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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 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 repesentation 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 $\phi_B(t)$. The force autocorrelation function $\phi(t)$ 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 $\phi_B(t)$ 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 $\phi_B(t)$ 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 $\phi(t)$. 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 $\phi(t)$. 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

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

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

$$D=\frac{k_BT}{m}\int_0^\infty \psi(t)dt, \tag{2}$$

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 the $\psi(t)$ (VACF) can be written as

$$\frac{d\psi(t)}{dt}=-\int_0^t \mathcal{K}(t-\tau)\psi(\tau)d\tau. \tag{3}$$

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

$$\tilde{\psi}(\omega)=-\frac{\psi(0)}{\omega+\tilde{\mathcal{K}}(\omega)}, \tag{4}$$

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

$$\tilde{\mathcal{K}}(\omega)=\left\langle \mathcal{QL}v_{1x}(0)\left|\frac{1}{\mathcal{QLQ}-\omega}\right|\mathcal{QL}v_{1x}(0)\right\rangle \Big/ \langle v_{1x}^2(0)\rangle. \tag{5}$$

In the above equation, $\mathcal{L}$ is the Liouville operator defined by

$$\begin{aligned}\mathcal{L}&=\mathcal{L}_0+\sum_{j<k}\mathcal{L}_1(jk)\\ &=-i\sum_j \frac{\mathbf{p}_j}{m}\cdot\frac{\partial}{\partial \mathbf{r}_j}-i\sum_{j<k}\mathbf{F}_{jk}\cdot\left[\frac{\partial}{\partial \mathbf{p}_j}-\frac{\partial}{\partial \mathbf{p}_k}\right],\end{aligned} \tag{6}$$

where $\mathbf{F}_{jk}=-\partial u(r_{jk})/\partial r_j$ is the force, $\mathbf{p}$ is momentum, and $\mathbf{r}_{jk}=|\mathbf{r}_j-\mathbf{r}_k|$. $\mathcal{Q}=1-\mathcal{P}$ is an operator orthogonal to projection operator $\mathcal{P}=\langle v_{1x}^2(0)\rangle^{-1}|v_{1x}(0)\rangle\langle v_{1x}(0)|$. 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 $\mathcal{L}$ rather than the projected one, $\mathcal{QLQ}$, which appears in Eq. (5). A simple way of doing this is by applying the identity

$$\frac{\omega}{\mathcal{L}-\omega}=-1+\frac{\mathcal{L}}{\mathcal{L}-\omega} \tag{7}$$

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

$$\begin{aligned}\tilde{\psi}(\omega)&=i\int_0^\infty dte^{i\omega t}\psi(t)\\ &=\left\langle v_{1x}(0)\left|\frac{1}{\mathcal{L}-\omega}\right|v_{1x}(0)\right\rangle,\end{aligned} \tag{8}$$

twice. This yields

$$\omega^2\tilde{\psi}(\omega)=\psi(0)[-\omega+\tilde{\phi}(\omega)], \tag{9}$$

where

$$\tilde{\phi}(\omega)=\left\langle \mathcal{L}v_{1x}(0)\left|\frac{1}{\mathcal{L}-\omega}\right|\mathcal{L}v_{1x}(0)\right\rangle \Big/ \langle v_{1x}^2(0)\rangle \tag{10}$$

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

$$\tilde{\mathcal{K}}(\omega)=\frac{\omega\tilde{\phi}(\omega)}{\omega-\tilde{\phi}(\omega)}. \tag{11}$$

Writing

$$\tilde{\phi}(\omega)=\phi'(\omega)+i\phi''(\omega), \tag{12}$$

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 $\tilde{\mathcal{K}}(\omega)$, respectively, given by

$$\mathcal{K}'(\omega)=\frac{\omega^2\phi'(\omega)-\omega(\phi'^2(\omega)+\phi''^2(\omega))}{[\omega-\phi'(\omega)]^2+\phi''^2(\omega)}, \tag{13}$$

and

$$\mathcal{K}''(\omega)=\frac{\omega^2\phi''(\omega)}{[\omega-\phi'(\omega)]^2+\phi''^2(\omega)}. \tag{14}$$

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

$$f(\omega)=2\psi''(\omega)=2\int_0^\infty \cos(\omega t)\psi(t)dt, \tag{15}$$

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

$$\psi''(\omega)=\frac{\mathcal{K}''(\omega)}{[\omega+\mathcal{K}'(\omega)]^2+[\mathcal{K}''(\omega)]^2}, \tag{16}$$

where

$$\tilde{\mathcal{K}}(\omega)=\mathcal{K}'(\omega)+i\mathcal{K}''(\omega). \tag{17}$$

Therefore, the time evolution of $\psi(t)$ can be obtained from

$$\psi(t)=\frac{1}{\pi}\int_0^\infty \cos(\omega t)f(\omega)d\omega. \tag{18}$$

The expression for the self-diffusion coefficient obtained from Eqs. (2) and (15) is given as

$$D=\frac{k_BT}{m}\frac{f(0)}{2}=\frac{k_BT}{m\mathcal{K}''(0)}. \tag{19}$$

This expression for the calculation of self-diffusion has been used frequently. However, it has been rarely used by expressing $\mathcal{K}''(0)$ in terms of the force autocorrelation function. In the present work, we use Eq. (14) to evaluate $\mathcal{K}''(0)$. We first note that $\phi(t)$ satisfies two exact relations given as

$$\int_0^\infty \phi(t)dt=0 \quad \text{and} \quad \int_0^\infty t\phi(t)dt=-1. \tag{20}$$

Using these relations and Eq. (14) in $\omega\rightarrow 0$ limit, we find that

$$\lim_{\omega\rightarrow 0}\mathcal{K}''(\omega)=\lim_{\omega\rightarrow 0}\frac{\omega^2}{\phi''(\omega)}=\frac{-2}{\int_0^\infty dt\phi(t)t^2}. \tag{21}$$

This provide us with another relation for the diffusion coefficient, given as

$$D=-\frac{k_BT}{2m}\int_0^\infty \phi(t)t^2dt. \tag{22}$$

This is still an exact result. To calculate self-diffusion from this expression, we need to know time evolution of the force autocorrelation function $\phi(t)$.

The exact calculation of $\phi(t)$ for a fluid consisting of interacting particles is not yet possible. However, Liouville operator appearing in Eq. (6) can be expanded using cluster expansion method [14]. Using this technique, the expression for binary contribution to $\phi(t)$ has been obtained by Pathak, Ranganathan, and Johnson [9]. The expression obtained for binary contribution to $\phi(t)$ is given [9] by

$$\phi_B(t)=\frac{n}{m2\sqrt{2}}\int\int d\mathbf{r}d\mathbf{p}G\left[\frac{p}{\sqrt{2}}\right]\frac{\partial g(r)}{\partial x}F_x(r(t)), \tag{23}$$

where $g(r)$ and $G(p)=(1/2\pi p_0^2)^{3/2}e^{-(p^2/2p_0^2)}$ with $p_0=(mk_BT)^{1/2}$ are, respectively, the static pair correlation function and the Maxwellian momentum distribution. The position vector $\mathbf{r}(t)$ and the momentum vector $\mathbf{p}(t)$ of a particle moving in a central potential field $u(r)$ obey Newton's equation of motion given by

$$\frac{1}{2}\frac{dp_x}{dt}=\frac{m}{2}\frac{d^2x}{dt^2}=F_x(r)=-\frac{\partial u(r)}{\partial x}, \tag{24}$$

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

In order to include the multiparticle contribution to $\phi(t)$, we examine its short-time expansion, which is given as

$$\phi(t)=V_2-V_4\frac{t^2}{2!}+V_6\frac{t^4}{4!}+\cdots, \tag{25}$$

where

$$V_{2n}=\left\langle \frac{d^n}{dt^n}v(t)\frac{d^n}{dt^n}v(t)\right\rangle \bigg/ (k_BT/m) \tag{26}$$

are essentially $2n$th 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 upto 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

$$\phi_B(t)=V_2-V_{42}\frac{t^2}{2!}+V_{62}\frac{t^4}{4!}+\cdots, \tag{27}$$

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

$$\begin{aligned}\phi(t)&=\phi_B(t)-\frac{t^2}{2}V_{43}\left(1-\frac{V_{63}+V_{64}}{6V_{43}}\frac{t^2}{2!}+\cdots\right)\\&\approx\phi_B(t)-At^2F_M(Bt),\end{aligned} \tag{28}$$

where $F(x)$ is a multiparticle correlation function even in x, and A and B are two parameters. In the present work, we take $F(x)$ 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

$$B=\frac{\dfrac{C_2}{C_1}\tilde{\phi}_B(0)}{1+\tilde{\phi}_1(0)} \quad \text{and} \quad A=\frac{B^3}{C_1}\tilde{\phi}_B(0), \tag{29}$$

where $\tilde{\phi}_B(0)=\int_0^\infty\phi_B(t)dt$, $\tilde{\phi}_1(0)=\int_0^\infty t\phi_B(t)dt$, $C_1=\int_0^\infty x^2\text{sech}(x)dx=\pi^3/8$, and $C_2=\int_0^\infty x^3\text{sech}(x)dx=11.8673$.

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

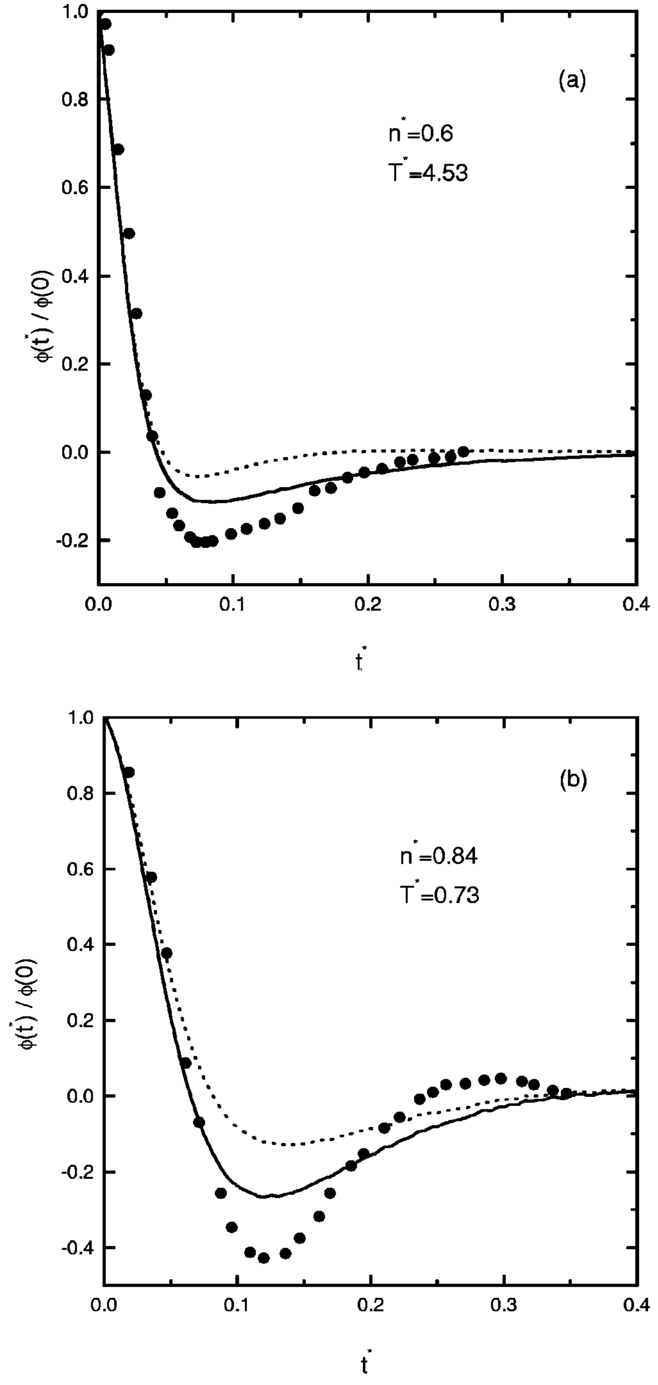

FIG. 1. Comparison of our results for the normalized force autocorrelation function $\phi(t^*)/\phi(0)$ (solid line) with those of molecular dynamics (solid circles) and binary contribution (dotted line) to it, for (a) $n^*=0.6$ and $T^*=4.53$ and (b) $n^*=0.84$ and $T^*=0.73$.

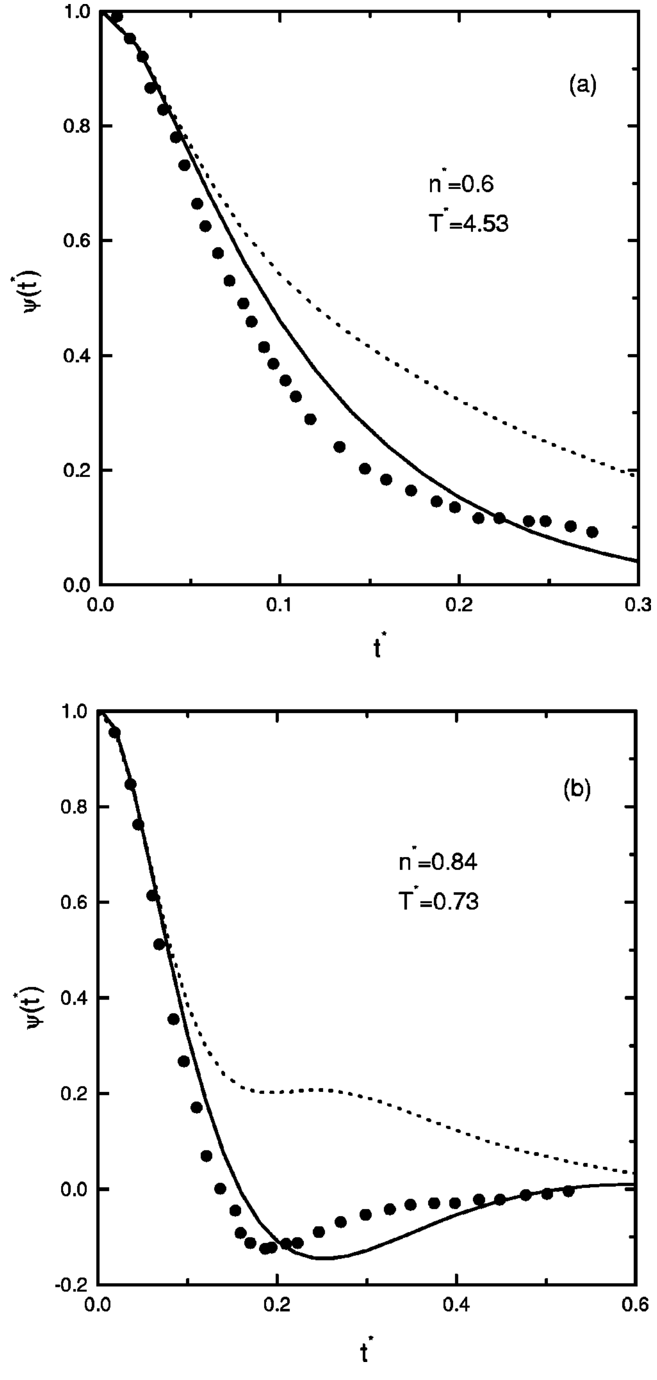

FIG. 2. Comparison of our results for the normalized velocity autocorrelation function $\psi(t^*)$ (solid line) with those of molecular dynamics (solid circles) and binary contribution (dotted line) to it, for (a) $n^*=0.6$ and $T^*=4.53$ and (b) $n^*=0.84$ and $T^*=0.73$.

to the function to do high accuracy integration on the optimized grid over about 15 iterations. A Verlet algorithm [17] is used to determine time dependent position and momentum coordinates. The dimensionless time variable used is $t^*=t/\tau$, with $\tau=\sqrt{m\sigma^2/\epsilon}$ (where σ and ϵ are two parameters of LJ fluids), and $\phi_B(t^*)$ is evaluated for $0\leqslant t^*\leqslant 1.0$. For $t^*\geqslant 1$, $\phi_B(t^*)$ almost approaches 0, as expected.

We calculate $\phi(t)$ from Eq. (28) by separately adding the multiparticle contribution to $\phi_B(t)$ 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 (V_{43}) 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 $T^*=k_BT/\epsilon$ 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 $\psi(t^*)$ for same densities and temperatures and compared the results with simulation results of Heyes in Figs. 2(a,b). The binary contribution to $\psi(t^*)$ is calculated by assuming that $\phi(t)\approx K(t)$ [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 [13] and also with the results from BC only. In Fig. 3, we plot $D^*n^*(D^*=D\sqrt{m/\sigma\epsilon})$ as a function of reduced density $n^*(=n\sigma^3)$ 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 $\phi(t)$.

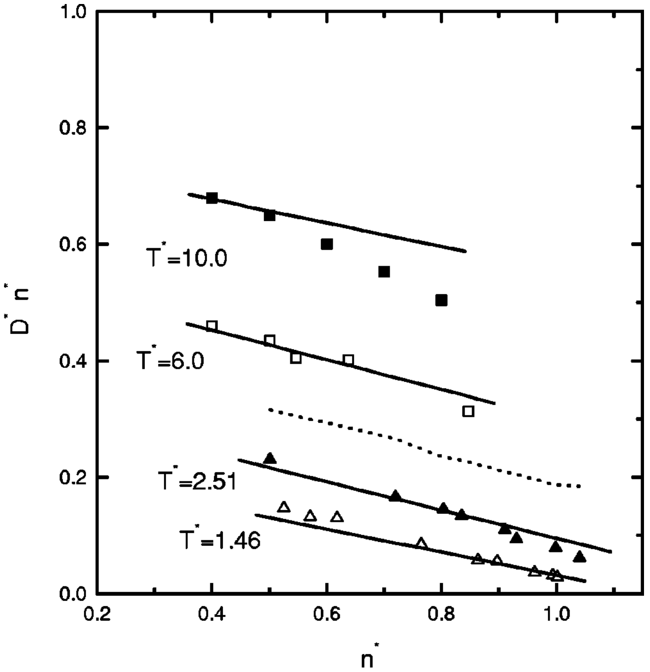

FIG. 3. Variation in the self-diffusion coefficient with reduced density for $T^*=1.46$, 2.51, 6.0, and 10.0. Our results are indicated by solid lines and those of molecular dynamics by symbols. Dotted line shows results due to binary contribution at $T^*=2.51$.

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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