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Longitudinal and bulk viscosities of Lennard-Jones fluids

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Abstract. Expressions for the longitudinal and bulk viscosities have been derived using Green Kubo formulae involving the time integral of the longitudinal and bulk stress autocorrelation functions. The time evolution of stress autocorrelation functions are determined using the Mori formalism and a memory function which is obtained from the Mori equation of motion. The memory function is of hyperbolic secant form and involves two parameters which are related to the microscopic sum rules of the respective autocorrelation function. We have derived expressions for the zeroth-, second- and fourth- order sum rules of the longitudinal and bulk stress autocorrelation functions. These involve static correlation functions up to four particles. The final expressions for these have been put in a form suitable for numerical calculations using low- order decoupling approximations. The numerical results have been obtained for the sum rules of longitudinal and bulk stress autocorrelation functions. These have been used to calculate the longitudinal and bulk viscosities and time evolution of the longitudinal stress autocorrelation function of the Lennard-Jones fluids over wide ranges of densities and temperatures. We have compared our results with the available computer simulation data and found reasonable agreement.

1. Introduction

A considerable amount of work has been done during the last three decades to study the transport coefficients of classical dense fluids. This has been possible owing to the combined efforts made as a result of experiments, computer simulations and theories. However, in most of the work attention has been paid to the study of the coefficients of self-diffusion and shear viscosity. The bulk viscosity of fluids which has relevance to the behaviour of fluids under rapid loading conditions has been least investigated. This may be due to the complications involved in its study. For example experimentally it cannot be measured directly. However, during the last decade this property of the fluids has been investigated by computer simulation techniques [1–3]. At present, sufficient information regarding the density and temperature dependences of bulk viscosity has been made available; hence the predictions of theories can be checked. For example the Enskog theory in which multiparticle correlated collisions are neglected overestimates the bulk viscosity by a factor of 2 and predicts the ratio of bulk viscosity to shear viscosity to be around 1.2 near solidification. However, molecular dynamics (MD) simulations on hard spheres produces a value for this ratio of around 0.34. In recent years, Brogelt *et al* [2] using the kinetic theory approach predicted a bulk viscosity which is at least 60% different from their simulation values. In fact at present there exist no tractable kinetic theory which can be used to predict

the bulk viscosity even for hard spheres and which is in agreement with the simulation data. The second approach which has now been used more frequently to study the transport and dynamics of the fluids is based on time correlation function (TCF) formalism. The time evolution of the TCF is generally calculated by introducing the memory function within the Mori memory function formalism [4, 5]. The advantage of this approach is that one can introduce an approximate form [6] of the memory function and can still preserve a number of properties of the TCF. Using this approach we have studied [7–10] the coefficients of self-diffusion, shear viscosity and thermal conductivity of Lennard-Jones (LJ) fluids. However, there exists no similar work on the calculation of bulk viscosity and hence of the respective TCF of interest. Therefore, in this paper we have studied the time evolution of the longitudinal stress autocorrelation (LSAC) and bulk stress autocorrelation (BSAC) functions and corresponding viscosities. We first derive expressions for the first three non-vanishing sum rules of the LSAC and BSAC functions. These have been put in a form suitable for numerical calculations. The numerical results have been obtained for the LJ potential at various densities and temperatures. These sum rules and a hyperbolic secant form of the memory function which is derivable from the Mori equation of motion have been used to study the longitudinal and the bulk viscosities of the LJ fluids. The results obtained have been compared with the simulation data of Heyes [1]. It is found that our results for the longitudinal viscosity are in good agreement with the simulation data. The bulk viscosity has been calculated using the sum rules of the BSAC function and also using its relation with the longitudinal and shear viscosities. The two methods have been found to provide similar results. The results for the bulk viscosity have been compared with the simulation data and are found to be in reasonable agreement except for densities close to the triple-point density. It is also noted that our approach predicts a bulk viscosity proportional to the square of the density in low-density limits which is in accordance with the predictions of kinetic theory.

The layout of the paper is as follows. In section 2 we present some of the general expressions. In section 3 we derive expressions for the sum rules of the LSAC and BSAC functions. In section 4, we derive the expression for the memory function. The expressions for the time evolution of the TCF and viscosities are also presented in section 4. In section 5 we present the calculations and results. In section 6 we summarize and conclude the work.

2. Generalities

The Green Kubo expression which relates the LSAC function $S^l(t)$ to the longitudinal viscosity η_l is given by

$$\eta_l = \frac{4}{3}\eta_S + \eta_B = \frac{1}{Vk_B T} \int_0^\infty dt S^l(t) \quad (1)$$

where

$$S^l(t) = \frac{1}{3} \langle J^{aa}(t) J^{aa}(0) \rangle \quad (2)$$

with

$$J^{ab} = \sum_{j=1}^N \left(\frac{p_{ja} p_{jb}}{m} + r_{ja} F_{jb} \right) - \delta_{ab} V \left(P + \frac{\partial P}{\partial \bar{E}} (E - \bar{E}) \right) \quad (3)$$

where a and b run over x, y and z . In the above equations, p_{ja}, r_{ja} and F_{ja} are the a th components of velocity, position and force, respectively, on the j th particle. The

angular brackets represent a canonical ensemble average. P , V , k_B , T and m are the average pressure, volume, Boltzmann constant, temperature and mass, respectively. The current chosen above is suitable for the canonical ensemble used in the present work. Expressions for \bar{E} and P in terms of pair potential $U(r)$ and pair distribution function $g(r)$ are given as

$$\bar{E} = \frac{3}{2}NkT + \frac{n}{2} \int dr g(r)U(r) \tag{4}$$

$$PV = k_B T - \frac{2\pi n}{3} \int_0^\infty dr \frac{dU(r)}{dr} r^3 g(r). \tag{5}$$

The second Green Kubo relation [11] which relates the bulk viscosity η_B directly to the so-called BSAC function $S^B(t)$ is given by

$$\eta_B = \frac{1}{Vk_B T} \int_0^\infty dt S^B(t) \tag{6}$$

where

$$S^B(t) = \frac{1}{9} \sum_a \sum_b \langle J^{aa}(t) J^{bb}(0) \rangle. \tag{7}$$

The shear viscosity η_S , which is related to the transverse stress autocorrelation (TSAC) function, is given by

$$\eta_S = \frac{1}{Vk_B T} \int_0^\infty dt S^S(t) \tag{8}$$

where

$$S^S(t) = \frac{1}{6} \sum_{a \neq b} \langle J^{ab}(t) J^{ab}(0) \rangle. \tag{9}$$

Expressions (1), (6) and (8) are derivable from the Navier–Stokes equation and therefore must be equivalent. However, this equivalence is not clear from the above expressions owing to the appearance of different combinations of products J^{ab} and J^{ab} . Therefore, in order to look for this equivalence and with the aim of studying the time-development of stress autocorrelation functions, we start by examining the short-time properties of these functions. The short-time expansion of $S(t)$ is given as

$$S(t) = S_0 - S_2 \frac{t^2}{2!} + S_4 \frac{t^4}{4!} - \dots \tag{10}$$

where S_0 , $-S_2$ and S_4 are the zeroth-, second- and fourth-order sum rules of the stress autocorrelation function in general. The expressions for the sum rules of the TSAC function has already been given in our earlier paper [8]. In the next section we present the results for sum rules of LSAC and BSAC functions.

3. Expressions for sum rules

3.1. Longitudinal stress autocorrelation function

The expressions for the zeroth-order sum rules of the LSAC function S_0^l is obtained by putting $t = 0$ in equation (2). The expression thus obtained is given as

$$S_0^l = 4(k_B T)^2 + \frac{2\pi n}{15} k_B T \int_0^\infty dr r^4 g(r) (3Ar^2 + 5B) - 5V \frac{dP}{d\bar{E}} (k_B T)^2 - (PV)^2 + \left(V \frac{dP}{d\bar{E}} \right)^2 (6(k_B T)^2 - \bar{E}^2) + 2PV^2 \frac{dP}{d\bar{E}} \left(\bar{E} - \frac{3}{2} k_B T \right). \tag{11}$$

The expression for S_2^l is obtained by evaluating the thermodynamic average:

$$S_2^l = \langle \dot{J}^{xx}(t) \dot{J}^{xx}(t) \rangle_{t=0} \quad (12)$$

where $\dot{J}^{xx}(t)$ is first time derivative of $J^{xx}(t)$. From the expression for $J^{xx}(t)$, one expects that the expression for S_2^l should contain static correlation up to four particles. However, it has been found that the four-particle contributions turn out to be zero under the pair potential approximation and successive use of the Yvon theorem:

$$\left\langle \frac{dU(r)}{dr} f(r) \right\rangle = k_B T \left\langle \frac{df(r)}{dr} \right\rangle$$

where $f(r)$ is a regular function of r . The final expression for S_2^l involves only the static pair and the triplet correlation functions. The expression obtained for S_2^l is given as

$$\begin{aligned} S_2^l = & \frac{4\pi k_B T n}{15m} \int_0^\infty r^2 g(r) dr [r^2(5B^2 + 3A^2r^4 + 6ABr^2) + k_B T(18Cr^4 + 165Ar^2 + 225B)] \\ & + \int_0^\infty r^2 dr \int_0^\infty r_1^2 dr_1 \int_{-1}^1 d\beta_1 g_3(\mathbf{r}, \mathbf{r}_1) \beta_1 [r r_1 (Ar^2 + B)(A_1 r_1^2 + 5B_1)] \\ & + 2\beta_1^2 A A_1 r^3 r_1^3. \end{aligned} \quad (13)$$

In the above expressions and in what follows, $g(r)$ and $g_3(\mathbf{r}, \mathbf{r}_1)$ are the static pair and the triplet correlation functions and

$$\begin{aligned} B &= \frac{1}{r} \frac{dU(r)}{dr} & A &= \frac{1}{r} \frac{dB}{dr} \\ C &= \frac{1}{r} \frac{dA}{dr} & D &= \frac{1}{r} \frac{dA}{dr}. \end{aligned} \quad (14)$$

The subscripts 1 on these imply that the argument of the potential $U(r)$ is replaced by r_1 . The fourth-order sum rule of the LSAC function is defined as

$$S_4^l = \langle \ddot{J}^{xx}(t) \ddot{J}^{xx}(t) \rangle_{t=0} \quad (15)$$

where $\ddot{J}^{xx}(t)$ is the second time derivative of $J^{xx}(t)$. The final expression for S_4^l involves the static pair, the triplet and the quadruplet contributions and is given as

$$\begin{aligned} S_4^l = & \frac{4\pi n}{15} \left(\frac{k_B T}{m} \right)^2 \int_0^\infty dr g(r) r^2 [54(k_B T)^2 (Dr^4 + 10Cr^2 + 15A) \\ & + k_B T(1890B^2 + 1504A^2r^4 + 2340ABr^2 + 216BCr^4 + 324Ar^6 + 18C^2r^8) \\ & + 2r^2(5B^3 + 9ab^2r^2 + 9A^2Br^4 + 3A^3r^6)] \\ & + 8\pi^2 n^2 \frac{(k_B T)^2}{15m^2} \int_0^\infty dr \int_0^\infty dr_1 \int_{-1}^1 d\beta_1 g_3(\mathbf{r}, \mathbf{r}_1) \\ & \times r^2 r_1^2 [k_B T(105(9BB_1 + 3BA_1r_1^2 + \frac{1}{3}AA_1r^2r_1^2(6\beta_1^2 + 1) + 3AB_1r^2) \\ & + 30(3B_1Cr^4 + 15AB_1r^2 + 3A_1Cr^4r_1^2\beta_1^2 + AA_1r^2r_1^2(9\beta_1^2 + 2) \\ & + 12rr_1\beta_1(3B_1Cr^2 + 15AB_1 + CA_1\beta_1r^2r_1^2(2\beta_1^2 + 1) + 11AA_1r_1^2) \\ & + 3(CC_1r^4r_1^2\beta_1^2(2\beta_1^2 + 1) + 2A_1Cr^4r_1^2(8\beta_1^2 + 1) + AA_1r^2r_1^2(28\beta_1^2 + 9))) \\ & + r(r + 4\beta_1r_1)(3AA_1B_1r^4 + 6ABB_1r^2 + 5B^2B_1) \\ & + rA_1B^2(r_1^3\beta_1 + 12rr_1^2(2\beta_1^2 + 1)) + 2A^2r^5r_1^2\beta_1(3\beta_1r + 4r_1(2\beta_1^2 + 1)) \\ & + 2Ar^3A_1r_1\beta_1B(3\beta_1r + 4r_1(2\beta_1^2 + 1)) \\ & - \frac{1}{2}[5r^2BB_1B_2 + BA_1B_2(3r_1^2 + r^2(2\beta_1^2 + 1)) + 3\beta_1^2r^4A_1AB_2r_1^2] \end{aligned}$$

$$\begin{aligned}
 & +BA_1A_2r_1^2r_2\beta_3(3\beta_1r^3 - 3r_1^3) - rr_1r_2(\beta_2 + 2\beta_1\beta_3) - 6r_1^2r_2\beta_3 \\
 & +\beta_1\beta_2r^4AA_1A_2r_1^2r_2^2(5\beta_3 - 2\beta_1\beta_2) + BB_1A_2r^2(3\beta_2^2r_2^2 + r_1^2(1 - \beta_1^2))] \\
 & +\frac{\pi n}{15}k_B T \left(\int_0^\infty dr r^4 g(r)(3Ar^2 + 5B) \right) \left(\frac{4\pi n}{3} \int_0^\infty dr r^2 g(r)(Ar^2 + 3B) \right)^2.
 \end{aligned} \tag{16}$$

The last term in equation (16) represents the approximate four-body contribution in terms of the static pair correlation function. The method of expressing the quadruplet contribution in terms of static pair contribution has already been explained in our earlier work [8, 9]. In the above equation $r_2 = |r_1 - r|$ and the subscripts 2 on A, B and C imply that the argument of the potential $U(r)$ is changed to r_2 . Further, β_1, β_2 and β_3 are cosines of the angles between r and r_1 , between r and r_2 and between r_1 and r_2 , respectively. These expressions for the sum rules of the longitudinal stress correlation function are expected to be quite useful in the study of the LSAC functions and hence for the longitudinal and bulk viscosities.

3.2. Bulk stress autocorrelation function

The expressions for the sum rules of the BSAC functions can also be obtained in a similar way. The results obtained for these are given below. The expressions for the zeroth-order sum of the BSAC function is given as

$$\begin{aligned}
 S_0^B &= \frac{8}{3}(k_B T)^2 + \frac{2\pi n}{9}k_B T \int_0^\infty dr r^4 g(r)(Ar^2 - B) - (PV)^2 \\
 &+ \left(V \frac{dP}{dE} \right)^2 (6(k_B T)^2 - \bar{E}^2) - 5V \frac{dP}{dE} (k_B T)^2 + 2PV^2 \frac{dP}{dE} \left(\bar{E} - \frac{3}{2}k_B T \right)
 \end{aligned} \tag{17}$$

The expression for the second-order sum rule is obtained to be

$$\begin{aligned}
 S_2^B &= \frac{4\pi n}{9m}(k_B T)^2 \int_0^\infty dr r^2 g(r)[(6Cr^4 + 45Ar^2 + 45B) + r^6(k_B T)^{-1}(Ar^2 + B)^2] \\
 &+ 8\pi^2 n^2 \frac{(k_B T)^2}{9m^2} \int_0^\infty dr \int_0^\infty dr_1 \int_{-1}^1 d\beta_1 g_3(\mathbf{r}, \mathbf{r}_1) r^2 r_1^2 (k_B T)^{-1} \\
 &\times rr_1 \beta (AA_1 r^2 r_1^2 + BA_1 r_1^2 + AB_1 r^2 + BB_1).
 \end{aligned} \tag{18}$$

The expression for the fourth-order sum rule of the BSAC function is given by

$$\begin{aligned}
 S_4^B &= \frac{4\pi n}{9} \left(\frac{k_B T}{m} \right)^2 \int_0^\infty dr g(r) r^2 [18(k_B T)^2 (Dr^4 + 10Cr^2 + 15A) \\
 &+ k_B T (390B^2 + 432A^2 r^4 + 620ABr^2 + 72BCr^4 + 108ACr^6 + 6C^2 r^8) \\
 &+ 2r^2 (B + Ar^2)^3 - 4B^3 r^2] \\
 &+ 8\pi^2 n^2 \frac{(k_B T)^2}{9m^2} \int_0^\infty dr \int_0^\infty dr_1 \int_{-1}^1 d\beta_1 g_3(\mathbf{r}, \mathbf{r}_1) \\
 &\times r^2 r_1^2 [(63(3BB_1 + BA_1 r_1^2 + AA_1 r^2 r_1^2 \beta_1^2 + AB_1 r^2) \\
 &+ 18(B_1 Cr^4 + 5AB_1 r^2 + A_1 Cr^4 r_1^2 \beta_1^2 + AA_1 r^2 r_1^2 (2\beta_1^2 + 1) \\
 &+ 8rr_1 \beta_1 (B_1 Cr^2 + 5AB_1 + CA_1 \beta_1 r^2 r_1^2 + 5AA_1 r_1^2) \\
 &+ 3r^2 r_1^2 (CC_1 r^2 r_1^2 \beta_1^2 + A_1 Cr^2 (2\beta_1^2 + 1) + A_1 Cr^2 (2\beta_1^2 + 1) + AA_1 (4\beta_1^2 + 7))]
 \end{aligned}$$

$$\begin{aligned}
& +k_B T^{-1}[4rr_1\beta_1(2AA_1Br^2r_1^2 + ABB_1r^2 + B^2B_1) + A_1B^2r_1^2 \\
& + 2A^2A_1r^4r_1^2 + BAB_1r_2 + A^2B_1r^4] + r_2(Ar^2 + B)^2(A_1r_1^2\beta_1^2 + B_2) \\
& - \frac{1}{2}[r^2BB_1B_2 + BA_1B_2r_1^2r^2\beta_1^2 + \beta_1^2r^4A_1AB_2r_1^2 + BA_1A_2r_1^2r_2^2\beta_3\beta_1\beta_2 \\
& + \beta_1\beta_2r^4AA_1A_2r_1^2r_2^2(2\beta_3 - \beta_1\beta_2) + BB_1A_2r^2\beta_2^2r_2^2 \\
& + AB_1B_2r^4 + AB_1A - 2r^4r_2^2\beta_3^2]]. \tag{19}
\end{aligned}$$

However, we note from equations (1), (6) and (8) these these sum rules can also be obtained from knowledge of the sum rules of $S^l(t)$ and $S^s(t)$. The relation between them is

$$S_{2n}^B = S_{2n}^l - \frac{4}{3}S_{2n}^s \tag{20}$$

where the subscript $2n$ represents the order of the sum rule. Since we have already derived the sum rules of the TSAC function, we can check the validity of equation (20). It is found that equation (20) can be used to derive the expressions for the sum rules of the BSAC function by knowing the sum rules of the longitudinal and transverse stresses. The validity of equation (20) also suggests the equivalence of equations (1) and (6) for the calculation of the bulk viscosity. Here, it may be noted that equation (20) is not apparent unless angular integration is completed. In the next section we derive expressions for the time evolution of the BSAC and LSAC functions and two viscosities using the Mori memory function formalism.

4. Theory

The time evolution of the stress autocorrelation functions is of fundamental importance in the study of relaxation of the momentum current fluctuations and in predicting the viscosities. The exact evaluation of the time evolution of any TCF is not yet possible except for a very simplified description of atomic motion. However, it has been shown by Mori that TCFs obey an equation of motion which determines their time evolution and is given by

$$\frac{dS(t)}{dt} + \int_0^t S(\tau)M_1(t-\tau) d\tau = 0 \tag{21}$$

where $S(t)$ is the stress autocorrelation function and $M_1(t)$ is the first-order memory function defined as

$$M_1(t) = \langle f_1(t)f_1^*(0) \rangle / \langle |f_1(0)|^2 \rangle \tag{22}$$

where

$$f_1(t) = \exp(iQ_1LQ_1t) Q_1J.$$

The operator $Q_1 (= 1 - P_1)$ projects onto the subspace orthogonal to the variable $J(t)$ and L is a Liouville operator. In order to calculate the time evolution of the autocorrelation function from equation (21), the fundamental theoretical quantity needed is the memory function $M_1(t)$. Since exact microscopic calculation of $M_1(t)$ is not yet possible, several phenomenological forms for it have been proposed in the literature. In the present work we follow our earlier work [7–10] and use

$$M_1(t) = a \operatorname{sech}(bt) \tag{23}$$

where $a = M_1(t=0) = \delta_1 = S_2/S_0$ and $b^2 = \delta_2 = S_4/S_2 - S_2/S_0$. This memory function is a solution of the non-linear equation given as

$$\frac{d^2M_1(t)}{dt^2} - b^2M_1(t) + \frac{2b^2}{a^2}M_1^3(t) = 0 \tag{24}$$

which is derivable [12] from the Mori equation of motion using two approximations.

The memory function given by equation (23) tends to a Gaussian and a simple exponential for short and long times, respectively. The analytical results [13] obtained for the TCF using the hyperbolic secant memory function has demonstrated the effect of the non-linearity reflected through equation (24) of the atomic motion on the time evolution of the autocorrelation function. The merits and demerits of the hyperbolic secant memory function have recently been investigated by Lee *et al* [14].

Defining the Fourier–Leplace transform as

$$\tilde{S}(\omega) = i \int_0^\infty \exp(i\omega t) S(t) dt. \tag{25}$$

The power spectrum of the stress autocorrelation function is given as

$$S''(\omega) = 2 \int_0^\infty \cos(\omega t) S(t) dt \tag{26}$$

where $S''(\omega)$ is the imaginary part of $S(\omega)$ and is obtained to be

$$S''(\omega) = \frac{S_0}{(\omega + M_1'(\omega))^2 + (M_1''(\omega))^2}. \tag{27}$$

M_1' and M_1'' are the real and imaginary parts, respectively, of the memory function $\tilde{M}_1(\omega)$ and are given as

$$M_1''(\omega) = (\pi a / 2b) \operatorname{sech}(\omega\pi / 2b) \tag{28a}$$

and

$$M_1'(\omega) = \frac{\pi a}{2b} \tanh\left(\frac{\pi\omega}{2b}\right) + \frac{a}{2} \left[\psi\left(\frac{1+i\omega}{4b}\right) - \psi\left(\frac{1-i\omega}{4b}\right) \right]. \tag{28b}$$

In the above equation, $\psi(x)$ is the Euler psi function.

The time dependence of $S(t)$ is obtained from the relation

$$S(t) = \frac{1}{\pi} \int_0^\infty \cos(\omega t) S''(\omega) d\omega. \tag{29}$$

The Green Kubo expression combined with equation (25) provides a general expression for the viscosity which is given as

$$\eta = \frac{-i}{V k_B T} \tilde{S}(\omega = 0). \tag{30}$$

Using equations (27) and (28) and values of a and b , we obtain

$$\eta = \frac{2n}{\pi k_B T} S_0 \sqrt{\frac{\delta_2}{\delta_1}}. \tag{31}$$

This expression will be used to calculate the longitudinal and bulk viscosities by using the corresponding values of the sum rules.

5. Calculations and results

In this section we present results for the time evolution of the LSAC function and longitudinal and bulk viscosities.

5.1. Longitudinal stress autocorrelation function and longitudinal viscosity

The input for the calculation of the sum rules of the LSAC functions consists of the interaction potential $U(r)$, the static pair correlation function and the triplet correlation function. For $U(r)$ we use the LJ potential which is representative of the inert fluids. The static pair correlation function has been calculated using the method of Sung and Chandler [15] based on optimized cluster theory. This $g(r)$ has been found [16] to be in good agreement with the MD data obtained for the LJ potential. For the triplet correlation function we have used a Kirkwood superposition approximation. This approximation has been tested and has been found [17, 18] to be suitable for the evaluation of the sum rules. The numerical integration has been done using the Gauss quadrature method. The accuracy of our numerical work is better than 5%. In order to see the relative importance of two- and three-particle contributions to the sum rule, we have presented these separately in table 1 for various reduced densities $n^* = n\sigma^3$ and temperatures $T^* = k_B T/\epsilon$; σ and ϵ are two parameters of the LJ potential of dimensions length and energy, respectively. In table 1 and in what follows, S_{nm}^l represents the m -body contribution to the n th sum rule of the LSAC function. It can be seen from table 1 that the three-body contribution is quite appreciable. It is noted that the ratio of the static triplet contribution to the static pair contribution to the second- and fourth-order sum rules increases with increase in density and decrease in temperature. Near the triple point this ratio has been found to be about 50%. Here it may be noted that in the present work we have ignored the terms in the zeroth-order sum rules which appear as a result of energy fluctuations because of complication involved in the calculation of $dP/d\bar{E}$.

Table 1. Values of the sum rules of the LSAC functions. S_{nm}^l represents the m -body contribution to the n th-order sum rule. S_0 , S_2 and S_4 are in units of ϵ^2 , $\epsilon^3/m\sigma^2$ and $\epsilon^4/m^2\sigma^4$, respectively. ϵ and σ are two parameters of the LJ potential.

T^*	n^*	S_0^l	$S_{22}^l \times 10^{-3}$	$S_{23}^l \times 10^{-3}$	$S_{42}^l \times 10^{-6}$	$S_{43}^l \times 10^{-6}$
0.730	0.844	60.46	31.95	-14.95	53.89	-20.36
1.000	0.720	66.55	40.77	-11.80	94.60	-19.80
1.230	0.419	42.15	26.99	-3.53	76.50	-7.32
1.190	0.584	59.83	39.41	-7.57	108.05	-14.95
1.160	0.844	113.07	90.80	-36.06	243.57	-72.54
1.830	0.500	89.52	81.16	-11.12	347.78	-34.76
1.810	0.600	114.53	109.44	-19.15	463.80	-58.30
1.810	0.700	146.74	153.88	-34.37	650.44	-103.71
1.840	0.743	165.45	186.81	-46.24	798.46	-141.86
2.500	0.500	142.13	168.96	-22.40	928.51	-92.38
2.500	0.600	183.31	236.64	-39.49	1295.20	-162.92
2.560	0.743	258.48	408.21	-95.61	2268.90	-391.21
2.500	0.803	276.46	478.85	-130.14	2599.30	-521.60
3.460	0.500	228.83	336.32	-44.85	2522.20	-238.02
3.410	0.600	286.99	480.06	-79.22	3603.80	-420.43
3.500	0.700	366.60	714.39	-147.69	5514.30	-785.56
3.540	0.803	436.54	1042.50	-272.08	8149.00	-1437.00
4.530	0.600	433.88	943.73	-149.38	9802.40	-1033.00
4.450	0.700	514.02	1262.40	-249.53	12840.00	-1660.20
4.450	0.803	595.91	1783.00	-440.01	18146.00	-2867.30

The time evolution of the normalized LSAC function determined from equations (29) and (27) is plotted in figure 1 for seven thermodynamic states. In figures 1(a) and 1(c)

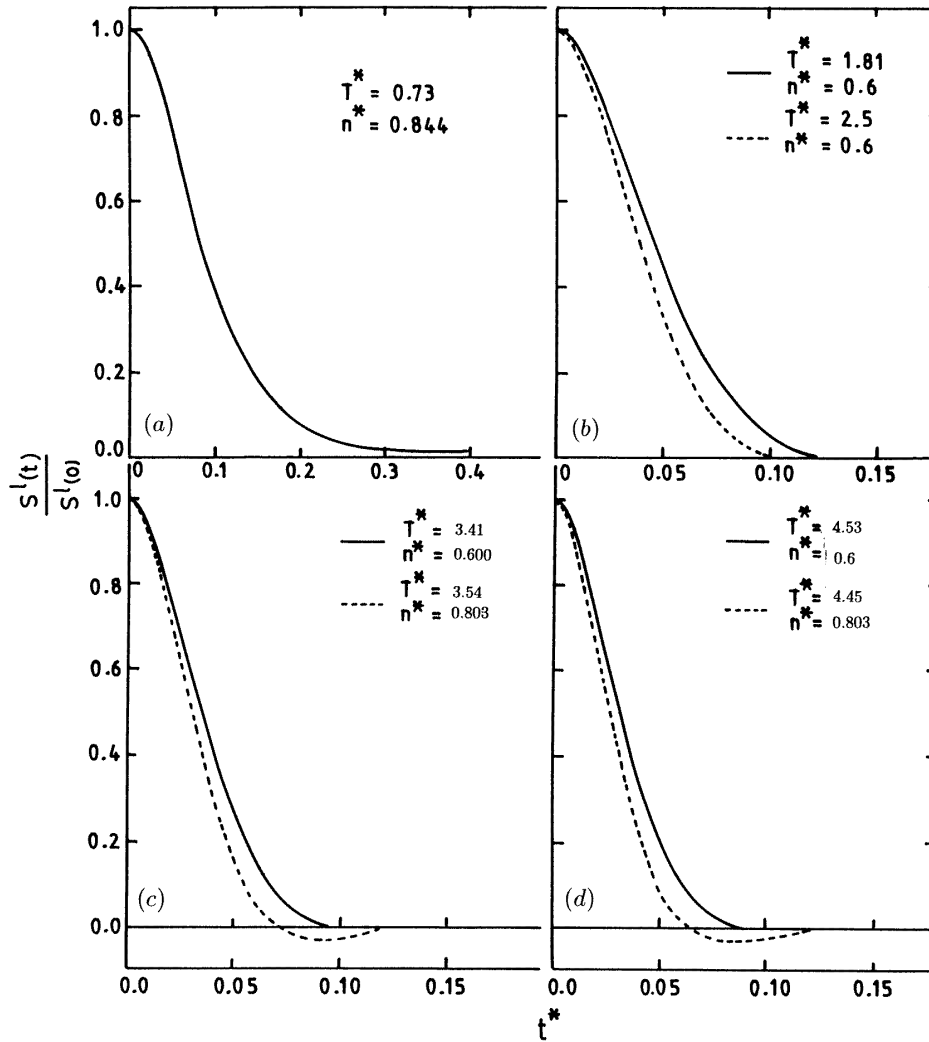


Figure 1. Variation in the normalized LSAC function with time t^* .

we have studied the effect of density on the time development of $S^l(t)$. It is seen that the effect of density is quite significant. The effect of increase in density on the time developments of $S_l(t)$ determine the importance of correlated collisions in determining the longitudinal viscosity. From our work on the shear viscosity we noted that the influence of correlated collisions was small for the shear viscosity. The longitudinal viscosity is the sum of the shear and bulk viscosities; therefore it seems that the effect of correlated collisions is more on the bulk viscosity than on the shear viscosity. This also suggests that the density dependence of bulk viscosity is stronger than the linear dependence. In figure 1(b) we have studied the effect of temperature on the development of the LSAC function. The repulsive part of the interaction potential becomes relatively more important at higher temperatures. Therefore, from figure 1(b) we found that the effect of the attractive part of the potential is also important in determining the longitudinal viscosity.

The longitudinal viscosity of the LJ fluids is calculated from equation (31) using the values of the sum rules from table 1. The results for $\eta_l^* = \eta\sigma^2(m\epsilon)^{-1/2}$ are presented in figure 2 for six isotherms. In figure 2 the full curves are results obtained from equation (31) and the MD results of Heyes [1] for $\eta_l = \frac{4}{3}\eta + \eta_B$ are shown as full circles. From figure 2, it is seen that our theory provides good agreement of the longitudinal viscosity with the MD data.

In order to see the relative importance of three- and many-particle contributions in estimating the longitudinal viscosity, we calculate it from equation (31), neglecting these contributions to sum rules. This is denoted by η_{l2}^* and is presented in table 2 for various densities and temperatures. We also present the results of η_l^* obtained including all contributions together with the MD results of Heyes. From table 2 we note that the effect of triplet and quadruplet correlations on the longitudinal viscosity increases with increase in density. It is also noted that the triplet contribution in estimating the longitudinal viscosity is between 15 and 55%.

Table 2. Values of the longitudinal viscosity for various values of the reduced densities n^* and T^* . $\eta_{l(2)}^*$ represent the longitudinal viscosity obtained from equation (31) by including only pair contributions to the sum rules. η_l^* is the longitudinal viscosity obtained by including pair as well as triplet contributions to the sum rules. $\eta_l^*(\text{MD})$ represent the MD data of Heyes [1].

T^*	n^*	$\eta_{l(2)}^*$	η_l^*	$\eta_l^*(\text{MD})$
0.733	0.844	2.87	6.51	5.51
1.23	0.419	0.67	0.80	0.71
1.16	0.844	2.83	5.56	5.01
1.81	0.600	1.45	1.86	1.64
1.81	0.700	1.94	2.72	2.47
1.84	0.743	2.11	3.09	3.05
2.50	0.500	1.00	1.50	—
2.56	0.743	1.91	2.73	2.91
3.46	0.500	1.11	1.34	0.98
3.41	0.60	1.47	1.86	1.68
3.54	0.803	1.95	2.98	3.40
4.53	0.600	1.52	1.92	1.96
4.45	0.700	1.84	2.49	2.35
4.45	0.803	1.94	2.90	3.39

5.2. Bulk viscosity

The sum rules of the BSAC function is obtained by knowledge of the sum rules of the LSAC and TSAC functions and using equation (20). The expressions and numerical value of the sum rules of the TSAC function are given in our earlier work. Using those values and the values given in table 1 for the LSAC function we obtain the values of the sum rules of the BSAC function. The results obtained are given in table 3 for various densities and temperatures. In table 3, S_{nm}^B represents the m -body contribution to the n th sum rule. From table 3 it is seen that the triplet contribution is quite significant. It is about 50% for the second-order sum rules whereas it is about 60% for the fourth-order sum rule at the triplet point. It decreases with increase in temperature and decrease in density.

The bulk viscosity is calculated from equation (31) using the values of sum rules from table 3 is given in table 4 in the fourth column for various values of n^* and T^* . The third column shows the results obtained for η_B^* calculated for the relation $\eta_B^* = \eta_l^* - \frac{4}{3}\eta_S^*$ using

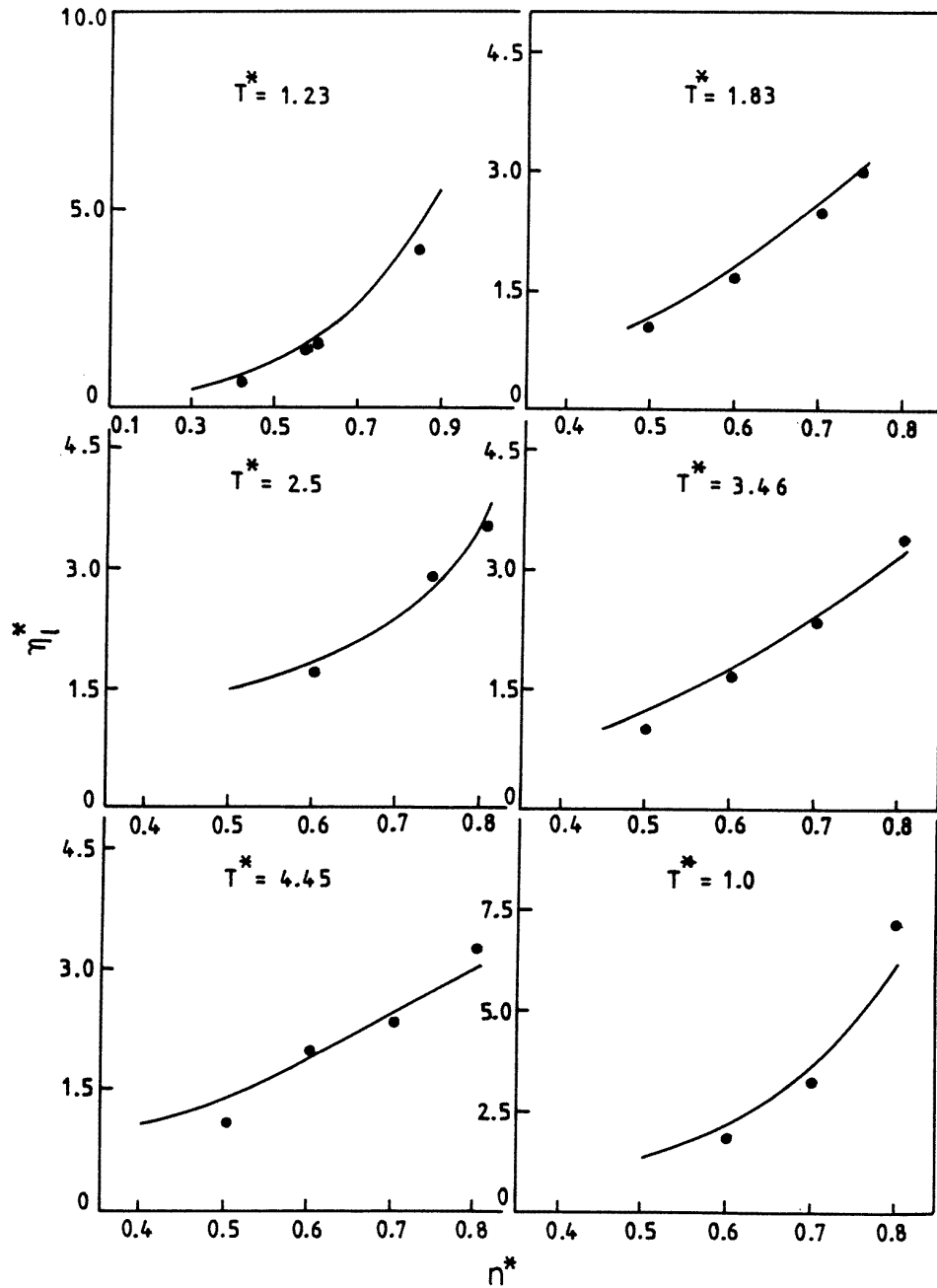


Figure 2. Variation in the longitudinal viscosity with density at various temperatures: —, our results; ●, results of the MD simulation of Heyes.

the values of η_l^* obtained in the previous section and η_S^* from our earlier work which were obtained using the same theory for the calculations. It is noted that the two results are quite close to each other except for a few thermodynamic states. The simulation results for the

Table 3. Values of the sum rules of the BSAC function. S_{nm}^B represents the m -body contribution to n th-order sum rule. The units are the same as those in table 1. T^* and n^* are the reduced temperature and density, respectively.

T^*	n^*	S_0^B	$S_{22}^B \times 10^{-3}$	$S_{23}^B \times 10^{-3}$	$S_{42}^B \times 10^{-6}$	$S_{43}^B \times 10^{-6}$
0.73	0.844	34.407	16.497	-8.58	24.6	-14.4
1.23	0.419	22.190	13.990	-2.12	39.1	-5.6
1.19	0.584	32.163	20.370	-4.33	55.2	-11.0
1.16	0.844	60.323	46.773	-19.50	124.8	-50.2
1.83	0.500	47.813	44.000	-6.75	188.3	-27.6
1.81	0.600	61.450	59.453	-11.09	253.8	-44.7
1.81	0.700	77.833	84.067	-18.98	353.9	-76.4
1.84	0.743	86.303	102.623	-25.11	434.7	-103.0
2.50	0.500	76.530	94.627	-14.41	496.3	-75.1
2.50	0.600	97.070	130.893	-23.93	676.0	-126.7
2.56	0.743	128.880	226.570	-54.33	1181.0	-288.6
3.46	0.500	119.403	176.937	-28.98	1263.9	-191.9
3.41	0.600	148.363	263.913	-49.58	1922.0	-332.1
3.50	0.700	180.577	394.363	-88.48	2971.4	-597.1
3.54	0.803	191.247	577.967	-155.99	4426.1	-640.0
4.53	0.600	219.720	544.943	-96.33	5835.1	-834.4
4.45	0.700	247.020	728.640	-153.73	7628.9	-1291.1
4.45	0.803	252.550	1034.937	-259.53	10879.9	-2134.8

bulk viscosity η_B^* (MD) [1] are given in the sixth column of table 4 for comparison. It can be seen from the table that our results are in reasonable agreement with the simulation data except for the density close to the triple-point density (0.844) where our results are rather different. In order to search for the reason for the difference between our values and the simulation values, we have calculated η_B^* from the relation $\eta_l^* - \frac{4}{3}\eta_S^*$ using the simulation values of η_S^* . This will avoid the error introduced using the theoretical value of the shear viscosity. For example, the result obtained at the triple point is now 2.47 compared with 3.92 obtained using the theoretical value of the shear viscosity. Comparing these results with the simulation result (1.47) we see that the results obtained now are certainly better. Finally in the fifth column we have studied the effect of three- and four-body contributions in determining the bulk viscosity. In table 4, $\eta_{B(2)}^*$ represents the bulk viscosity obtained from equation (31) including only the pair distribution contribution to the sum rules. It is found that the effect of the triplet contribution is a maximum at the triple-point density and it decreases with decrease in density and increase in temperature. It is also noted that $\eta_{B(2)}^*$ is surprisingly close to η_B^* (MD). However, this should not imply that the multiparticle correlations are not important for determining the bulk viscosity.

The theoretical results for η_B^* which are given in the fourth column of table 3 are compared with MD simulation data in figure 3. From the figure it is seen that, although our results are close to the MD results, the curvature of theoretical curves for η_B^* versus n^* changes gradually from concave to convex with increase in T^* . MD data are not always sufficient to show a linear dependence of η_B^* on n^* . It may be recalled that η_B^* varies as n^{*2} for dilute gases. It is also known that other transport coefficients do show a non-linear dependence on density. The difference in variation of our calculated η_B^* from MD data could be due to the neglect of energy fluctuation terms in the sum rules, which is probably important at high temperatures and densities, or due to the inadequacy of our model memory function.

Table 4. Values of the bulk viscosities. η_B^* represents the bulk viscosities obtained from equation (31) obtained using all the contributions to the sum rules taken from table 3. $\eta_{B(2)}^*$ is obtained by including only two-body contribution to sum rules. $\eta_B^*(\text{MD})$ represents the MD data of Heyes. η_B^* given in the third and seventh columns are obtained by taking theoretical values of longitudinal viscosity given in table 2 (fourth column) and the theoretical and MD values of the shear viscosities, respectively.

T^*	n^*	$\eta_B^* = (\eta_l - \frac{4}{3}\eta_S^*)$	η_B^*	$\eta_{B(2)}^*$	$\eta_B^*(\text{MD})$	$\eta_B^* = (\eta_1^* - \frac{4}{3}\eta_S^*(\text{MD}))$
0.733	0.844	3.92	3.59	1.682	1.47	2.47
1.23	0.419	0.43	0.43	0.355	0.36	0.46
1.19	0.584	0.96	0.96	0.723	0.78	0.94
1.16	0.844	0.299	2.96	1.568	1.55	2.09
1.83	0.500	0.635	0.635	0.524	0.52	0.65
1.81	0.600	0.981	0.980	0.770	0.78	0.99
1.81	0.700	1.336	1.342	0.993	1.05	1.29
1.84	0.743	1.41	1.44	1.030	1.25	1.29
2.50	0.500	0.602	0.603	0.499	—	—
2.50	0.600	0.852	0.855	0.679	0.77	0.82
2.56	0.743	1.032	1.105	0.796	1.18	1.00
3.46	0.500	0.691	0.687	0.558	0.48	0.82
3.41	0.600	0.883	0.889	0.693	0.82	0.99
3.50	0.700	1.015	1.057	0.770	0.98	1.08
3.54	0.803	0.894	1.03	0.622	1.34	0.90
4.53	0.600	0.840	0.866	0.678	0.72	0.67
4.45	0.700	0.906	0.991	0.727	1.02	1.15
4.45	0.803	0.532	0.856	0.567	1.50	0.90

5.3. Low-density limit

It is of interest to point out that our theory gives a non-zero value of longitudinal viscosity in the low-density limit. Using $P = 2\bar{E}/3V$ and $\bar{E} = 3NkT/2$ for a dilute gas, it is found that in the $n \rightarrow 0$ limit

$$S_0^l = \frac{4}{3}(k_B T)^2 + O(n) \quad (32)$$

$$S_2^l = F_1 n \quad (33)$$

$$S_4^l = F_2 n \quad (34)$$

where F_1 and F_2 are independent of densities and depend on the temperature and interatomic potential. Their explicit expressions can be easily obtained from equations (13) and (16) with the understanding that $g(r)$ will have a low-density value. Substituting for S_0^l , S_2^l and S_4^l from equations (32)–(34) in equation (31), we obtain

$$\eta_l = \frac{2}{\pi}(k_B T)^3 \left(\frac{16}{9}\right) \left(\frac{F_2}{F_1^3}\right)^{1/2} \quad (35)$$

which is clearly finite. Here it may be noted that our theory also predicts the density-independent value of shear viscosity in the dilute gas limit.

It is also of great interest to study the dilute gas limit of the bulk viscosity as it is known that the bulk viscosity is zero for an ideal gas. Employing the procedure used above in deriving equations (32)–(34), it is noted that in the case of an ideal gas

$$\langle J_{aa} \rangle = 2E$$

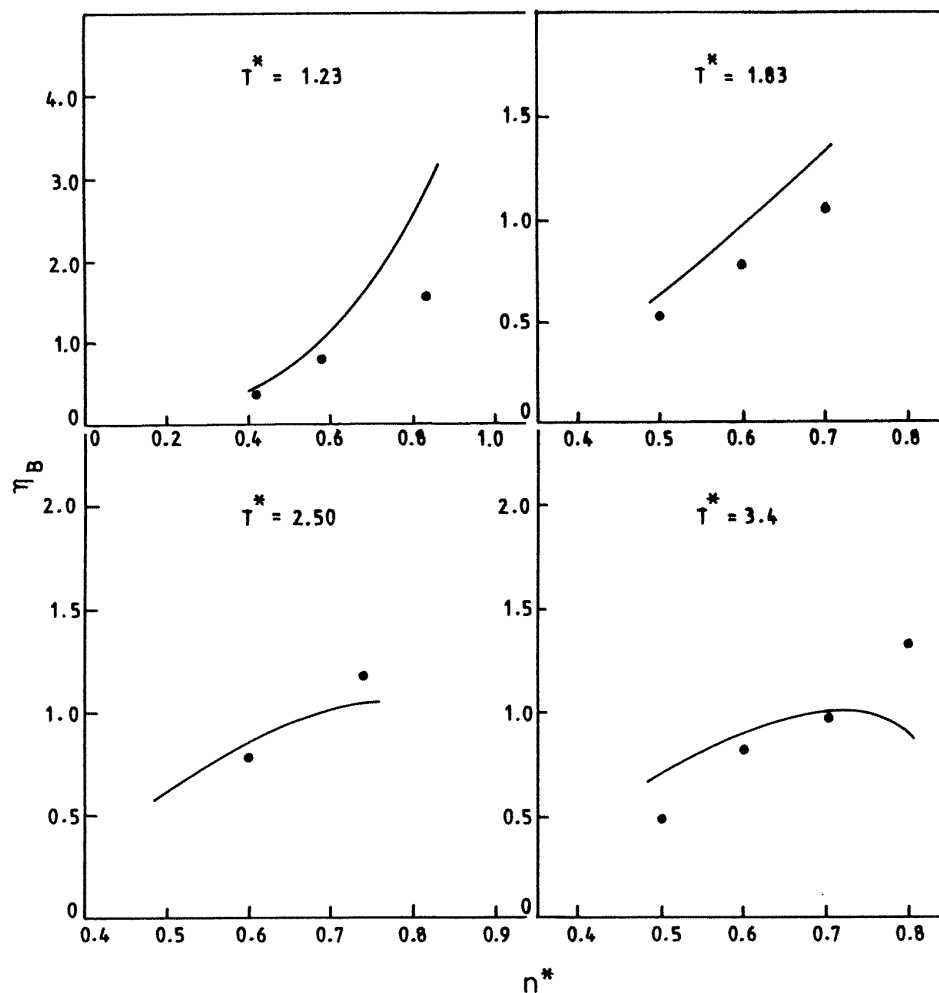


Figure 3. Variation in the bulk viscosity with density at various temperatures: —, our results; ●, MD data of Heyes.

and

$$\eta_B = \frac{1}{9Vk_B T} \sum_a \sum_b \int_0^\infty dt \left\langle \left(\frac{p_{ia}^2}{m} - \frac{p_{ia}^2}{m} \right) \left(\frac{p_{jb}^2(t)}{m} - \frac{p_{jb}^2}{m} \right) \right\rangle \quad (36)$$

which clearly vanishes. This result can also be obtained from the sum rules of BSAC function given in section 3.2. It is noted from equation (17) that, for a non-interacting gas, S_0^B vanishes, which in turn results in a zero values of the bulk viscosity.

On the other hand, for the $n \rightarrow 0$ limit it is noted that

$$S_0^B = nX_1 \quad (37)$$

$$S_2^B = nX_2 \quad (38)$$

$$S_4^B = nX_3 \quad (39)$$

where X_1 , X_2 and X_3 can be obtained from equations (17)–(19) by using the dilute gas value of $g(r)$. Substituting equations (37)–(39) in equation (31), we obtain

$$\eta_B = \frac{2}{\pi} \frac{n^2}{k_B T} \frac{X_1^{3/2}}{X_2} \sqrt{X_3 X_1 - X_2^2} \quad (40)$$

which predicts that η_B tends to n^2 in agreement with kinetic theory. Thus it is gratifying to see that our approach reproduces the exact density dependence of these viscosities for an ideal gas as well as those predicted for dilute and dense fluids.

6. Summary and conclusion

In this paper we have derived expressions for the sum rules of the LSAC and BSAC functions. These have been evaluated numerically for the LJ potential for various densities and temperatures. These results for the sum rules and Mori memory function formalism have been used to study the time evolution of the LSAC and BSAC functions and the corresponding viscosities. By studying the density and temperature dependences of these we have found that both correlated collisions and the attractive part of the potential play important roles in determining the bulk viscosity and hence the longitudinal viscosity. We have found that our theory provides good agreement of the longitudinal viscosity with the simulation results. The results for bulk viscosity are generally in reasonable agreement with the simulation data except for a few thermodynamic points where they are not. Our theory also predicts the exact low-density limit of both η_l and η_B .

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