Many-body correlations versus mode-coupling effects in the dynamics of dense gases

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Time dependent contributions due to the triplet and quadruplet correlation functions have been combined with microscopically determined contribution due to the pair correlation function for the transverse stress correlation function. Comparison of the results with simulation data shows that contributions due to two- and three-body static correlation functions are sufficient to understand the viscous dynamics of dense gases. However, close to the triple point, it becomes necessary to include the contribution due to the four-body correlation function. The contribution due to the mode coupling effect has been contrasted with the contribution due to three- and four-body correlation functions. It is noted that the mode coupling contribution plays a similar role as that due to many-body correlation functions.

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I. INTRODUCTION

A lot of work has been done to understand transport phenomena in dense gases and liquids through time correlation functions. Time correlation functions provide informations about the atomic motions at different times. Theoretical attempts have been made to provide more and more accurate predictions of the time evolution of time correlation functions (TCF) and of transport coefficients [1–5]. In many of these attempts, the memory function (MF), appearing in Mori's memory function equation for the calculation of time evolution of TCF, has been a fundamental quantity to be evaluated. A MF can be studied [1,2] either in the phase space or in space-time framework. In space-time framework a TCF/MF can be calculated using cluster expansion technique [6] but so far it has been possible to derive expressions for binary contribution only [7,8]. These microscopic expressions for hard sphere fluids have provided Enskog results for the transport coefficients [7]. For Lennard-Jones (LJ) fluids such a theory, as expected, could explain results of the time correlation function and of transport coefficients only for dilute gases. The binary contribution can be combined with contributions due to higher order static correlation functions so as to make theory applicable to dense fluids. Recently, we have developed a method to combine the microscopic binary contribution to the triplet and quadruplet contributions but for time correlation function of the force acting on a tagged particle [9]. It was found that higher order correlations play an important role for a fluid near the triple point density. It is expected that the role of higher order static correlations can be examined with more authenticity by studying the collective (viscous) phenomena rather than single particle motion. Moreover, the study of viscous phenomena is of significant importance in liquids and glassy phase. Following our earlier work [9], in the present work we write transverse stress autocorrelation function (TSAC) as sum of time dependent contributions due to the static pair, triplet, and quadruplet correlation functions. Having the microscopic expression for the time dependent pair (binary) contribution now, we add to it the time dependent contributions due to triplet and quadruplet correlation functions. It is found that the results obtained for the time development of the TSAC function and for the

shear viscosity are in very good agreement with MD data [10]. Slowing down of the TSAC function at large time is very well explained by contributions due to the higher order static correlation functions.

Alternatively, one of the acceptable theory which accounts for slow dynamics at long time is the mode-coupling theory [11]. Mode-coupling effects start playing a role even at thermodynamics states close to the triple point [12]. The mode-coupling contribution to an autocorrelation function has earlier been combined with the fast decaying contribution which has relevance at short times [13]. So far, only phenomenological forms [14] for the fast decaying part have been chosen. Therefore, it is important to examine how microscopically determined binary contribution could be combined with mode-coupling calculation to provide a useful theory. In the present work, we make an attempt in this direction. By adding the microscopic contribution due to the pair correlation function to the mode-coupling contribution, it is found that it requires modification at intermediate times. From the analysis of short time properties of the TSAC function, a new way of combining the contribution due to the mode-coupling with the pair and triplet correlation function has been derived. Results of this method have been found to explain the viscous dynamics of liquids at the triple point of LJ fluids. The mode-coupling contribution has been compared with the time dependent contribution due to triplet and quadruplet correlation functions. It has been realized that the mode-coupling method is one of the ways to express the dynamical many-body correlation functions. It is expected that the present work is also useful for linking short time and long time dynamics in supercooled liquids and glasses.

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. THEORETICAL FORMALISM

The transverse stress autocorrelation function, $S(t)$ is related to the shear viscosity, η via Green-Kubo relation [1]

$$\eta = \frac{1}{Vk_BT}\int_0^\infty S(t)dt,\tag{1}$$

with

$$S(t) = \langle J_{xy}(t)J_{xy}(0)\rangle, \tag{2}$$

and

$$J_{xy}(t) = \sum_{i=1}^{N}\left[mv_{ix}(t)v_{iy}(t) + F_{iy}(t)x_i(t)\right], \tag{3}$$

where V, k_B, and T are the volume, the Boltzmann constant and the temperature, respectively. $F_{ix}(t)$, $v_{ix}(t)$, and $x_i(t)$ are the x component of force, velocity and position of ith particle at time t. The angular brackets represent a canonical ensemble average. The variable, $J_{xy}(t)$ appearing in the Green-Kubo expression is the sum of the kinetic and the potential part. Consequently, there are three distinct contributions to the shear viscosity; a purely kinetic part, corresponding to transport of momentum via displacement of particle; a purely potential term arising due to interparticle interaction, and kinetic-potential term. Since in liquids and dense gases, potential-potential contribution to the shear viscosity is dominated [15], we consider only the potential part of $J_{xy}(t)$ in the present work.

The microscopic expression [7] for the contribution only due to static pair correlation function to the potential-potential part $S_b^{pp}(t)$ of $S(t)$ is given by

$$S_b(t) = \frac{nk_BT}{4\sqrt{2}P_0^2}\int\int d\mathbf{r}d\mathbf{p}\,G\left(\frac{p}{\sqrt{2}}\right)\frac{\partial g(r)}{\partial y}x(0)x(t)F_y[r(t)], \tag{4}$$

where $x(t)$ and $F_x(t)$ are the x component of position and force of the particle. $g(r)$ and $G(p) = (1/2\pi P_0^2)^{3/2}\exp(-p^2/2P_0^2)$ with $P_0 = (mk_BT)^{1/2}$ are the static pair correlation function and Maxwellian distribution function, respectively. The time evolution of the position vector $\mathbf{r}(t)$ is governed by Newton's law in the form

$$\ddot{x}(t) = \dot{p}_x(t) = \frac{2}{m}F_x(r) = -\frac{2}{m}\frac{\partial u(r)}{\partial x}, \tag{5}$$

where $u(r)$ is the two-body central potential. In Eq. (4) and in what follows, we have suppressed the superscript pp. Equation (4) contains the effect of uncorrelated binary collision only. The derivative of $g(r)$ appears in Eq. (4) and hence the density dependence is more complicated than the explicit linear dependence. This expression has been successful in understanding the dynamics of fluid only at low density [7]. To make theory applicable for dense fluids, it is necessary to include the contribution due to higher order correlation functions.

In order to include the contributions due to the triplet and quadruplet correlation functions to $S(t)$, we examine its short time expansion given by

$$S(t) = S_0 - S_2\frac{t^2}{2!} + S_4\frac{t^4}{4!} - S_6\frac{t^6}{6!} + \cdots, \tag{6}$$

where S_0, $-S_2$, S_4, and $-S_6$ are zeroth, second, fourth, and sixth frequency sum rules of the potential-potential part of the TSAC function. Expressions for the sum rules up to fourth order of the TSAC function are already known [16]. It was noted that S_0, S_2, and S_4 involve static correlation functions up to two, three, and four particles, respectively. Therefore, we write Eq. (6) as

$$S(t) = S_{02} - (S_{22} + S_{23})\frac{t^2}{2!} + (S_{42} + S_{43} + S_{44})\frac{t^4}{4!}$$
$$- (S_{62} + S_{63} + S_{64} + S_{65})\frac{t^6}{6!} + \cdots, \tag{7}$$

where S_{mn} represents n-body contribution to the mth sum rule. Expression (4) contains in it only two-body contribution due to all the nonvanishing sum rules and has the following short time expansion:

$$S_b(t) = S_0 - S_{22}\frac{t^2}{2!} + S_{42}\frac{t^4}{4!} - S_{62}\frac{t^6}{6!} + \cdots. \tag{8}$$

From the expansions (7) and (8), one finds that

$$S(t) = S_b(t) - \frac{t^2}{2!}S_{23}\left(1 - \frac{S_{43}}{6S_{23}}\frac{t^2}{2!} + \cdots\right)$$
$$+ \frac{t^4}{4!}S_{44}\left(1 - \frac{S_{64}}{30S_{44}}t^2 + \cdots\right) - \cdots$$
$$= S_b(t) - S_{23}\frac{t^2}{2}G_3(t) + S_{44}\frac{t^4}{4!}G_4(t) - \cdots, \tag{9}$$

where $G_n(t)$ contains only n-body contribution with the following expansion:

$$G_n(t) = \sum_{m=0}^{\infty}(-1)^m\frac{S_{2n-4+2m,n}}{S_{2n-4,n}}\frac{(2n-4)!}{(2n-4+2m)!}t^{2m}, \quad n \ge 3. \tag{10}$$

In Eq. (10), m is a positive integer. The expansion (9) is exact provided $2n$th sum rule contains static correlations up to $(2+n)$th order, which is known to be correct for the sum rules at least up to sixth order. Equation (9) expands $S(t)$ in terms of time dependent contributions due to all possible cluster of particles. First term in Eq. (9) represents the time dependent two-body contribution, whereas second and third terms explicitly represent contributions due to correlations among three and four particles, respectively. Contributions due to second and higher terms are important at high density and low temperature when particles experience the caging effect. It is noted from Eq. (9) that the contribution due to the triplet correlation builds as $t^2(1-At^2)$ and due to the quadruplet correlation as $t^4(1-Bt^2)$, implying that many-body correlations are important at larger times. Equation (9) is a useful result for studying the role played by many-body correlations in dynamics of fluids and also provides some insight about how binary and long time effects can be combined.

Alternatively, the fast decaying two-body contribution can be combined additively with mode-coupling effects, i.e., contribution due to coupling of slowly varying collective variables. In this approach stress correlation function can be written as [14,15]

$$S(t) = S_b(t) + S_{mc}(t), \qquad (11)$$

where $S_{mc}(t)$ represents the mode-coupling contribution. In the present work, we use the following expression for the mode-coupling contribution given by [15]

$$S_{mc}(t) = \frac{k_B T}{60\pi^2} \int dq q^4 \left(\frac{s'(q)}{s(q)}\right)^2 \left[1 - \left(\frac{F_0(q,t)}{F_s(q,t)}\right)^2\right]\left(\frac{F(q,t)}{s(q)}\right)^2, \qquad (12)$$

where $s(q)$ is static structure factor and $s'(q)$ its first derivative, $F(q,t)$ is intermediate scattering function, $F_s(q,t)$ is its self-part, and $F_0(q,t) = \exp[-(k_B T/2m)q^2 t^2]$ is the free particle limit common to both F and F_s. Here, we have followed the work of Balucani [15] who has simplified Eq. (12) by considering the main contribution to the integral in a narrow range of wave vectors around q_m, q_m being the value of wave vector q at the main peak of $s(q)$. The final simplified expression for $S_{mc}(t)$ is given by

$$S_{mc}(t) = \frac{k_B T}{60\pi^2 \Delta} q_m^4 2\alpha \left[1 - \left(\frac{F_0(q_m,t)}{F_s(q_m,t)}\right)^2\right]\exp\left(-\frac{2B(q_m)t}{s_\pm}\right), \qquad (13)$$

where the structure factor $s_\pm = s(x_\pm)$ with

$$x_\pm^2 = \left(1 + \frac{2[s(q_m) - 1]}{e}\right)\bigg/\left(1 + \frac{[s(q_m) - 1]}{2e}\right) \qquad (14)$$

and

$$B(q_m) = \frac{2k_B T}{\sqrt{\pi m}}\frac{q_m^2}{[\Omega_l^2(q_m) - \Omega^2(q_m)]^{1/2}}. \qquad (15)$$

In Eq. (15), quantities $\Omega_l^2(q_m)$ and $\Omega^2(q_m)$ are explicitly given by

$$\Omega_l^2(q_m) = \frac{3q_m^2 k_B T}{m} + \omega_E^2[1 - j_0(q_m\sigma) + 2j_2(q_m\sigma)], \qquad (16)$$

$$\Omega^2(q_m) = \frac{q_m^2 k_B T}{ms(q_m)}, \qquad (17)$$

where ω_E^2 is Einstein frequency, $j_0(x)$ and $j_2(x)$ are zeroth and second order spherical Bessel functions. In Eq. (13)

$$\alpha = b^2 \int_0^\infty dx \frac{x^2 \exp(-x^2)}{\{1 - b[1 - \exp(-x^2/2)]\}^2}, \qquad (18)$$

with $x = (q - q_m)/\Delta$, Δ being the width of the peak of $h(q)$ $[=s(q) - 1]$ and $b = 1 - [s(q_m)]^{-1}$. In order to calculate $S_{mc}(t)$ from Eq. (13), we need self-scattering function, $F_s(q,t)$. For the calculation of $F_s(q,t)$, we had followed the Mori-continued fraction representation and have truncated the hierarchy at second stage by introducing the appropriate memory function. The expression obtained for the self-part of dynamical structure factor is given by

$$S_s(q,\omega) = \frac{2\delta_1 M_2''(q,\omega)}{[\omega^2 - \delta_1 + \omega M_2'(q,\omega)]^2 + [\omega M_2''(q,\omega)]^2}, \qquad (19)$$

where $M_2'(q,\omega)$ and $M_2''(q,\omega)$ are real and imaginary parts of the Fourier-Laplace transform of the memory function $M_2(q,t)$. For the memory function, we use a phenomenological form $M_2(q,t) = a\,\mathrm{sech}(bt)$ with $a = \delta_2$, $b^2 = \delta_3$. δ_1, δ_2, and δ_3 are related to frequency sum rules of $S_s(q,\omega)$ up to second, fourth, and sixth order, respectively. The expression for second, fourth, and sixth frequency sum rules are available in the literature [17]. $F_s(q,t)$ is finally calculated from

$$F_s(q,t) = \frac{1}{\pi} \int_0^\infty S_s(q,\omega)\cos(\omega t)d\omega. \qquad (20)$$

It has been found from Eq. (12) that $S_{mc}(t)$ varies as t^4 for small time. Equations (11) and (9) then imply that even t^2 terms are not properly taken care of, as S_{23} does not appear in Eq. (11). In view of this we propose

$$S(t) = S_b(t) - S_{23}\frac{t^2}{2}G_3(t) + S_{mc}(t). \qquad (21)$$

Equation (21) contains contributions due to static pair and triplet correlation to all sum rules and long time contribution provided by the mode-coupling term, $S_{mc}(t)$. In the next section, we shall be obtaining results from Eqs. (9), (11), and (21) to understand the role played by contribution due to many-body correlation function and mode-coupling contribution by evaluating $S(t)$ for different densities and temperatures.

III. RESULTS AND DISCUSSION

A. Many-body correlation's contribution

The calculation of $S_b(t)$ involves the integration over six variables and requires inputs like $g(r)$, $x(t)$, $r(t)$ and interatomic potential. For pair correlation function, $g(r)$, we have used theoretical results of Sung and Chandler [18]. Verlet like algorithm [19] has been used to evaluate $x(t)$ and $r(t)$ from Eq. (5) for Lennard-Jones potential. The time step t^* $[=t/\tau$ with $\tau = (m\sigma^2/\epsilon)^{1/2}$ where σ and ϵ are two parameters of LJ potential] taken in the Verlet algorithm is 0.005. For the evaluation of integral, we have used the Monte Carlo method [20]. The integration is performed over a set of the initial configuration. The results obtained are shown in Figs. 1–4 as dotted lines at four thermodynamic states, (i) $n^* = 0.844$, $T^* = 0.72$ (near triple point); (ii) $n^* = 0.844$, $T^* = 1.26$; (iii) $n^* = 0.422$, $T^* = 1.26$; and (iv) $n^* = 0.211$, $T^* = 1.26$. Henceforth, these states will be referred to as states I, II, III, and IV, respectively. $n^* = n\sigma^3$ and $T^* = k_B T/\epsilon$ are, respectively, the reduced density and the reduced temperature. It can be seen from Figs. 1–4 that the binary contribution is not sufficient to explain the time evolution of the potential-potential contribution to the TSAC function even at intermediate times. For example, from Fig. 1, it is observed that the binary contribution, $S_b(t)$ is in agreement only up to $t^* = 0.02$ with MD simulation data [10]. Therefore, it becomes essential to include contributions due to higher order static
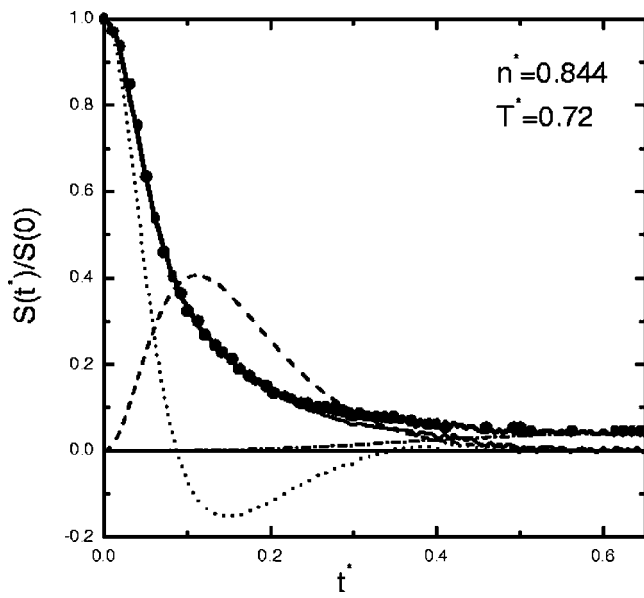
FIG. 1. The potential-potential part of TSAC function $S(t^*)/S(0)$ as a function of reduced time $t^*[=t(\epsilon/m\sigma^2)^{1/2}]$; at $T^*=0.72$ and $n^*=0.844$. Showing separately contributions from two-body (dotted), three-body (dashed), four-body (dashed-dotted) correlations and summed up contributions of two- and three-body (full) and two-, three-, and four-body (thick solid) correlations. Solid circles are MD data [10].

correlation functions. In order to calculate the time-dependent triplet contribution to TSAC function, we use $G_3(t)=\mathrm{sech}(\omega_3 t)$ in the present work. The parameter ω_3 can readily be obtained from coefficients of the expansion (10), we find $\omega_3=\sqrt{S_{43}/6S_{23}}$. Expressions for S_{23} and S_{43} are already available [16]. We prefer $\mathrm{sech}(\omega_3 t)$ over the simple exponential function due to its symmetric property which is one of the requirements of expansion (10). For the triplet

FIG. 2. Same as Fig. 1, but for $T^*=1.26$ and $n^*=0.844$ and without the four-body contribution.
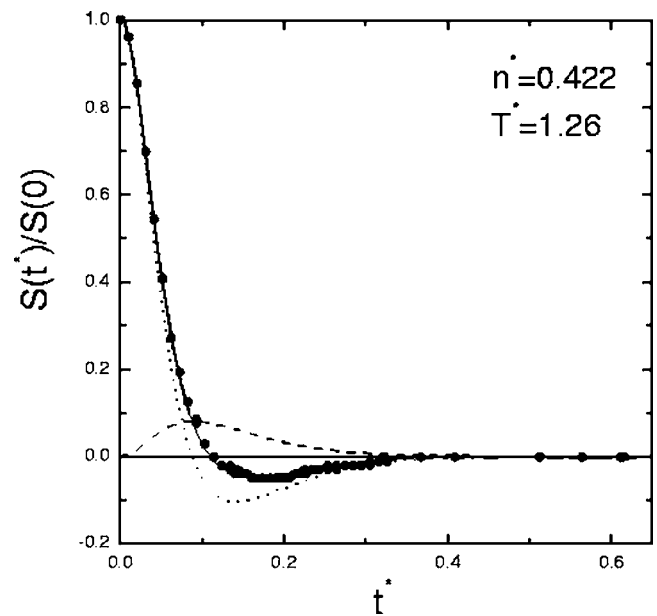

FIG. 3. Same as Fig. 2, but for $T^*=1.26$ and $n^*=0.422$.

correlation function, we have used the Kirkwood superposition approximation. This approximation has been tested earlier [21] by comparing the results with molecular dynamic results for the triplet contribution to the second sum rule of the transverse stress autocorrelation function and fourth sum rule of velocity autocorrelation function. It was found that this approximation overestimates the triplet contributions up to 35 percent. But the error involved in estimating total frequency sum rules is not substantial (10%–15%) as the triplet contribution itself is up to 35% of the binary contribution. The error decreases with increase in temperature and decrease in density. It was found that the error involved at density about one-half of the triple point density reduces to
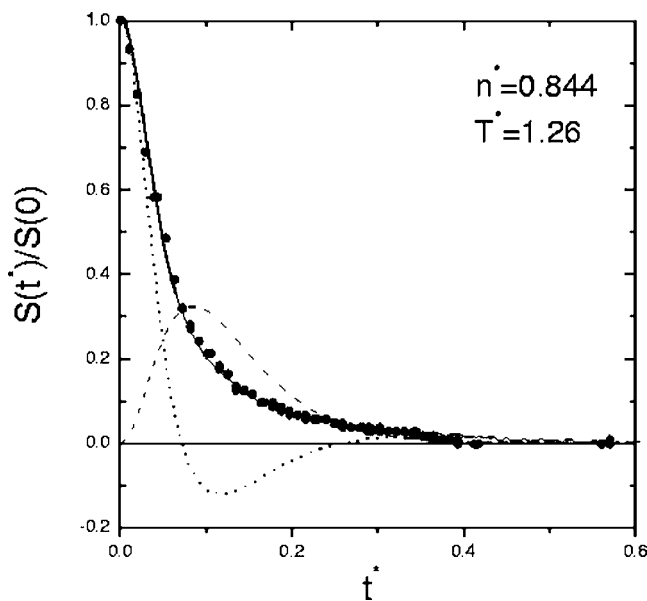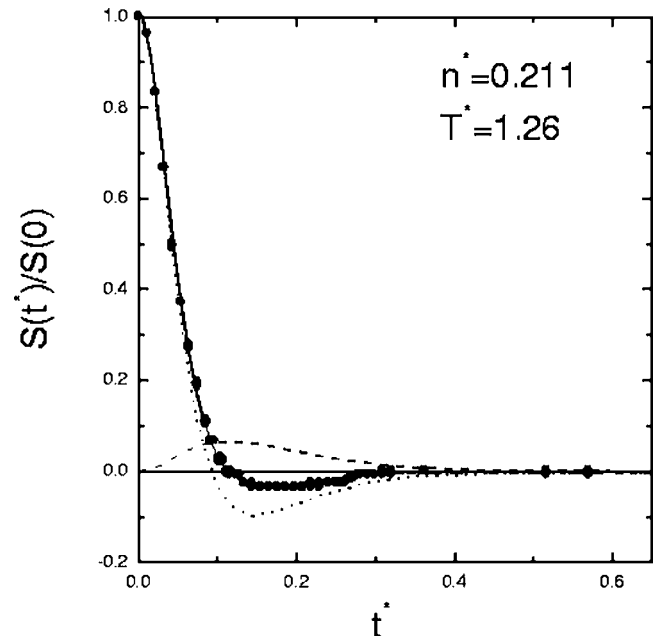

FIG. 4. Same as Fig. 2, but for $T^*=1.26$ and $n^*=0.211$.

TABLE I. Results of S_{23} (in units of $\epsilon^3/m\sigma^2$), $\omega_3 (= \sqrt{S_{43}/6S_{23}})$ (in units of $\sqrt{\epsilon/m\sigma^2}$), S_{43} [in units of $(\epsilon^4/m^2\sigma^4) \times 10^6$], and S_{42} [in units of $(\epsilon^4/m^2\sigma^4) \times 10^6$] for various densities and temperatures.

State	T^*	n^*	$-S_{23}$	ω_3	$-S_{43}$	S_{42}
I	0.72	0.844	5106	18.6	10.59	27.81
II	1.26	0.844	15492	24.3	54.88	166.80
III	1.26	0.422	1109	23.0	3.52	44.26
IV	1.26	0.211	285	18.0	0.55	21.56

about 5% which is about the same as that of the numerical error. The results obtained using this approximation for the static triplet correlation function along with parameter ω_3 are given in Table I for four of the thermodynamic states. In Table I, we also present corresponding results of two-body contribution to the fourth sum rule, i.e., S_{42}. It can be seen from the table that S_{43}/S_{42} decreases as one moves from the triple point toward the critical point. The time dependent three-body contribution as evaluated from Eq. (9) is shown in Figs. 1–4 as dashed lines. It can be seen from Figs. 1–4 that resultant of the binary and triplet contributions shown as full lines, improve agreement with simulation data [10] significantly. In fact, results are in very good agreement with MD data for all densities at $T^*=1.26$. However, near the triple point, the sum of two- and three-body contributions is in good agreement with the simulation data only up to $t^* =0.22$, i.e., up to one and one-half times of the Enskog relaxation time (≈ 0.16) at the same thermodynamic state. Therefore, at the triple point it appears that it is necessary to add the contribution due to four particles also. In the present work, we estimate it through $G_4(t) = \text{sech}(\omega_4 t)$. The expression for ω_4 is obtained to be $\sqrt{S_{64}/30S_{44}}$. Since nothing is known about the quadruplet contribution to sixth sum rule, we have fitted parameters S_{44} and ω_4 so as to get correct MD value of the shear viscosity. The contribution due to the static quadruplet correlation function is shown as the dashed-dotted line in Fig. 1. The result obtained by combining two-, three-, and four-body contributions is shown as thick full line in Fig. 1 and is in good agreement with MD simulation data [10]. It is also noted that the four-body correlation's contribution starts building only at larger times, implying that it plays a significant role only in liquids and glasses in which long time effects are important. It is also noted that near the triple point, the values of t^* at which pair, triplet and quadruplet contributions to $S(t)$ are one-half of their maxima are 0.045, 0.225, and 0.360. Whereas at densities $n^*=0.844$,

0.422, and 0.211 for $T^*=1.26$, the values of t^* at which pair and triplet contributions to $S(t)$ are one-half of their maxima are 0.035, 0.172; 0.041, 0.182; and 0.042, 0.233.

Results obtained for the potential-potential contribution to the shear viscosity are given in Table II. In Table II, we have given the contribution to shear viscosity due to pair (η_b), triplet (η_3), and quadruplet (η_4) correlations, separately. η in Table II represents sum of all contributions considered. It can be seen from the table that ratio of the binary (η_b) and the triplet contribution (η_3) to the total value of the shear viscosity varies from 17 to 68 percent and from 56 to 31 percent for the states I–IV. It is also seen that triplet correlations plays more important role than the pair correlation near the triple point density. Thus, it is realized that the three- and four-body contributions play a more important role at triple point as these are able to account for slowing down of the stress autocorrelation function. Having found good agreement of the shear viscosity ($\eta_b + \eta_3$) with MD data (η_{MD}) for thermodynamic states II–IV and from the good description of $S(t)$, it can be said that the pair and triplet contributions are sufficient to explain viscous dynamics of dense fluids. However, at the triple point, it is necessary to include the four-body contribution. All other higher order contributions are small and are useful when only long time effects are important. One of the reasons for the involvement of higher body correlation functions near the triple point density is that particles stay for much longer times in cages formed by their neighbors before they find positions at next nearest neighbor distances.

B. Mode-coupling contribution

Calculations for the mode-coupling contribution requires the knowledge of $F_s(q,t)$, sum rules, and in turn the knowledge of static pair correlation function. The static pair correlation function obtained [20] using optimized cluster series

TABLE II. Results for shear viscosity in units of 10^{-6} Pas for argon. η_b, η_3, η_4, η, and η_{MD} represent the shear viscosity due to binary contribution, three-body contribution, four-body contribution, sum of all these contributions, and the simulation result [10]. The value in parentheses denotes the shear viscosity at $T^* =1.26$ and $n^*=0.211$ calculated from the area under the MD curve of $S(t)$ [10].

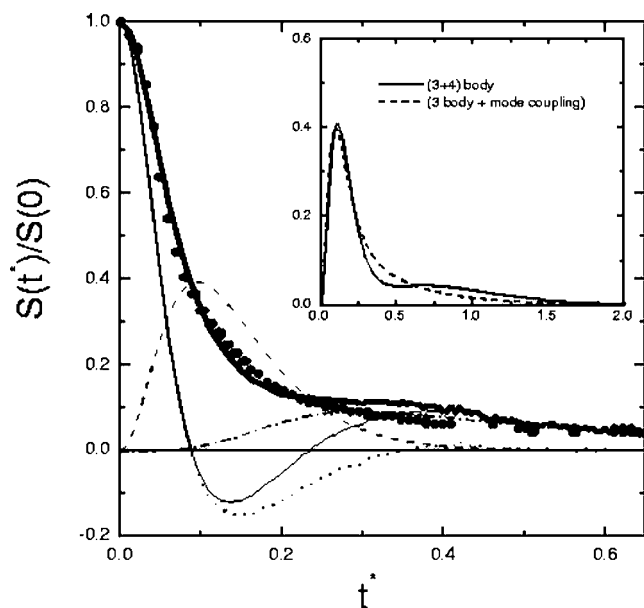| State	T^*	n^*	η_b	η_3	η_4	η	η_{MD}
I	0.72	0.844	51.75	163.04	74.74	289.53	289.6
II	1.26	0.844	71.08	127.28		198.36	191.0
III	1.26	0.422	11.77	5.36		17.13	18.9
IV	1.26	0.211	3.13	1.43		4.56	3.6(4.6)

FIG. 5. The potential-potential part of TSAC function $S(t^*)/S(0)$ as a function of reduced time t^*; at $T^*=0.72$ and $n^*=0.844$. The dashed-dotted line, solid line, thick solid line, and solid circles represent the mode-coupling contribution, the sum of two-body and mode-coupling contributions, the sum of two-body, three-body, and mode-coupling contributions and MD data [10], respectively. The inset contains the comparison of the sum of three-body and mode-coupling contributions as dashed line and the sum of three- and four-body contributions shown as solid line.

expansion for LJ potential has been used to determine the various sum rules required in the evaluation of $F_s(q,t)$. The result obtained for the mode-coupling contribution has been plotted in Fig. 5 for the thermodynamic state I as dashed-dotted line, whereas dotted line represents the binary contribution. The sum of the two contributions is shown by the solid line in Fig. 5. The results are compared with simulation data [10] and reveal a significant improvement in long time behavior of $S(t)$. However, large discrepancies at intermediate times suggest that the binary and the mode coupling contributions cannot be just added to study the complete time development of $S(t)$. Therefore, we add triplet correlation's contribution to improve intermediate behavior of $S(t)$ and follow Eq. (21). For $G_3(t)$, we use the same phenomenological form, i.e., $\text{sech}(\omega_3' t)$. Since mode-coupling contribution as given by expression (13) varies as t^4 for small time, it may, therefore, contain part of the triplet contribution building as t^4 to the sum rules. If we satisfy up to fourth sum rules by including up to quadruplet contribution, we obtain

$$\omega_3' = \sqrt{\frac{S_{43} + S_{44} - C_1}{6 S_{23}}}, \tag{22}$$

with

$$C_1 = \lim_{t \to 0} \frac{S_{mc}(t)}{t^4}.$$

The value of C_1 [in units of $(\epsilon^4/m^2\sigma^4) \times 10^6$] is found to be 0.73. The values of ω_3' (in units of $\sqrt{\epsilon/m\sigma^2}$) appearing in Eq. (22) is obtained to be 21.5 so as to get MD simulation value of the shear viscosity. The result obtained due to the second term in Eq. (21) is shown in Fig. 5 as the dashed line. It yields rapid increase in viscosity due to slowing down of the stress correlation function. The results obtained by adding all contributions are shown as thick full line which is in satisfactory agreement with simulation data [10] (solid circles). The satisfactory agreement implies that mode-coupling contribution can be combined with contribution due to the pair and triplet contributions, though mode-coupling contribution carries part of the triplet contribution starting as t^4. It can also be seen that the role played by mode coupling is not very different from that played by the triplet and higher order static correlation functions at long time. This becomes more evident from Fig. 5 (inset), wherein we have plotted sum of triplet and quadruplet contributions as solid line and sum of the second term of Eq. (21) and the mode-coupling contribution is shown as dashed line. Thus, it can be said that different relaxations arise due to different dynamical contributions due to two-, three-, and four-body correlation functions and are essential to understand the viscous dynamics in dense fluids and supercooled liquids.

IV. SUMMARY AND CONCLUSION

In the present work, transverse stress correlation function has been expanded as a series with time-dependent terms representing contribution due to all possible cluster of particles. The expression for the static pair correlation's contribution has been numerically calculated for the transverse stress correlation function of Lennard-Jones (LJ) fluid within cluster expansion technique. The results obtained on adding three-body contribution to it when compared with the simulation data reveal a significant improvement in behavior of the transverse stress correlation function and in the shear viscosity. It is also found that contributions due to two- and three-body static correlation functions are sufficient to understand the viscous dynamics of dense gases. However, close to the triple point, it is necessary to include contribution due to the four-body correlation function. The contribution due to the mode coupling has been found to play a similar role as that by the triplet and quadruplet correlation functions. Thus, the mode coupling can be thought of as one of the ways of describing the dynamical many-body correlation functions. The origin of different relaxation times in liquids is thus due to various dynamical many-body correlations.

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