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## Theory of transport coefficients of simple fluids

K Tankeshwar<sup>†</sup>, K N Pathak<sup>†</sup> and S Ranganathan<sup>‡</sup>

<sup>†</sup> Department of Physics, Panjab University, Chandigarh-160 014, India

<sup>‡</sup> Department of Mathematics and Computer Science, Royal Military College of Canada, Kingston, Ontario K7K 5L0, Canada

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**Abstract.** We report exhaustive calculations of the density and temperature dependences of the time evolution of the velocity, transverse stress and energy current density correlation functions and the corresponding transport coefficients for Lennard–Jones fluids over wide ranges of densities and temperatures. The calculated results are compared with the recent molecular dynamics data. Overall, good agreement has been achieved.

### 1. Introduction

With the aim of studying the atomic transport properties of monatomic liquids and dense gases in terms of a given interatomic potential, we have derived the molecular expressions for the first three non-vanishing sum rules of the velocity autocorrelation (VAC) (Tankeshwar *et al* 1987), transverse stress autocorrelation (TSAC) (Tankeshwar *et al* 1988) and energy current density autocorrelation (ECDAC) (Tankeshwar *et al* 1989) functions. The fourth non-vanishing sum rule of the VAC function has also been derived. The expressions for these coefficients involve the interatomic potential and the static correlation functions up to five particles. Owing to non-availability of sufficient information about the static triplet and higher particle correlation functions, we have used the superposition approximation (SA) and a low-order decoupling approximation (Tankeshwar *et al* 1987) for these, respectively. Our final expressions involve only the static pair correlation function  $g(r)$  and have been put into the form which is readily calculable for a given potential and  $g(r)$ . These have been calculated for Lennard–Jones (LJ) fluids using  $g(r)$  from the optimised cluster theory of Sung and Chandler (1974) for some ranges of densities and temperatures. Using these results and Green Kubo formulae for the transport coefficients and memory function formalism with the  $\text{sech}(bt)$  form of the memory function, we have calculated the coefficients of the self-diffusion, shear viscosity and thermal conductivity. The results obtained have been compared with molecular dynamics (MD) data (Heyes 1983, 1984) available up to 1984.

In the present work, the validity of the SA and low-order decoupling approximation used in obtaining the numerical results of the frequency sum rules has been checked by performing some MD calculations and using already existing MD data (Lee and Chung 1982, Toxvaerd 1984). The errors involved in numerical values of sum rules due to these approximations have been found to be not very significant. In this paper we have also studied the density and temperature dependences of the time evolution of the VAC, TSAC

and ECDAC functions. This was not done in our earlier work. The results for the time evolution of these autocorrelation functions are also compared with MD data wherever available. It is found that the effect of density dependence on the normalised VAC function is strong and it is moderate for the ECDAC function. It is found to be rather weak for the normalised TSAC function. On the other hand, for the temperature dependence it is found that its effect is strong for the VAC function, moderate for the TSAC function and rather small for the ECDAC function. These results are quite important and provide us with information about the importance of the correlated collisions and the attractive part of the potential in the theory of atomic transport in fluids.

In order to see the quality of results over the entire fluid range, we have calculated the transport coefficients for several more densities and temperatures. These are compared with recent MD data (Heyes 1988). Generally, good agreement has been achieved. The present work provides a comprehensive picture for the time evolution of the time correlation functions and the transport coefficients for whole of the fluid range of LJ system.

In section 2 we briefly present the theory and the model for the memory function. The calculations and results are given in section 3. In section 4 we present the conclusions.

## 2. Theory

### 2.1. Generalities

The transport coefficients of mass (diffusion), momentum (viscosity) and energy (thermal conductivity) can be written as Green Kubo integrals (Boon and Yip 1980, Hansen and McDonald 1986) of an appropriate time correlation function. Explicitly these are given as

$$\mu = K \int_0^{\infty} dt C(t) \quad (1)$$

where  $\mu$  is a generalised transport coefficient and  $K$  is some thermodynamic constant. The autocorrelation function  $C(t)$  is defined as

$$C(t) = \langle A(t)A(0) \rangle \quad (2)$$

where  $A(t)$  is an appropriate dynamical variable. The angular brackets in equation (2) represent the thermodynamic average. If  $A(t)$  is the velocity of the particle, the corresponding transport coefficient is the self-diffusion coefficient given by

$$D = \frac{k_B T}{m} \int_0^{\infty} V(t) dt \quad V(t) = \frac{\langle v_{1x}(t)v_{1x}(0) \rangle}{\langle v_{1x}^2 \rangle} \quad (3)$$

where  $v_{1x}$  is the  $x$  component of the velocity of the particle labelled 1. The TSAC function is related to the shear viscosity defined as

$$\eta = \frac{1}{Vk_B T} \int_0^{\infty} S(t) dt \quad S(t) = \langle J_{xy}(t)J_{xy}(0) \rangle \quad (4)$$

where

$$J_{xy}(t) = \sum_i [mv_{ix}(t)v_{iy}(t) + F_{iy}(t)x_i(t)]. \quad (5)$$

In equation (5),  $F_{ix}(t)$ ,  $v_{ix}(t)$  and  $x_i(t)$  are the  $x$  components of force on, velocity of and

position of the  $i$ th particle at time  $t$ . Similarly the thermal conductivity coefficient  $\lambda$  is related to the ECDAC given by

$$\lambda = \frac{1}{Vk_B T^2} \int_0^\infty E(t) dt \quad E(t) = \langle J_x^c(t) J_x^c(0) \rangle \quad (6)$$

$$J_x^c(t) = \sum_i \left( \frac{p_i^2}{2m} v_{ix}(t) + \frac{1}{2} \sum_{i \neq j} U_{ij} v_{ix}(t) - \frac{1}{2} \sum_{i \neq j} \frac{\partial U_{ij}}{\partial r_{ij}} \hat{r}_{ij} \cdot v_i(t) \right) \quad (7)$$

where the total interaction potential  $U(r) = \frac{1}{2} \sum_{i \neq j} U_{ij} = \frac{1}{2} \sum_{i \neq j} U(|r_i - r_j|)$ ,  $r_{ij} = r_i - r_j$  and  $\hat{r}_{ij} = r_{ij}/r_{ij}$ . In the above equations,  $n$ ,  $k_B$ ,  $m$  and  $V$  are the density, Boltzmann constant, temperature, atomic mass and volume of the system, respectively. The above expressions for the transport coefficients are quite general and valid for any density and temperature.

The exact evaluation of the time correlation functions is not yet feasible except for very simple cases and for some models of fluids. However, at the molecular level the time evolution of the time correlation function can be obtained using the generalised Langevin equation

$$\frac{\partial C(t)}{\partial t} = - \int_0^t M_1(t - \tau) C(\tau) d\tau \quad (8)$$

where  $M_1(t)$  is the first-order memory function or relaxation kernel. In order to calculate the time correlation function from equation (8) the fundamental theoretical quantity to be calculated is the memory function  $M_1(t)$ . It follows from the technique used in deriving equation (8) that  $M(t)$  also satisfies an equation similar to equation (8). A generalisation of this leads to

$$\frac{\partial M_n(t)}{\partial t} = - \int_0^t M_{n+1}(t - \tau) M_n(\tau) d\tau \quad n = 1, 2, 3, \dots \quad (9)$$

where  $M_n(t)$  is the  $n$ th-stage memory function. The Fourier Laplace transform of equation (8) coupled with equation (9) provide the continued-fraction representation, namely

$$\tilde{C}(\omega) = -C(0)/[\omega + \tilde{M}_1(\omega)] \quad \tilde{M}_n(\omega) = -\delta_n/[\omega + \tilde{M}_{n+1}(\omega)] \quad (10)$$

where  $\delta_n = M_n(0)$  and these are called Mori coefficients. These are related to coefficients in the short-time expansion of the time correlation function given by

$$C(t) = C_0 - C_2(t^2/2!) + C_4(t^4/4!) - C_6(t^6/6!) + \dots \quad (11)$$

where  $C_0$ ,  $-C_2$ ,  $C_4$  and  $-C_6$  are the frequency sum rules of the spectral function of the time correlation function. The sum rules are exactly expressible in terms of the static correlation functions and the interatomic potential. The expressions for a few of these coefficients for the VAC, TSAC and ECDAC functions have already been obtained by us

(Tankeshwar *et al* 1987, 1988, 1989). The coefficients  $\delta_n$  and  $C_{2n}$  are related. The first few  $\delta_n$  are given as

$$\delta_1 = C_2/C_0 \quad \delta_2 = C_4/C_2 - C_2/C_0 \quad \delta_3 = (C_6/C_2 - C_4^2/C_2^2)/\delta_2. \tag{12}$$

The frequency spectrum  $f(\omega)$  of the time correlation function is defined as

$$f(\omega) = 2\tilde{C}''(\omega) = 2 \int_0^\infty \cos(\omega t) C(t) dt \tag{13}$$

where  $\tilde{C}''(\omega)$  is the imaginary part of  $\tilde{C}(\omega)$ .  $C(t)$  can be obtained from

$$C(t) = \frac{1}{\pi} \int_0^\infty \cos(\omega t) f(\omega) d\omega. \tag{14}$$

The generalised Green Kubo expression (1) can be written in terms of  $\tilde{C}(\omega)$  as

$$\mu = -iK\tilde{C}(0). \tag{15}$$

The problem of calculation of time correlation functions and hence transport coefficients now reduces to the calculation of the appropriate memory function.

### 2.2. Model for the memory function

In order to calculate  $C(\omega)$ , it is necessary to truncate the hierarchy of equation (10) at some suitable stage. Higher-order  $\tilde{M}_n(\omega)$  are more complicated objects mathematically owing to the restricted time evolution of fluctuating forces appearing in the expressions for  $\tilde{M}_n(\omega)$ . Therefore, one normally restricts the discussion to a first- or second-stage memory function. Although we have a microscopic expression for the memory function, its calculation is not simple and amounts to a solution of a many-body problem (Boon and Yip 1980, Hansen and McDonald 1986). Therefore, several phenomenological forms of the memory function have been proposed in the literature (Martin and Yip 1968) and an extensive review of these has been given by Boon and Yip (1980). In this work we use a phenomenological form (Tankeshwar *et al* 1987, 1988, 1989) given by

$$M_1(t) = a \operatorname{sech}(bt). \tag{16}$$

This choice of the memory function enables us to incorporate its short-time behaviour exactly and its exponential behaviour for large times is also a desired feature (Levesque and Verlet 1970). The parameters  $a$  and  $b$  in equation (16) can be determined by requiring that the first two coefficients in the expansion of equation (16) and the actual memory function are the same. We obtain

$$a = \delta_1 \quad b^2 = \delta_2. \tag{17}$$

Defining

$$\tilde{M}_1(\omega) = \tilde{M}'_1(\omega) + i\tilde{M}''_1(\omega) = i \int_0^\infty \exp(i\omega t) M_1(t) dt \tag{18}$$

we have

$$\tilde{M}'_1(\omega) = (\pi a/2b) \tanh(\pi\omega/2b) + i(a/2b)\{\psi[(b + i\omega)/4b] - \psi[(b - i\omega)/4b]\} \tag{19a}$$

$$\tilde{M}''_1(\omega) = (\pi a/2b) \operatorname{sech}(\pi\omega/2b) \tag{19b}$$

where  $\psi(x)$  is the Euler psi function. The expression obtained for the frequency spectrum  $f(\omega)$  is given by

$$f(\omega) = 2\delta_0 \tilde{M}_1''(\omega) / \{[\omega + \tilde{M}_1'(\omega)]^2 + [\tilde{M}_1''(\omega)]^2\}. \quad (20)$$

The time correlation function  $C(t)$  can be calculated using equations (20) and (14) and hence the expression for the transport coefficients is obtained to be

$$\mu = (2/\pi)(\delta_0/\delta_1)\sqrt{\delta_2} K. \quad (21)$$

On the other hand, if we truncate the hierarchy of equation (10) at the second stage and assume

$$M_2(t) = \delta_2 \operatorname{sech}(\sqrt{\delta_3}t). \quad (22)$$

The expression obtained for  $f(\omega)$  is given by

$$f(\omega) = 2\delta_0 \delta_1 \tilde{M}_2''(\omega) / \{[\omega^2 - \delta_1 + \omega \tilde{M}_2'(\omega)]^2 + [\omega \tilde{M}_2''(\omega)]^2\} \quad (23)$$

where  $\tilde{M}_2'(\omega)$  and  $\tilde{M}_2''(\omega)$  are the real and imaginary parts of  $\tilde{M}_2(\omega)$ . The resulting expression for the generalised transport coefficient is obtained as

$$\mu = (\pi/2)K(\delta_0/\delta_1)(\delta_2/\sqrt{\delta_3}). \quad (24)$$

We use equations (21) and/or (24) to calculate the transport coefficients and equations (14) and (20) or (23) to study the time evolution of the time correlation functions.

### 3. Calculations and results

We now present the numerical evaluation of the time evolution of the VAC, TSAC and ECDAC functions and use them to calculate the corresponding transport coefficients.

#### 3.1. Velocity autocorrelation function and diffusion coefficient

The calculations of  $\delta_1$ ,  $\delta_2$  and  $\delta_3$  appearing in the continued fraction for the Fourier Laplace transform of the VAC function require knowledge of the static correlation functions for two, three and four particles, respectively. The explicit expressions for  $\delta_1$ ,  $\delta_2$  and  $\delta_3$  are given in our earlier work (Tankeshwar *et al* 1987). There we used the SA and a low-order decoupling approximation for the static triplet and quadruplet correlation functions, respectively, to obtain the numerical values. In order to check the validity of the SA in estimating  $\delta_2$ , now we have made MD simulation of the triplet contribution to the fourth-frequency sum rules of the VAC function. The expression which we have used to evaluate the triplet contribution is

$$V_{43} = \frac{1}{Nm^2} \left\langle \sum_{j,k} \sum_{\alpha} U_{x\alpha}(r_{ij}) U_{x\alpha}(r_{ik}) \right\rangle \quad (25)$$

where  $N$  is the number of particles and

$$U_{\alpha\beta} = \partial^2 U(r_{ij}) / (\partial r_{i\alpha} \partial r_{j\beta}). \quad (26)$$

The interaction potential  $U(r_{ij})$  used in our calculations is the LJ potential with parameters  $\epsilon/k_B = 201.9$  K and  $\sigma = 3.57$  Å<sup>-1</sup>. These parameters are representative of fluid krypton. We have simulated 108 particles of mass  $m = 139.44 \times 10^{-24}$  g (the mass of a Kr atom)

**Table 1.** Comparison of MD and SA results for  $V_{43}$  and  $S_{23}$  at  $T^* = 1.47$ .

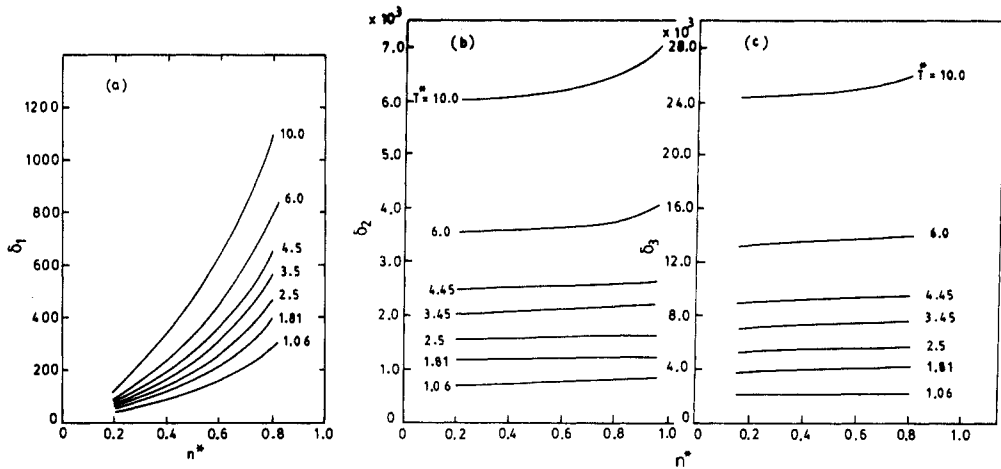
$n^*$	$V_{43} (10^{52} \text{ s}^{-2})$		$S (10^{36} \text{ cm}^2 \text{ s}^{-1})$	
	MD	SA	MD	SA
0.482	0.0259	0.0256	0.038	0.044
0.628	0.0568	0.0595	0.082	0.105
0.844	0.22	0.24	0.32	0.44

**Table 2.** Comparison of MD results (Lee and Chung 1982) and our results for the Mori coefficients  $\delta_n$  (measured in units of  $m\sigma^2/\epsilon$ ) of the VAC function. The values in parentheses represent the MD values of Toxvaerd (1984).

$n^*$	$T^*$	$\delta_1$		$\delta_2$		$\delta_3$	
		MD	Ours	MD	Ours	MD	Ours
0.85	0.727	273.8	272.1	563.0	588.74	1 793.0	1 440.7
0.85	0.778	287.8	282.4	606.0	617.96	2 045.0	1 594.4
0.85	4.76	793.1	798.6	3204.0	3103.1	11 850.0	10 995.0
0.85	4.66	774.6	789.2	3151.0	3046.3	11 670.0	10 757.0
0.75	1.134	252.4	255.2	801.0	794.6	2 640.0	2 422.1
0.75	1.104	250.5	251.5	796.0	777.2	2 596.0	2 358.3
0.75	5.267	644.5 (640.4)	645.6	3442.0 (3482.0)	3324.7	12 690.0 (13 130.0)	12 171.0
0.75	5.122	621.5	634.4	3316.0	3237.0	12 310.0	11 814.0
0.65	1.457	216.0	218.9	995.0	950.3	3 303.0	3 075.0
0.65	1.430	217.7	216.7	968.0	936.7	3 201.0	3 022.5
0.65	5.084	470.1	476.4	3241.0	3151.5	11 730.0	11 587.0
0.65	5.026	465.2	472.3	3201.0	3116.9	11 740.0	11 444.3
0.30	1.575	80.5	81.1	1066.0	1006.6	3 501.0	3 201.6

to calculate equation (25). The details of MD calculations have been given by Pathak *et al* (1985). The results are shown in table 1 for three densities  $n^* = n\sigma^3$  at  $T^*(k_B T/\epsilon) = 1.47$  along with the results obtained using the SA. From table 1 we find that the error involved in  $V$  by using SA is not significant.

In order to see the effect of the SA and low-order decoupling approximation on the numerical values of  $\delta_2$  and  $\delta_3$ , we compare our results in table 2 with already existing MD data of Lee and Chung (1982) and Toxvaerd (1984). We have used theoretically generated  $g(r)$  (Sung and Chandler 1974) for our calculations. From table 2, we have found that, for  $\delta_2$  which involves the triplet correlation function, the difference between our and the MD results is within the numerical error (5%). The error in estimating which involves up to a quadruplet correlation function is less than 10% except near the triple point where it is about 20%. Further, the percentage error in  $\delta_2$  and  $\delta_3$  decreases with decrease in density. Finally, we find that the use of the SA and a low-order decoupling approximation have an insignificant effect on the calculations of the total (including all the contributions) frequency sum rules. The results obtained for  $\delta_1$ ,  $\delta_2$  and  $\delta_3$  are plotted in figures 1(a), 1(b) and 1(c), respectively. In figures 1(b) and 1(c) it is seen that  $\delta_2$  and



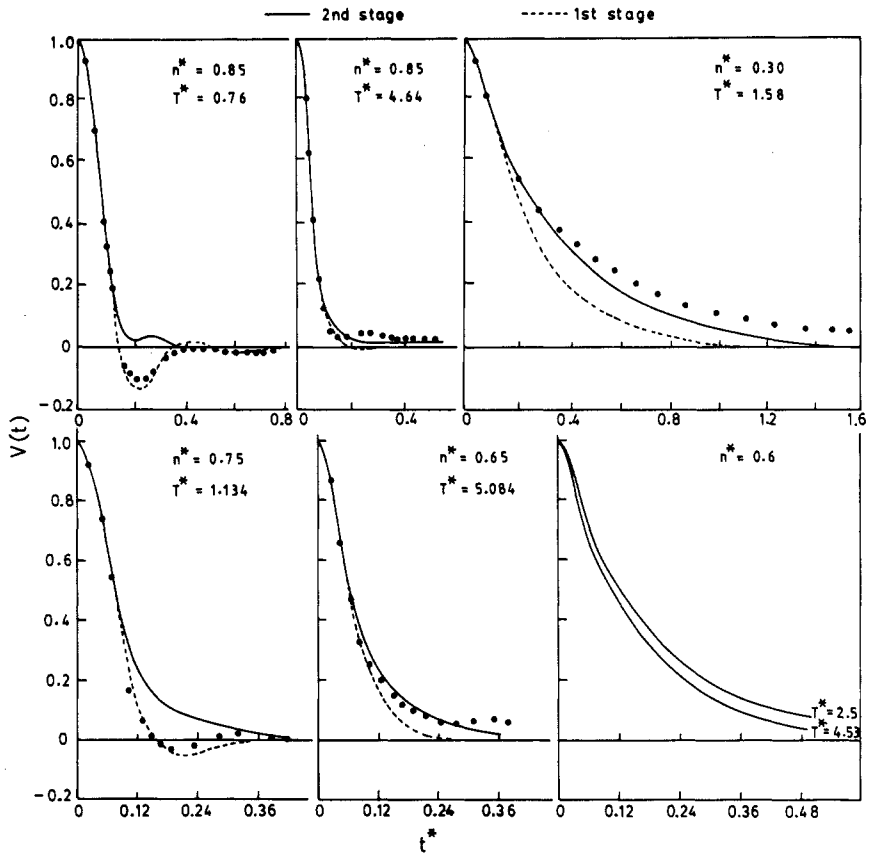
**Figure 1.** The variation in the Mori coefficients (a)  $\delta_1$ , (b)  $\delta_2$  and (c)  $\delta_3$  in units of  $m\sigma^2/\epsilon$  for the VAC function with density  $n^*$  for the different temperatures indicated against each curve.

$\delta_3$  are almost independent of density.  $\delta_3$  has been found to be linear in temperature ( $\delta_3 = CT^*$ ), whereas  $\delta_2$  deviates slightly from its linear behaviour. In contrast,  $\delta_1$  is strongly density and temperature dependent. From the behaviour of  $\delta_1$ ,  $\delta_2$  and  $\delta_3$  with density and temperature and equations (21) and (24) for the self-diffusion coefficient we expect that the density dependence of  $D$  is solely determined by  $\delta_1$ .

The time evolution of the VAC function  $V(t)$  has been calculated using equations (14), (20) and (23). The results obtained from equations (14) and (20) are shown as broken curves, whereas  $V(t)$  obtained using equations (14) and (23) are shown as full curves in figure 2 for six thermodynamic states. The MD results (Kushick and Berne 1973, Lee and Chung 1982) are represented as full circles. It can be seen from figure 2 that the results obtained using equation (20) (first stage of the continued fraction) for  $f(\omega)$  are in good agreement with MD data at low temperatures and high densities. On the other hand, the results obtained using equation (23) for  $f(\omega)$  (at the second stage of the continued fraction) are in good agreement for temperatures greater than the critical temperature. The results obtained for  $V(t)$  using two different expressions (equations (20) and (23)) for  $f(\omega)$  suggests that it is not only the form of the memory function which matters in determining the time development of the correlation function but also the stage at which the continued fraction is truncated. This has also been noted before (Kahol *et al* 1977) and needs further investigation. From our analysis of the time evolution of the VAC function, we have found that there is dramatic effect of density on the form of the VAC function. It exhibits a well known negative plateau (back-scattering) in the vicinity of the triple point. This result is incompatible with the Enskog hard-sphere theory in which the VAC function decays exponentially for all the densities and temperatures.

The results for the diffusion coefficients  $D^* = D(m/\epsilon\sigma)^{1/2}$  are obtained from equation (24) and  $D^*n^*$  are plotted in figure 3 as a function of density for four isotherms. The MD results of Heyes (1983, 1988) are also shown there. For a dilute gas,  $D^*n^*$  is almost constant. With increasing density the particles will be arrested in their cages formed by neighbouring particles and this results in a decrease in  $D^*n^*$  with increasing density as can be seen from figure 3. The temperature dependence of the diffusion





**Figure 2.** Variation in the normalised VAC function  $V(t)$  with time  $t^* = t(\epsilon/m\sigma^2)$  obtained for six thermodynamic states: —, results obtained from equation (14) and (23); ---, results from equations (14) and (20); ●, MD results (Kushick and Berne 1973, Lee and Chung 1982).

constants are presented in figure 4 for five densities along with the corresponding computer simulation (Heyes 1983, 1988) data. It can be seen from figures 3 and 4 that the agreement is satisfactory. The present work along with our earlier work predict the value of the self-diffusion coefficients over the entire fluid range except near the triple point, in agreement with MD results. Our theory also provides a good description of the density and the temperature dependences of the self-diffusion coefficient.

*3.2. Transverse stress autocorrelation function and shear viscosity*

The Mori coefficients  $\delta_0$ ,  $\delta_1$  and  $\delta_2$  for the TSAC function have been calculated using a procedure similar to that used for the Mori coefficients of the VAC function. We have also calculated the triplet contribution to  $\delta_1$ , using the MD method from the expression given by

$$S_{23} = \frac{1}{Nm^2} \left\langle \sum_{i,j,k} x_{ij}x_{ik} \sum_{\alpha,\beta} \left\{ U_{\alpha\beta}(r_{ij})U_{\alpha\beta}(r_{ik}) - \sum_{\alpha} U_{x\alpha}(r_{ij})U_{x\alpha}(r_{ik}) \right\} \right\rangle. \tag{27}$$

The details of the MD calculation are the same as described in section 3.1. The MD results

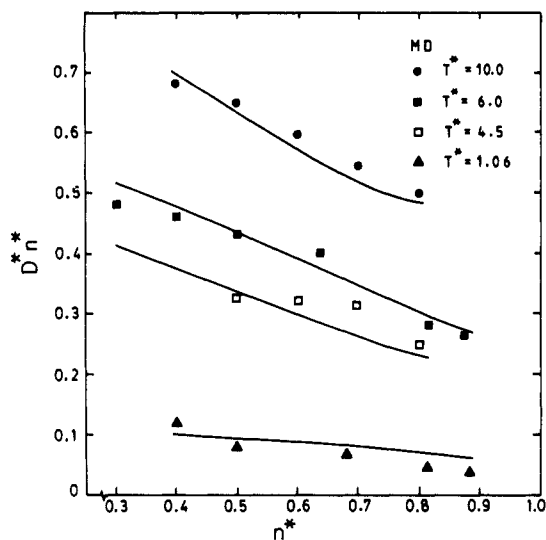


Figure 3. Variation in the diffusion coefficients with density at various temperatures: —, our results; ●, ■, □, ▲, MD results.

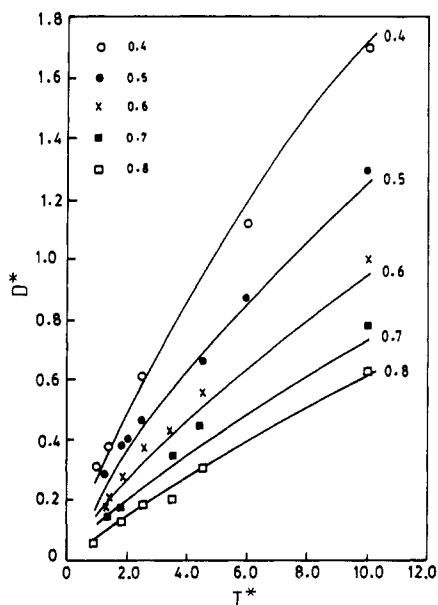
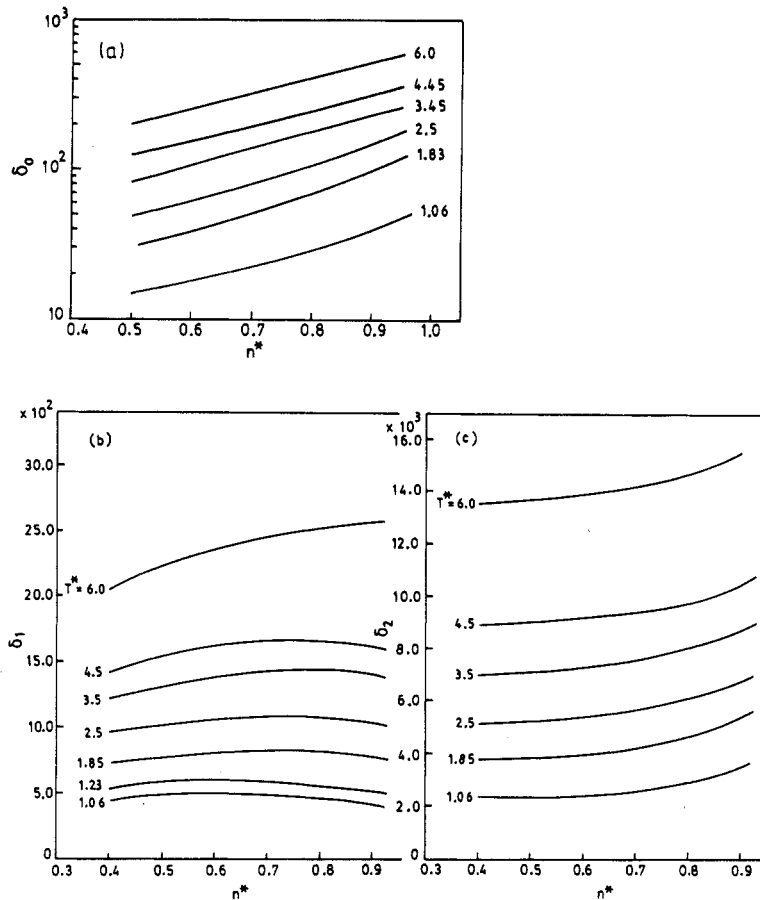


Figure 4. Variation in diffusion coefficients with temperature: —, our results; ○, ●, ×, ■, □, MD results.

are shown in table 1 along with the results obtained using the SA. From table 1, we have found that the ratio of  $(S_{23})_{SA}$  and  $(S_{23})_{MD}$  for  $n^* = 0.482, 0.628$  and  $0.844$  are 1.16, 1.28 and 1.38, respectively. These indicate that the SA overestimates the triplet contribution but the error involved in estimating the total frequency sum rule is insignificant.

In order to see the density and temperature dependences of Mori coefficients  $\delta_0, \delta_1$  and  $\delta_2$  for the TSAC function, we have plotted these in figures 5(a), 5(b) and 5(c), respectively. From figure 5(a) it can easily be seen that  $\delta_0$  depends strongly on density and temperature, whereas  $\delta_1$  is only weakly dependent on density but strongly depends on temperature. Specifically, for temperatures  $T^*$  up to 4.5, initially  $\delta_1$  increases slightly with increasing density and then becomes almost constant and finally shows a small decrease. For higher temperatures it has been found that  $\delta_1$  increases with increase in density for all the densities investigated here. It can be seen from figure 5(c) that  $\delta_2$  increases with increase in density for all densities and is almost linear in temperature, i.e.  $\delta_2 = BT^*$ .

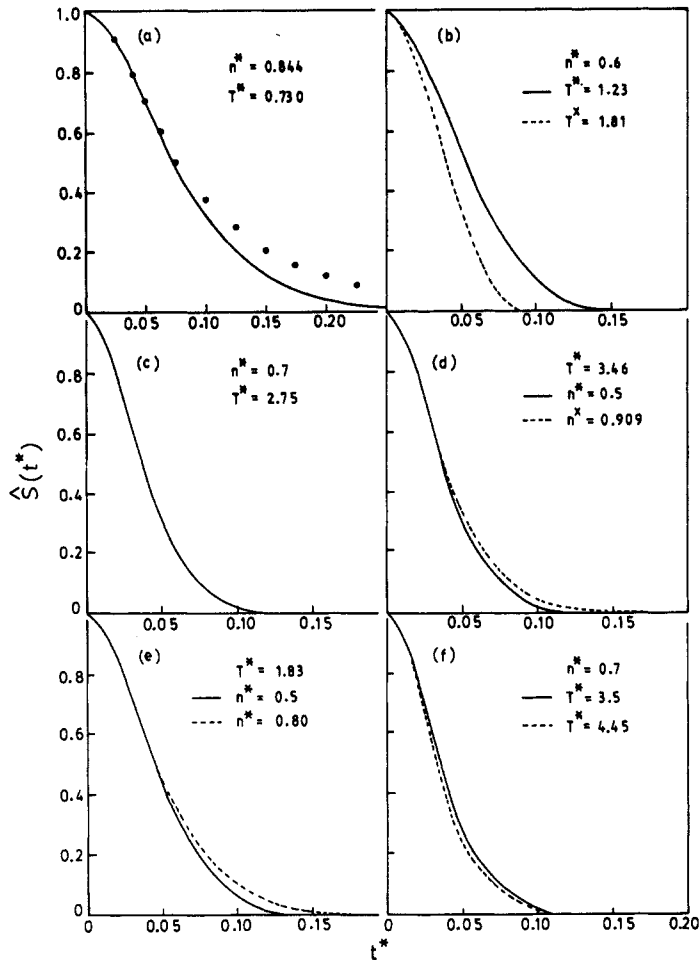
The time evolution of the TSAC function is determined from equations (14) and (20) using the respective values of  $\delta_n$ . The time development of the normalised TSAC function is plotted in figure 6 as full curves for ten thermodynamic states. The results obtained are compared with the MD data of Heyes (1983) which are available only at the triple point. We have found that our theory provides reasonable agreement with the MD data. In figures 6(b) and 6(c) we have shown the temperature dependence of the decay of the TSAC function. The effect of temperature on the time dependence of the TSAC function was found to be quite significant. In figures 6(d) and 6(f) we have presented the results for the density dependence of  $S(t)$ . It can be noted that the time evolution of  $S(t)$  is not affected by the change in density for times less than  $0.04t^*$  but, for times greater than



**Figure 5.** Variation in (a)  $\delta_0$ , (b)  $\delta_1$  and (c)  $\delta_2$  in units of  $m\sigma^2/\epsilon$  for the TSAC function with density for the different temperatures indicated against each curve.

$0.04t^*$ , the decay of  $S(t)$  is found to slow down with increase in the density. We have also found that the effect of temperature on the area under the normalised  $S(t)$  curve is greater than the effect of density. This implies that inclusion of correlated collisions is not as important as the modification of the hard-sphere diameter in hard-sphere theories. It is consistent with the use of the effective hard-sphere diameter in the Enskog theory used by Heyes (1988) who has obtained reasonable results for the shear viscosity. Our results show no negative region (back-scattering effect) in the time development of  $S(t)$  even at the triple point, in agreement with the MD data.

The shear viscosity of the LJ fluids has been calculated using equation (21) with  $K = n/k_B T$ . The results obtained for  $\eta^* = \eta\sigma^2(m\epsilon)^{-1/2}$  have already been plotted in our earlier work (Tankeshwar *et al* 1988) for six isotherms. In order to see the quality of the results of our theory for the entire fluid range, the results obtained for a few more thermodynamic states are plotted in figure 7. In the present work we have also studied the temperature dependence of the shear viscosity. It is given in figure 8. From our earlier work as well as from the present paper we have found that the  $\text{sech}(bt)$  form of the memory function provides a good density dependence of the shear viscosity.



**Figure 6.** Variation in the normalised TSAC function  $\hat{S}(t)$  with  $t^*$  for different densities and temperatures: —, ---, our results; ●, MD results (Heyes 1983).

However, for the temperature dependence of  $\eta$  we have found that the results are in reasonable agreement for densities  $n^*$  up to 0.7. The temperature dependence of  $\eta$  is not well determined by our theory in the vicinity of the triple-point density. This result is consistent with our earlier conclusion that in the vicinity and at the triple point a Gaussian model for  $M_1(t)$  provides better results than the results obtained using the  $\text{sech}(bt)$  form of the memory function.

### 3.3. Energy current density autocorrelation function and thermal conductivity

The Mori coefficients for the ECDAC function have been calculated for different densities and temperatures.  $\delta_0$  as a function of density is plotted in figure 9(a) for different values of  $T^*$ . From the figure it can easily be seen that  $\delta_0$  shows strong dependences on density and temperature. From figures 9(b) and 9(c) it can be seen that  $\delta_1$  and  $\delta_2$  are both increasing functions of density and temperature.  $\delta_2$  is found to be almost linear in

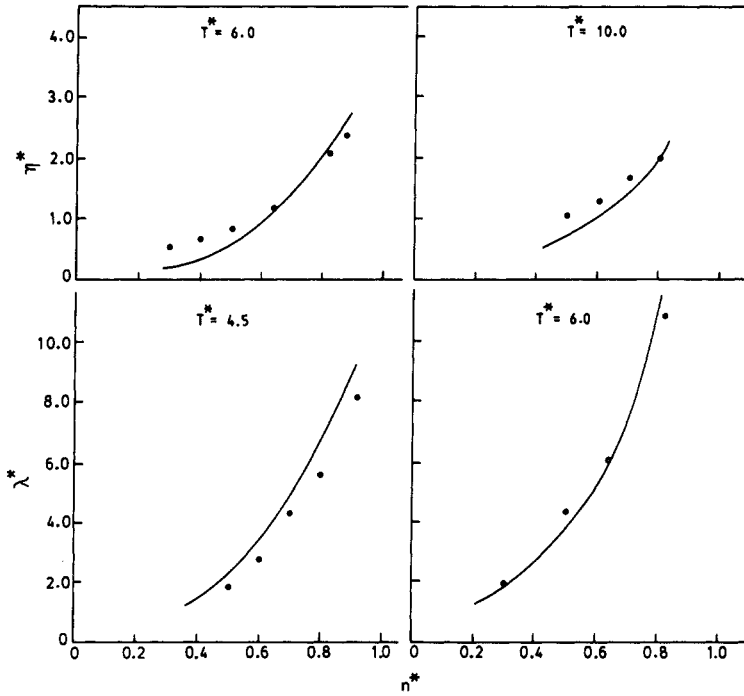


Figure 7. Variation in the shear viscosity  $\eta^*$  and the thermal conductivity  $\lambda^*$  with density: —, our results; ●, MD results (Heyes 1988).

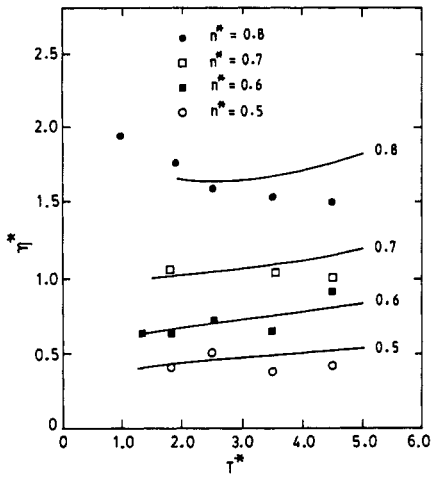


Figure 8. Variation in  $\eta^*$  with temperature for different densities indicated against each curve and set of symbols: —, our results; ●, ○, ■, □, MD data of Heyes (1983, 1988).

density. Further the enhancement of  $\delta_1$  with increase in density is found to be greater at high temperatures than at low temperatures.

In order to study the temperature and density dependences of the time evolution of the ECDAC function, we plot the normalised  $E(t)$  in figure 10. In figures 10(a) and 10(c) we have shown the temperature dependence of  $E(t)$ . It can be seen that the area under

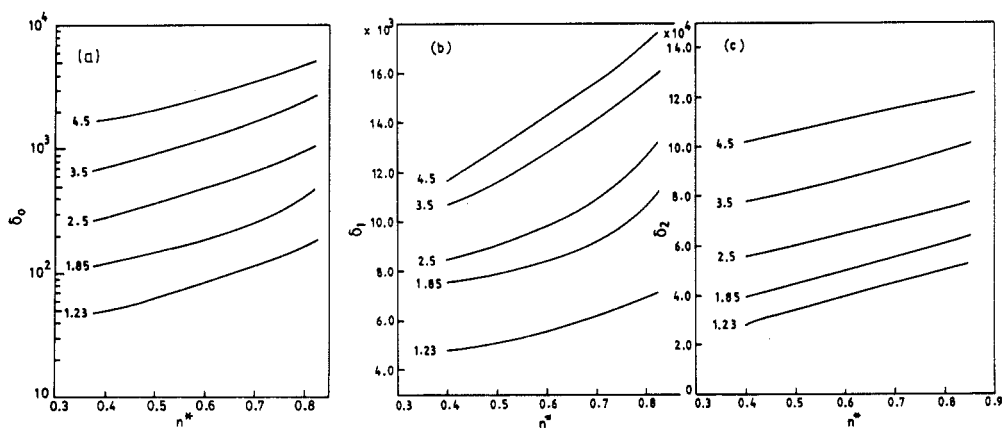


Figure 9. Variation in (a)  $\delta_0$ , (b)  $\delta_1$ , and (c)  $\delta_2$  in units of  $m\sigma^2/\epsilon$  for the ECDAC function with density for the different temperatures indicated against each curve.

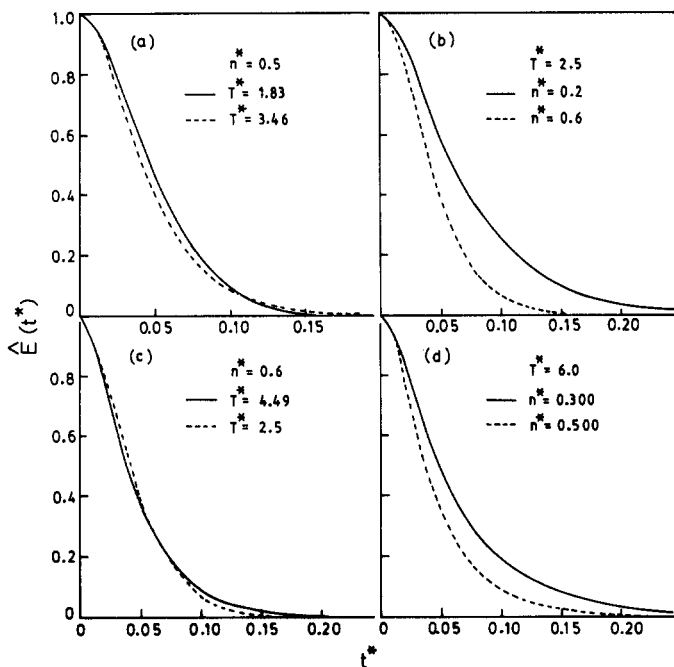
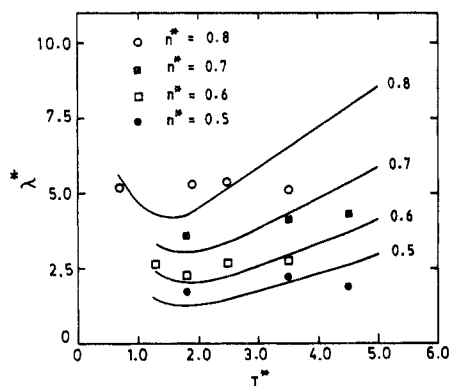


Figure 10. Variation in the normalised ECDAC correlation function with  $t^*$  for various densities and temperatures.

the  $E(t)$  curve for different temperatures at a given density is almost constant. From this we can say that the attractive part of the LJ potential does not play a significant role in determining the decay of  $E(t)$ . On the other hand, from figures 10(b) and 10(d), we find that the change in density affects the decay of  $E(t)$  significantly. Further, the decay of  $E(t)$  slows down with increase in density. This probably indicates that the inclusion of correlated collisions are important in the hard-sphere theories.



**Figure 11.** Temperature dependence of the thermal conductivity  $\lambda^*$  for densities indicated against each curve and set of symbols: —, our results;  $\circ$ ,  $\blacksquare$ ,  $\square$ ,  $\bullet$ , MD data of Heyes (1984, 1988).

The predicted results for  $\lambda^* = \lambda(m/\varepsilon)^{1/2} (\sigma^2/k_B)$  are plotted in figure 7 for two isotherms. From earlier and present results we have found that our predictions for the thermal conductivity provide a reasonable density dependence over the entire fluid range. The temperature dependence of the thermal conductivity is shown in figure 11 for four densities. The temperature dependence of  $\lambda$  is found to be reasonable except in the vicinity of the triple-point density where agreement between the MD results and our results are not very satisfactory.

#### 4. Conclusions

In this paper, we have presented a simple model for predicting the coefficients of the self-diffusion, shear viscosity and thermal conductivity of simple fluids. The theory is based on Mori's continued-fraction representation of the time correlation function in terms of the memory function. For the memory function we have proposed a  $\text{sech}(bt)$  form, the parameters of which have been determined using the frequency sum rules. The validity of the SA and the low-order decoupling approximation used in obtaining the numerical results of the frequency sum rules have been checked by performing some MD calculations and comparing our results with already existing MD data (Lee and Chung 1982, Toxvaerd 1984). The error involved owing to these approximations in the total frequency sum rules has been found to be insignificant. The numerical results presented in the present paper as well as in our earlier work (Tankeshwar *et al* 1987, 1988, 1989) now provide results for the transport coefficients (*i.e.*  $D$ ,  $\eta$  and  $\lambda$ ) over essentially the whole of the fluid range. The results are compared with the available MD data and generally good agreement is achieved. It is found that the density dependence of the transport coefficients is well described in our theory. The temperature dependence of the self-diffusion coefficient is found to be quite satisfactory. However, only a limited success has been achieved for the temperature dependence of the shear viscosity and the thermal conductivity.

We have also studied the effect of the density and temperature of the time correlation functions appearing in the Green Kubo formulae of the coefficients of self-diffusion, shear viscosity and thermal conductivity. It is found that the effect of the density dependence of the normalised VAC function is strong and it is less strong for the normalised EDCAC function. The density dependence of the normalised TSAC function is found to be rather weak. These results are important in the sense that these determine

the importance of the influence of the correlated collisions on transport properties. This implies that the influence of correlated collisions is a maximum for the self-diffusion coefficient, moderate for the thermal conductivity and small for the shear viscosity. This is in accordance with the predictions of the hard-sphere theory (Heyes 1988) which could not explain the self-diffusion coefficient and thermal conductivity of LJ fluids. We have also found that the effect of the temperature on the VAC function is strong. It is moderate for the TSAC function and small for the ECDAC correlation function. Since the repulsive part of the interaction potential becomes relatively more important at higher temperature, we therefore conclude that the attractive part of potential is important in determining the self-diffusion coefficient of LJ fluids.

In conclusion, it is gratifying to see that a simple theory without any adjustable parameter has predicted the results for the transport coefficients which are in agreement with the MD data over a wide fluid range. The results are not very satisfactory near the triple point. The theory uses only an interatomic potential and a theoretically generated static pair correlation function as input.

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### References

- Boon J P and Yip S 1980 *Molecular Hydrodynamics* (New York: McGraw-Hill)  
Hansen J P and McDonald I R 1986 *Theory of Simple Liquids* (New York: Academic)  
Heyes D M 1983 *J. Chem. Soc. Faraday Trans. II* **79** 1741  
— 1984 *J. Chem. Soc. Faraday Trans.* **80** 1363  
— 1988 *Phys. Rev. B* **37** 5677  
Kahol P K, Chaturvedi D K and Pathak K N 1977 *Physica A* **87** 192  
Kushick J and Berne B J 1973 *J. Chem. Phys.* **59** 3732  
Lee L L and Chung Ting Horng 1982 *J. Chem. Phys.* **77** 4650  
Levesque D and Verlet L 1970 *Phys. Rev. A* **2** 2514  
Martin P C and Yip S 1968 *Phys. Rev.* **170** 151  
Pathak K N, Ranganathan S, Bansal R and Bruns W 1985 *Phys. Rev. A* **31** 960  
Sung S and Chandler D 1974 *Phys. Rev. A* **9** 1688  
Tankeshwar K, Pathak K N and Ranganathan S 1987 *J. Phys. C: Solid State Phys.* **20** 5749  
— 1988 *J. Phys. C: Solid State Phys.* **21** 3607  
— 1989 *J. Phys. Condens. Matter* **1** 6181, 6193  
Toxvaerd S 1984 *J. Chem. Phys.* **81** 5131