autocorrelation function, i.e., $\phi_B(t)$ given by Eq. (23) involves six-dimensional integral over function of potential, pair distribution function, and the time dependence of position and momentum. We have used Monte Carlo method of multiple integration to evaluate this six-dimensional integral. We perform Monte Carlo integration by a user-supplied [16] 6-dimensional function over a rectangular volume specified by the region of 12-dimensional vector consisting of 6-dimensional “lower left” coordinates of the region, followed by 6-dimensional “upper right” coordinates. The various appropriate inputs used for this integration are $\Delta t^* = 0.0050$, with each iteration approximately with 5000 calls.
FIG. 1. Comparison of our results for the normalized force autocorrelation function \( \phi(t^*)/\phi(0) \) (solid line) with those of molecular dynamics (solid circles) and binary contribution (dotted line) to it, for (a) \( n^* = 0.6 \) and \( T^* = 4.53 \) and (b) \( n^* = 0.84 \) and \( T^* = 0.73 \).

FIG. 2. Comparison of our results for the normalized velocity autocorrelation function \( \psi(t^*)/\psi(0) \) (solid line) with those of molecular dynamics (solid circles) and binary contribution (dotted line) to it, for (a) \( n^* = 0.6 \) and \( T^* = 4.53 \) and (b) \( n^* = 0.84 \) and \( T^* = 0.73 \).

We calculate \( \phi(t) \) from Eq. (28) by separately adding the multiparticle contribution to \( \phi_2(t) \) obtained above. Parameters \( A \) and \( B \) are determined from Eq. (29). It is found that parameter \( A \) thus obtained is of the order of the three-body contribution to the fourth-sum rule \( \langle F_3 \rangle \) obtained by using superposition approximation. It may be noted that like many-body correlation effects, \( A \) and \( B \) also increase with increase in density. The results obtained for \( \phi(t^*) \) are plotted in Figs. 1(a,b) for two different densities and temperatures at (a) \( n^* = 0.6, T^* = 4.53 \) and (b) \( n^* = 0.84, T^* = 0.73 \) (triple point),
where \( n^* = n \sigma^3 \) and \( T^* = k_B T / e \) are, respectively, the reduced density and the reduced temperature. We have compared our results with molecular dynamics (MD) results of Heyes [18] and with the results obtained solely due to binary contribution to \( \phi(t) \). A significant improvement is found over binary contribution results, as can be noted from the Figs. 1(a,b).

From \( \phi(t) \) obtained above, we have calculated the velocity autocorrelation function \( \phi^*(t) \) for same densities and temperatures and compared the results with simulation results of Heyes in Figs. 2(a,b). The binary contribution to \( \phi^*(t) \) is calculated by assuming that \( \phi^*(t) = \Phi^*(t) \) [9], from expressions (16) and (18). The results are also given in Figs. 2(a,b). It can be seen from Fig. 2 that a significant improvement has resulted for both the thermodynamic states and clearly shows the importance of multiparticle correlation effects, especially at high densities.

We have also calculated the self-diffusion coefficient from Eq. (22) and compared our results with simulation results [11] and also with the results from BC only. In Fig. 3, we plot \( D^*(n^*) = D^*(n / \sqrt{m / \sigma^3}) \) as a function of reduced density \( n^* \) for four isotherms. Dotted line shows the results obtained using binary contribution only, at \( T^* = 2.51 \). It can be seen that our results are much closer to MD results, as compared to BC results over a wide range of temperatures and densities. Hence, we have successfully added the multiparticle contribution to the microscopically determined binary contribution results of the force autocorrelation function \( \phi(t) \).

IV. SUMMARY AND CONCLUSION

In this paper, we have written the space-time memory function as a sum of two parts: one associated with binary contribution, descriptive of short-time behavior, and the other associated with multiparticle dynamics, which becomes important at longer times. The results of microscopic calculations involving only binary contribution are alone sufficient to explain the properties of system at low density. But for dense fluids, it is known that multiparticle effects are necessary to predict the dynamical and transport properties. But till now it was not possible to combine the microscopic calculations of binary contribution with that of multiparticle contribution. So, in our present work, we have taken a step ahead in this direction and added the multiparticle contribution separately to the microscopically obtained binary contribution to the force autocorrelation function (FACF). We have taken the multiparticle correlation function as a two-parametric phenomenological function. The two parameters of multiparticle correlation function are exactly obtainable from two exact conditions for FACF. As expected, one of the parameters obtained has been found to be of the order of the three-body contribution to the fourth-sum rule using superposition approximation.

We have also calculated the velocity autocorrelation function from the FACF. Self-diffusion coefficients have been obtained from the time evolution of the FACF at various densities and temperatures. Predicted results for the VACF and self-diffusion coefficients are compared with computer simulation data and show a significant improvement over binary contribution results. The improvements over the results of binary contribution calculations clearly demonstrate the role of multiparticle correlations. Further, our study suggests that systematic inclusion of multiparticle contribution is desirable to understand the dynamics of fluids in terms of interatomic potential.

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Role of many-body correlations in dynamics of liquids

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I. INTRODUCTION

Dynamics of simple liquids exhibit most of the important features of complex systems which makes them excellent candidates to test theories for understanding the basic phenomena responsible for many of their properties. There exists an enormous amount of research work in which dynamics of the simple fluids like Ar/Kr have been investigated covering a wide range of densities and temperatures. One of the aims of such studies has been to extend the available theories for dilute gases in predicting properties of dense gases and liquids. During the last few decades, efforts have been made to extend these theories to supercooled liquids and glasses. One of the theoretical methods to study self- or collective phenomena in these systems is the evaluation of an appropriate time correlation function (TCF). A TCF has been commonly calculated using memory function formalism [1,2] either in the phase-space or in the space-time framework. There exists a mode-coupling theory for calculating memory function which has been successful in understanding the dynamics of both liquid state [3] and glassy phase [4]. On the other hand, exact properties, i.e., sum rules of the time correlation function, can be calculated to understand the microdynamics of dense gases. Such studies [5], which have been using memory function with a single relaxation time, revealed that only first few sum rules are sufficient to obtain a reasonable value of the transport coefficients in simple systems. These studies have also emphasized the role played by triplet and quadruplet correlation functions. However, to understand the dynamics of the system at different length and time scales, two relaxation time models have met with more success [6]. Recently, a memory function with three relaxation times has been used [7] to explain the line shape of the dynamical structure factor of liquid metals. Though these two or three relaxation times have been assigned some physical meaning, it is not yet possible to extract these contributions from the first principle.

An alternative approach for calculating a TCF is through developing models for it without making use of the memory function. One successful approach is due to Zwanzig [8] who proposed to separate the stable packed configuration of the system from the vibrational one. Such an approach exploited by other workers [9] too have predicted good results as far as the transport coefficients are concerned. Microscopically, a TCF can be calculated directly using the cluster expansion technique [10] but so far it has been possible to calculate the binary contribution only. Recently, we have combined [14] the binary contribution determined in a microscopic way with the multiparticle contribution for the force autocorrelation function. This method has provided a good description of the velocity autocorrelation function and self-diffusion coefficient. In spite of the success of various models and theories, it is still not known how to combine the contributions due to two particles, three particles, four particles, and so on. It is also important to investigate whether these different contributions are responsible for the requirement of two, three or, a multirelaxation function to explain the dynamics of liquids. Therefore, in the present work, we express a time correlation function as a time series in terms of the cluster expansion of a Liouville operator. Three and four particle contributions have been estimated by using superposition approximation. It is shown that at intermediate densities, at least two relaxations are needed corresponding to two and three particle correlations. On the other hand, at the thermodynamic state close to the triple point, at least three relaxation times are needed; a third one is attributed to the four particle correlations.

The layout of the paper is as follows. In Sec. II we present the theory. Results obtained are discussed in Sec. III. The paper is summed up in Sec. IV.

II. THEORY

A time correlation function $C(t)$ of any dynamical variable $A(t)$ defined as

$$C(t) = \langle A^*(t)A(0) \rangle,$$  \hspace{1cm} (1)

can be expressed as a Taylor series expansion,
In the above equation, \( M_{2n} \) is the second order sum rule and is defined as
\[
M_{2n} = \left( \frac{\partial}{\partial \phi} A(t) \right) \left. \frac{\partial}{\partial \phi} A(t) \right|_{\phi=0}.
\]

The time dependence of any dynamical variable \( B(t) \) is determined through the Liouville equation
\[
\frac{\partial B(t)}{\partial t} = i [\mathcal{L}, B(t)],
\]
where \( \mathcal{L} \) is the Liouville operator defined by
\[
\mathcal{L} = \mathcal{L}_0 + \sum_{j<k} \mathcal{L}_{jk} = -\sum_j \frac{\partial}{\partial r_j} \sum_m F_{jm} \left[ \frac{\partial}{\partial \phi_j} \frac{\partial}{\partial \phi_m} \right],
\]
with \( F_{jm} = -\partial v_j(r_j-r_m) / \partial r_m \), the force, and \( r_m = r_j - r_k \), \( v_j \) is the potential.

For \( A(t) = dB(t)/dt \), the Fourier-Laplace transform of \( C(t) \) can be written as
\[
\tilde{C}(\omega) = \left( \mathcal{L} B(0) \right) \left. \frac{1}{\mathcal{L} - \omega} \right|_{\phi=0} \mathcal{L} B(0).
\]

The binary contribution to \( C(t) \) can be obtained using the well established cluster expansion technique [10]. The cluster expansion formula is
\[
\frac{1}{\mathcal{L} - \omega} \approx \frac{1}{\mathcal{L}_0 - \omega} + \sum_{j<k} \left[ \frac{1}{\mathcal{L}_0 + \mathcal{L}_{jk} - \omega - \mathcal{L}_0 - \omega} \right] + \ldots
\]

The first term involves the free propagation and the second term contains a sum over a pair of particles. Microscopic expressions for the binary contribution to time correlation functions of force on a tagged particle, transverse, and longitudinal current correlation functions have already [11-13] been obtained. The binary contribution \( C^{(2)}(t) \) contains complete information about the two particle contribution to all the sum rules and can be expanded as
\[
C^{(2)}(t) = \sum_{n=0} (-1)^n M^{(2n)} \frac{t^{2n}}{2n!}.
\]

where \( M^{(2n)} \) represents the \( n \)th body contribution to second sum rule. Using the knowledge [5] that each sum rule of second order contains the contribution of the static correlation functions up to \((2n+1)\)th order, we obtain from Eqs. (2) and (8)
\[
C(t) = C^{(2)}(t) + \sum_{n=0} (-1)^n M^{(2n+1)} \frac{t^{2n}}{2n!} + \sum_{n=0} (-1)^n M^{(2n+2)} \frac{t^{2n+2}}{2n!} + \ldots
\]

The first term represents the time dependent two body contribution, the second term only the three body contribution, the third term only the four body contribution, and so on.

Replacing each individual summation in Eq. (9) by a time dependent function, we obtain
\[
C(t) = C^{(2)}(t) - M^{(3)} \frac{t^3}{2!} + C^{(3)}(t) + M^{(4)} \frac{t^4}{4!} C^{(4)}(t) - \ldots,
\]

where \( C^{(n)}(t) \) represents the \( n \) body time dependent contribution. The above equation expands a TCF in terms of time dependent contributions due to all possible clusters of particles.

The formalism presented here is applicable to time correlation functions like that for the force on a tagged particle, transverse, and longitudinal current correlation functions. However, in the present work, we consider \( A(t) \) as force on a tagged particle, i.e., \( m(d/dt)v(t) \); \( v(t) \) is the velocity of the tagged particle at time \( t \). Using Mori’s projection operator procedure, the relation between the velocity autocorrelation function \( \phi(\omega) \) and the first order memory function \( \tilde{K}(\omega) \) in Fourier-Laplace space can be written as
\[
\tilde{\phi}(\omega) = \frac{\phi(0)}{\omega + i \tilde{K}(\omega)}.
\]

The memory function is related [14] to the force autocorrelation function \( \tilde{C}(\omega) \) as
\[
\tilde{K}(\omega) = \frac{\omega \tilde{C}(\omega)}{\omega - \tilde{C}(\omega)}.
\]

Writing
\[
\tilde{C}(\omega) = C(\omega) + i C'(\omega),
\]
where \( C(\omega) \) and \( C'(\omega) \) are the real and imaginary parts of \( \tilde{C}(\omega) \), we obtain expressions for the real and imaginary parts of \( \tilde{K}(\omega) \), respectively, given by
\[
K'(\omega) = \frac{\omega^2 C'(\omega) - \omega C(\omega) + C^2(\omega)}{[\omega - C(\omega)]^2 + C'^2(\omega)},
\]
and
\[
K''(\omega) = \frac{\omega^2 C'(\omega)}{[\omega - C(\omega)]^2 + C'^2(\omega)}.
\]

The Green-Kubo expression for the self-diffusion coefficient is given as
\[
D = \frac{k_B T}{m K''(0)},
\]

where \( k_B \), \( T \), and \( m \) are the Boltzmann constant, temperature, and atomic mass of the particle, respectively. In order to calculate \( K''(0) \) from Eq. (15), we make use of the following relations
FIG. 1. Variation of the force autocorrelation function \( C(t*)/C(0) \) with reduced time \( t = t(e/m\sigma^2)^{1/2} \); at \( T* = 0.73 \) and \( n* = 0.84 \). The dotted line represents \( C^2(t*)/C(0) \), the dashed line represents the sum of two and three body contributions. The full line represents the sum of two, three, and four body contributions. The solid circles are MD results [17]. The dashed-dotted line is the contribution due to quadruplet correlation.

\[
\lim_{\omega \to 0} C'(\omega) = -\lim_{\omega \to 0} \int_0^\infty C(t)\sin(\omega t)dt = 0, \quad (17)
\]

and

\[
C'(\omega) = \int_0^\infty C(t)\cos(\omega t)dt = \int_0^\infty C(t)[\cos(\omega t) - 1]dt. \quad (18)
\]

For writing the above equation, we have used the following exact relation [1]:

\[
\int_0^\infty C(t)dt = 0. \quad (19)
\]

Using Eqs. (17) and (18) in Eq. (15), we obtain

\[
\lim_{\omega \to 0} \mathcal{C}(\omega) = -\lim_{\omega \to 0} \frac{\omega^2}{C''(\omega)} \int_0^\infty C(t)\lim_{\omega \to 0} \left( \frac{\sin(\omega t)}{\omega} - 1 \right)dt
\]

\[
= -\frac{2}{\int_0^\infty dtC(t)^2}. \quad (20)
\]

Equations (20) and (16) provide us a relation for the diffusion coefficient given [14] as

\[
D = -\frac{k_BT}{2m} \int_0^\infty C(t)\frac{d^2r}{dt^2}dt. \quad (21)
\]

This relation has been verified to provide the same results [14] as that obtained using the Green-Kubo formula for self-diffusion. An alternative derivation of Eq. (21) is presented in the Appendix. To calculate self-diffusion from this expression we need to know the time evolution of the force autocorrelation function \( C(t) \). The contribution due to the pair correlation is given [11] by

\[
C^2(t) = -\frac{n}{m^2\sigma^2} \int dr dp G \frac{\partial g(r)}{\partial x} F_x(r(t)), \quad (22)
\]

where \( g(r) \) and \( G(p) = (1/2\pi\rho_0)^{3/2}e^{-\rho_0^2/2p^2} \) with \( \rho_0 = (mk_BT)^{1/2} \) are, respectively, the static pair correlation function and the Maxwellian momentum distribution. The position vector \( r(t) \) and the momentum vector \( p(t) \) of a particle moving in a central potential field \( u(r) \) obey the Newton's equation of motion given by

\[
\frac{1}{2} \frac{dp_x}{dt} = \frac{m}{2} \frac{d^2x}{dt^2} = F_x(r), \quad \frac{1}{2} \frac{dp_y}{dt} = \frac{m}{2} \frac{d^2y}{dt^2} = F_y(r), \quad \frac{dp_z}{dt} = \frac{dF_z}{dt}, \quad (23)
\]

where \( x, p_x, \) and \( r \) are the initial values of these quantities at time \( t=0 \).

III. RESULTS AND DISCUSSION

The six dimensional integral in Eq. (22) has been evaluated using the Monte Carlo method [15] and the Verlet algorithm [16] for the evaluation of \( r(t) \) for the Lennard-Jones

\[
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\]
fluid. The microscopic contribution due to the two body correlation is shown in Figs. 1 and 2 as dotted lines at \( T^* = 0.6 \), \( \sigma^* = 0.84 \), and at \( T^* = 4.53 \) and \( \sigma^* = 0.6 \), respectively (where \( \sigma \) and \( \epsilon \) are two parameters of Lennard-Jones potential). It can be seen from the figures that the pair contribution is in agreement with molecular dynamics (MD) simulation data [17] (solid circles) only up to \( t^* \) = 0.03. Therefore it becomes essential to include contributions due to the higher order static correlation function. The three body contribution \( C^3(t) \) is estimated so as to include exactly the triplet contribution to the sum rules of the force autocorrelation function up to fourth order. We assume \( C^3(t) = \text{sech}(\alpha t) \) with \( \alpha = (M^3_q / 6M^3_q)^{1/2} \). We prefer \( \text{sech}(\alpha t) \) over the simple exponential function due to its symmetric property which is one of the requirements of the expansion [10]. For the calculation of \( M^3_q \) and \( M^3_q \), we have used the Kirkwood superposition approximation for the static triplet correlation function. The values of \( M^3_q \) [in units of \( (\epsilon/\sigma^2) \)] and \( a \) [in units of \( (\epsilon/\sigma^2)^{1/2} \)] are 49.13794 and 16.22 at \( T^* = 0.73 \) and \( n^* = 0.84 \) and 75.697.6 and 27.04 at \( T^* = 4.53 \) and \( n^* = 0.6 \). The value of \( a \) at \( T^* = 4.53 \) and \( n^* = 0.6 \) is obtained by adjusting the value of \( M^3_q \) by about 20% which is within the error limit due to the superposition approximation [5]. The results obtained by combining two and three body contributions are shown as dashed curves in Figs. 1 and 2. It can be seen from the Fig. 2 that at \( T^* = 4.53 \) and \( n^* = 0.6 \), the dashed curve is in very good agreement with molecular dynamics results [17]. This implies that contributions due to four and higher body correlation functions to \( C(t) \) will have a negligible effect due to their cancellation nature. However, at the triple point, it is noticed that the triplet contribution is effective in correcting the behavior of \( C(t) \) up to \( t^* \approx 0.09 \) as can be judged from comparison with MD data. Therefore at the triple point it appears that it is necessary to add \( C^3(t) \), i.e., the contribution due to four particles. In the present work, we estimate it through a faster decaying function than \( \text{sech}(\alpha t) \), i.e., \( \exp(-bt) \). The value of \( b \) can be determined from the quadruplet contribution to the sum rules and is given as \( \sqrt{M^4_q / 30M^3_q} \). The expression for \( M^4_q \) is available and can be determined using a decoupling approximation [18]. Since nothing is known about \( M^4_q \), we have fitted this and \( M^3_q \) so as to obtain the MD value of \( D \). It was found that the fitted value of \( M^4_q \) is about 15% less than the value predicted by using the decoupling approximation for the quadruplet correlation function in the fourth sum rule of \( C(t) \).

The results obtained by including contributions up to four particles is shown as a full line in Fig. 1, and are in good agreement with MD simulation results (solid circles) up to \( t^* = 0.3 \). It can be seen from the Fig. 1 that \( C(t) \) becomes positive at the triple point at around \( t^* = (\epsilon/\sigma^2)^{1/2} = 0.24 \). This positive lobe is responsible for the rapid fall of \( D \) while approaching the triple point. It is further noted that this positive contribution is arising due to the four body static correlation function and is shown separately as a dashed-dotted line in Fig. 1. Therefore, in a supercooled or glassy state of matter, the four particle contribution is expected to play an important role as it is responsible for the arrest of a tagged particle in the cage formed by a cluster of particles. It is also noted that the four body correlation's contribution starts building only at larger times, implying that these play a vital role in cases where long time effects are quite important. For example, at the triple point, values of \( t^* \) at which pair, triplet, and quadruplet contributions to \( C(t) \) are half of their maxima are 0.035, 0.053, and 0.144, whereas at \( n^* = 0.6 \) and \( T^* = 4.53 \), corresponding values of \( t^* \) for pair and triplet contributions are 0.021 and 0.032. At the triple point and at thermodynamic states close to it, the correlation among more than four particles may have a negligible contribution due to the canceling effect.

In order to understand the wide role played by three and four body contributions, we have also studied the behavior of \( C(t) \) at the critical point of Lennard-Jones fluids. The results obtained for \( C^4(t) \) and that by adding the multiparticle contribution [14] are shown in Fig. 3 as a dashed line and full line, respectively. Since MD results of \( C(t) \) at the critical point is not available, the full line is made to satisfy the two exact conditions \( \int_0^t C(t)dt = 0 \) and \( \int_0^t C(t)dt = -1 \) by adjusting the values of parameters in the multiparticle contribution. It is then found that this predicts the self-diffusion coefficient in good agreement with the MD simulation. It can be seen from Fig. 3 that the two curves are closer to each other than found at the thermodynamic states studied earlier, implying that on further diluting a gas, only the two particle correlation's contribution would be sufficient.

IV. SUMMARY AND CONCLUSION

Summing up, in the present work, it is shown that a TCF can be written as a time series of contributions due to all possible clusters of particles. Each term is associated with at
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least one relaxation time corresponding to contributions due to static correlations of two particles, three particles, four particles, and so on. It is shown that for a TCF of force acting on a tagged particle, it is essential to include the contribution due to the quadruplet correlation function at the triple point. However, at low densities and/or high temperature, only two and three particle contributions are sufficient. Our work systematically demonstrates that as one goes towards the triple point from the critical point, the role played by multiparticle correlation becomes imperative and hence requires more numbers of relaxation times.

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APPENDIX

We present here an alternate method for deriving Eq. (21). The Green-Kubo expression for the self-diffusion coefficient \[ D_{\text{self}} \] is given as

\[
D = \frac{k_B T}{m} \left( \frac{1}{t} \int_0^t \phi(t') dt' \right), \tag{A1}
\]

where \( \phi(t) \) is the normalized velocity autocorrelation function. Integrating Eq. (A1) by parts, we get

\[
D = \frac{k_B T}{m} \int_0^t \phi(t') dt' - \frac{k_B T}{m} \int_0^t \frac{d\phi(t')}{dt} dt = \frac{k_B T}{m} \int_0^t \phi(t') dt'. \tag{A2}
\]

Again integrating Eq. (A2) by parts, we get

\[
D = \int_0^t \frac{d^2 \phi(t')}{dt^2} \, dt' = \frac{k_B T}{2m} \int_0^t \frac{d^2 \phi(t')}{dt^2} \, dt'. \tag{A3}
\]

\(-d^2 \phi(t)/dt^2 = C(t)\) is a force autocorrelation function; we obtain

\[
D = \frac{k_B T}{2m} \int_0^t C(t') dt'. \tag{A4}
\]

In obtaining Eqs. (A2) and (A4), it is required that \( f(t) \) vanishes faster than \( t^{-1} \) for \( t \rightarrow \infty \).

Force and Velocity Autocorrelation Functions of Liquid Metal

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Force and velocity autocorrelation functions of liquid rubidium at six thermodynamic states along liquid-vapour co-existence curve have been studied by calculating time dependent contributions due to static pair, triplet and quadruplet correlations, separately. Binary contribution has been obtained using microscopic expression [1] based on cluster expansion technique. The numerical calculations have been performed [2] using Monte-Carlo method of multiple integration and Verlet algorithm for evaluating time evolution of force. For interatomic potential, we have used Ashcroft pseudopotential with Ichimaru screening and for static pair correlation function, we have used corresponding computer simulation data [3]. Time correlation function of force acting on a tagged particle has been written as a time series containing time dependent contributions due to two, three and four body cluster of particles. Three and four body time dependent contributions have been estimated by phenomenological functions where parameters can be determined from contributions of three and four body static correlations to the sum rules of velocity autocorrelation function. It is found that close to the critical and at intermediate temperatures, contributions due to two and three body static correlation are sufficient. However near the melting point, contribution due to four-body static correlation function is essential to explain velocity and force autocorrelation functions as has been judged by comparing our results with those obtained from computer simulation[3] and predictions of earlier theoretical investigation [4].


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