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# Transport coefficients of classical dense fluids: a simple approach

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**Abstract.** We have used theoretical values of the sum rules in the information theory for the transport coefficients from work of Heyes and Powles, and have found that there is no noticeable improvement in the results for the diffusion coefficient of a Lennard-Jones fluid over their results obtained using an indirect method for the evaluation of the sum rules. We also propose a phenomenological form involving two parameters for the time development of the time correlation function. The parameters are determined from the frequency sum rules of the respective time correlation function to incorporate exactly its short-time behaviour. The values of the sum rules and Green–Kubo expressions are used to determine self-diffusion, shear viscosity and thermal conductivity of Lennard-Jones fluids over wide ranges of density and temperature. A reasonable agreement with computer simulation data is obtained for all the transport coefficients.

## 1. Introduction

Transport coefficients of simple classical fluids expressed in terms of appropriate time correlation functions are obtainable from computer simulation experiments for a given interaction potential representative of the fluid. Exhaustive computer simulation data for the self-diffusion, shear viscosity and thermal conductivity coefficients are now available [1–3] for a large number of thermodynamic states over the whole of the phase diagram of Lennard-Jones (LJ) fluids. Theoretically, attempts have been made recently to develop quantitatively accurate theories [4–6] of these transport coefficients using mainly the Mori memory function formalism [7, 8]. This approach, which was originally developed by Martin and Yip [9], involves choosing a phenomenological form for first- and/or second-order memory functions, and has been widely used to predict the transport coefficients. The parameters of the memory function were generally determined using the theoretically calculated frequency sum rules of the spectral function of the time correlation function (TCF). Overall these attempts have been quite successful in predicting the transport coefficients as was judged by their comparison with the simulation data over large ranges of density and temperature of the LJ fluid. Recently, Heyes and Powles [10] applied information theory, which involves optimization of the spectral function of the TCF itself, rather than the memory function. So-called second-, fourth- and sixth-order information theories involve frequency sum rules up to the second, fourth and sixth orders, respectively. These sum rules were obtained by them with the help of computer simulation and pre-knowledge of the time correlation function itself. But very recently Heyes *et al* [11] suggested that, if sum rules are obtained from the theory, one is likely to get better estimates of transport coefficients than those obtained by them using fourth-order information theory. This, then, may avoid the use of sixth-order information theory. Therefore, one of the motivations of

the present work is to use theoretical sum rules in fourth-order information theory and to see the improvement over the results of Heyes and Powles. In fact, the use of theoretical sum rules makes information theory more useful and complete. We have found that the use of theoretical sum rules does not improve the results obtained by Heyes and Powles. In addition to this, in the present work we use a phenomenological form involving two parameters for the time correlation function. Parameters are determined from the sum rules to incorporate exactly the short-time behaviour of the TCF. These have then been used to determine self-diffusion, shear viscosity and thermal conductivity of LJ fluids over wide ranges of density and temperature. The results obtained have been compared with computer simulation results. It has been found that the model used provides very good agreement for the self-diffusion coefficient. The agreement for shear viscosity and thermal conductivity with simulation results is also quite reasonable.

The layout of the paper is as follows. In section 2 we present the theory. The proposed model is also given there. In section 3, results and discussion are presented. The conclusion is given in section 4.

## 2. Theory

### 2.1. Generalities

The transport coefficients of mass (diffusion), momentum (viscosity) and energy (thermal conductivity) in terms of Green-Kubo integrals [7, 8] of an appropriate TCF can be written as

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

where  $\tau$  is the generalized transport coefficient and  $K$  is some thermodynamic constant. The normalized autocorrelation function  $\hat{C}(t)$  is defined as

$$\hat{C}(t) = \langle A(t)A(0) \rangle / \langle A^2 \rangle \quad (2)$$

where  $A(t)$  is an appropriate dynamic variable. In the above equation the angular brackets represent the ensemble average. The power spectrum of  $\hat{C}(t)$  is defined as

$$p(\omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \hat{C}(t) e^{i\omega t} dt \quad (3)$$

so that

$$\tau = \langle A^2 \rangle K \pi p(0). \quad (4)$$

Inverting equation (3), we have

$$\hat{C}(t) = \int_{-\infty}^{\infty} p(\omega) e^{-i\omega t} d\omega = 1 - (t^2 M_2/2!) + (t^4 M_4/4!) - \dots \quad (5)$$

where

$$M_{2n} = \int_{-\infty}^{\infty} \omega^{2n} p(\omega) d\omega. \quad (6)$$

If  $A(t)$  is the velocity of the tagged particle, then the corresponding transport coefficient is the self-diffusion coefficient, given by

$$D = \frac{k_B T}{m} \int_0^\infty V(t) dt. \quad (7a)$$

The velocity autocorrelation (VAC) function is given by

$$V(t) = \langle v_{1x}(t)v_{1x}(0) \rangle / \langle v_{1x}^2 \rangle \quad (7b)$$

where  $v_{1x}$  is the  $x$  component of the velocity of the particle labelled as 1. The transverse stress autocorrelation (TSAC) function  $S(t)$  is related to the shear viscosity defined as

$$\eta = \frac{1}{V k_B T} \int_0^\infty S(t) dt \quad S(t) = \langle J_{xy}(t)J_{xy}(0) \rangle \quad (8)$$

where

$$J_{xy}(t) = \sum_{i=1}^N [m v_{ix}(t)v_{iy}(t) + F_{iy}(t)x_i(t)]. \quad (9)$$

In equation (5)  $F_{ix}(t)$ ,  $v_{ix}(t)$  and  $x_i(t)$  are the  $x$  components of force, velocity and position of the  $i$ th particle at time  $t$ . Similarly the thermal conductivity coefficient  $\lambda$  is related to the energy current density autocorrelation (ECDAC) function  $E(t)$ , as

$$\lambda = \frac{1}{V k_B T^2} \int_0^\infty E(t) dt \quad E(t) = \langle J_x^e(t)J_x^e(0) \rangle \quad (10)$$

where

$$J_x^e(t) = \sum_{i=1}^N \frac{p_i^2}{2m} v_{ix}(t) + \frac{1}{2} \sum_{i \neq j} u_{ij} v_{ix}(t) - \frac{1}{2} \sum_{i \neq j} \left( \frac{\partial u_{ij}}{\partial r_{ij}} \right) \hat{r}_{ij} \cdot v_i(t) \quad (11)$$

with

$$u(r) = \frac{1}{2} \sum_{i \neq j} u_{ij} = \frac{1}{2} \sum_{i \neq j} u(|r_i - r_j|); \quad r_{ij} = r_i - r_j$$

and

$$\hat{r}_{ij} = r_{ij}/r_{ij}.$$

The exact evaluation of TCF is not yet feasible except for very simple cases because this amounts to solving a complicated many-body problem. Therefore, a number of closures have been suggested in the past to calculate the transport coefficients, for the TCF itself or for the memory function appearing in the Mori-Zwanzig formalism. In the next subsection we consider one such closure.

## 2.2. Information theory

This method involves the optimization of  $p(\omega)$  using a finite number of sum rules. If  $M_2$  and  $M_4$  are known then we have

$$p(\omega) = N^{-1} \exp[-(\gamma\omega^2 + \mu\omega^4)] \quad (12)$$

and

$$\tau = K\pi^{1/2} \left[ (2\mu)^{-1/4} \exp(\gamma^2/8\mu) D_{-1/2} \left( \gamma/\sqrt{2\mu} \right) \right]^{-1} (A^2). \quad (13)$$

In these equations  $\gamma$  and  $\mu$  are related to  $M_2$  and  $M_4$  and  $D_{-\alpha-1/2}$  is a parabolic cylindrical function. Equation (13) is subject to the restriction that  $M_4 \leq 3M_2^2$ . However, for  $M_4 \geq 3M_2^2$  from non-classical information theory [12] we have

$$p(\omega) = N^{-1} [\exp(\beta + \gamma\omega^2) - 1]^{-1} \quad (14)$$

and

$$\tau = \frac{K(A^2)(\pi\gamma)^{1/2}}{S_1(1 - e^\beta)} \quad (15)$$

where

$$S_i = \sum_{n=1}^{\infty} \exp[(1-n)\beta] n^{(1/2)-i} \quad (16)$$

and  $\gamma$  and  $\beta$  are determined from the following equations

$$M_2 = S_2/2\gamma S_1$$

and

$$M_4 = 3S_3/4\gamma^2 S_1. \quad (17)$$

For details of information theory, readers should refer to the work of Heyes and Powles [10, 11]. In the next section we use equations (13) and (15) to calculate the transport coefficient using the theoretically generated sum rules and compare our results with that of Heyes and Powles [10] along with the computer simulation results.

## 2.3. A phenomenological model

In the present work, we propose a simple phenomenological form of the TCF given as

$$\hat{C}(t) = \text{sech}(t/\tau_1) \cos(\omega_1 t) \quad (18)$$

so that the normalized spectrum is given as

$$p(\omega) = \tau_1 \frac{\cosh[(\pi/2)\omega\tau_1] \cosh[(\pi/2)\tau_1\omega_1]}{\cosh(\pi\tau_1\omega) + \cosh(\pi\tau_1\omega_1)}. \quad (19)$$

The expression for the transport coefficient is obtained as

$$\tau = \langle A^2 \rangle K(\pi/2) \tau_1 \operatorname{sech}(\pi \omega_1 \tau_1 / 2). \quad (20)$$

In order to calculate  $\tau$  we estimate  $\omega_1$  and  $\tau_1$  using the short-time properties of the normalized TCF given by equation (6). Comparing the short-time expansion of equation (18) with equation (15) we obtain

$$\tau_1^{-2} = (M_4/M_2) - M_2 \quad (21a)$$

and

$$\omega_1^2 = (5M_2 - M_4/M_2). \quad (21b)$$

From the above expression we find that  $\omega_1^2$  is negative for  $M_4/M_2^2 > 5$  so that  $\omega_1$  becomes imaginary and then

$$\hat{C}(t) = \operatorname{sech}(t/\tau_1) \cosh(\omega_1' t) \quad (22)$$

where  $(\omega_1')^2 = -\omega_1^2$ .

The expression for the power spectrum is modified to

$$p(\omega) = \tau_1 \frac{\cos[(\pi/2)\omega_1' \tau] \cosh[(\pi/2)\tau_1 \omega]}{\cosh(\pi \tau_1 \omega_1') + \cos(\pi \tau_1 \omega)} \quad (23)$$

and for the transport coefficient we obtain

$$\tau = \langle A^2 \rangle K(\pi/2) \tau_1 \operatorname{sech}(\pi \omega_1' \tau_1 / 2). \quad (24)$$

The model presented in this subsection has theoretical origin, as has been demonstrated in the work on the self-diffusion coefficient by Tankeshwar *et al* [6]. The model is based on separating the configurational space of the fluid system into vibrational and structural parts and dividing the many-body system into a number of cells. Then the  $\operatorname{sech}(t/\tau_1)$  is the waiting-time distribution for the cell jump and  $\cos(\omega_1 t)$  is the normal-mode contribution, where  $\tau_1^{-1}$  and  $\omega_1$  are respectively jumping and vibrational frequencies. This model has provided very satisfactory results for self-diffusion coefficients for various systems [13–17] as has been judged by their comparison with computer simulation or experimental results. In this paper we have used the same functional form in a phenomenological sense to see its applicability for the prediction of shear viscosity and thermal conductivity.

### 3. Results and discussion

In order to calculate the transport coefficients from equations (13) or (15) and from (20) or (24), we require  $M_0$ ,  $M_2$  and  $M_4$  as inputs. The general expressions for these sum rules have been obtained for the VAC, TSAC and ECDAC functions by Tankeshwar *et al* [4]. The expressions for these sum rules involve the interatomic potential and static correlation functions up to five particles. Owing to limited information about static triplet and higher particle correlation functions, the superposition approximation and a low-order decoupling approximation were used, respectively. The final expressions have been put into a form

that is readily calculable for a given potential and a static pair correlation function at any thermodynamic state of the fluid. The values of these sum rules have been tabulated in earlier work [4]. It may be noted that the superposition approximation used here has provided [4] a good estimate of the triplet contribution to  $M_4$  of VAC function as was judged by their comparison with simulation results. Using these values of the sum rules in the information theory and the model presented in section 2.3, we calculate the self-diffusion coefficient, shear viscosity and thermal conductivity of LJ fluids for wide ranges of density and temperature. We also present below a comparison of results obtained for the self-diffusion coefficient from information theory using theoretical values of sum rules with those obtained by Heyes and Powles using sum rules generated from information of the TCF by computer simulation. Here it may be noted that we have not made such a comparison for shear viscosity and thermal conductivity as we know the sum rules of the VAC function more accurately than those of TSAC and ECDAC function, which involve higher-order static correlation functions.

### 3.1. Self-diffusion coefficient

In the present work, with the intention of using the values of the sum rules calculated from their theoretical expressions in the information theory, we have calculated the self-diffusion coefficient from equation (13) or (15). The results thus obtained for  $D^* = D(m\varepsilon/\sigma^2)^{1/2}$ , where  $\sigma$  and  $\varepsilon$  are two parameters of the LJ fluid, have been compared with results obtained by Heyes and Powles [10] using the same theory but an indirect method for the evaluation of the sum rules. A comparison is given in table 1 for a few densities  $n^* = n\sigma^3$  and temperatures  $T^* = k_B T/\varepsilon$ . From table 1 we find that our results agree very well with those obtained by Heyes and Powles [10]. Therefore, one may conclude that use of the theoretical values of sum rules makes no improvement over the results obtained by Heyes and Powles [10] as was expected by them. For the sake of comparison of results of our model with information theory we also present below some results for self-diffusion coefficients calculated from the model presented in section 2.3.

Table 1. Values of the self-diffusion coefficients<sup>a</sup> at different temperatures  $T^*$  and densities  $n^*$ .

| $T^*$ | $n^*$ | $D_I^*$ | $D_{IH}^*$ | $D_{SC}^*$ | $D_{MD}^*$ |
|-------|-------|---------|------------|------------|------------|
| 0.720 | 0.848 | 0.057   | 0.056      | 0.042      | 0.029      |
| 1.060 | 0.731 | 0.108   | 0.108      | 0.092      | 0.091      |
| 1.060 | 0.821 | 0.085   | 0.084      | 0.067      | 0.060      |
| 1.830 | 0.500 | 0.329   | 0.342      | 0.337      | 0.382      |
| 1.810 | 0.600 | 0.245   | 0.265      | 0.239      | 0.273      |
| 1.810 | 0.700 | 0.185   | 0.194      | 0.170      | 0.191      |
| 1.900 | 0.801 | 0.147   | 0.151      | 0.125      | 0.131      |
| 2.480 | 0.500 | 0.431   | 0.452      | 0.448      | 0.471      |
| 2.500 | 0.803 | 0.185   | 0.190      | 0.162      | 0.173      |
| 3.500 | 0.700 | 0.324   | 0.326      | 0.311      | 0.331      |

<sup>a</sup>  $D_I^*$  = diffusion coefficients obtained from information theory using theoretical sum rules.  $D_{IH}^*$  = results of Heyes and Powles using the same theory.  $D_{SC}^*$  = results of equations (20) or (24).  $D_{MD}^*$  = computer simulation results of Heyes [1].

The detailed results are given in our earlier work [6]. The  $\omega_1$  and  $\tau_1$ , which are parameters of the model TCF, are calculated from equation (21). We also note that  $\tau_1$  remains constant for a given temperature whereas  $\omega_1$  decreases with increase in density. It implies that the effect of increase of density is to decrease the vibrational frequency

of a particle in a more densely packed cell. On the other hand, for a given density it is found that  $\tau_1$  decreases and  $\omega'_1$  increases with increase in temperature. It implies that the effect of increase of temperature is to increase the jumping frequency and vibrational frequency, which seems to be plausible. Using the values of  $\omega_1$  and  $\tau_1$  we calculate  $D^*$  from equations (20) and (24); results for  $D^*$  are given in table 1 for a few densities and temperatures. It can be noted that our model provides a better estimate of self-diffusion coefficient than the information theory, especially near the triple point.

### 3.2. Shear viscosity

In order to calculate shear viscosity from equations (20) and (24) we calculate  $\omega_1$  and  $\tau_1$  by using the values of the sum rules of the TSAC function from the work of Tankeshwar *et al* [4]. It has been found that, for the TSAC function,  $S(t)$  always decays monotonically in time and no backscattering-like effect has been observed. It has also been noted that, for a given temperature,  $\tau_1$  remains almost constant whereas  $\omega'_1$  increases with increase in density. On the other hand  $\tau_1$  decreases with increase in temperature for a given density. It implies that the effect of increase of temperature is to increase the jumping frequency. The values of  $\omega'_1$  and  $\tau_1$  thus obtained have been used to calculate shear viscosity of LJ fluids from equation (24) with  $K = n/k_B T$ . The results obtained for  $\eta^* = \eta \sigma^2 (m \epsilon)^{-1/2}$  are given in figure 1 for eight isotherms for various densities. In figure 1 the results obtained from equation (24) are shown as full curves whereas the simulation data of Heyes [1,3] are shown as full circles for comparison. It can be seen from figure 1 that the results of our model are generally higher than the simulation data except for  $T^* = 6.0$  and  $10.0$  at  $n^*$  less than  $0.8$ . Here it may be noted that up to  $T^* = 4.5$  the shear viscosity results of the simulation are from a non-equilibrium molecular dynamics method [1] whereas for  $T^* = 6.0$  and  $10.0$  the simulation results were obtained using the Green-Kubo method [3]. In order to look for a reason behind the disagreement between our results and simulation results, we investigate the long-time behaviour of equation (22), which is given as

$$\hat{S}(t) = \exp(-t/\tau_1) \exp(\omega'_1 t)$$

where  $\omega'_1$  and  $\tau_1$  are positive. This function is the product of a decreasing and an increasing function of time, which makes  $S(t)$  decay slowly in the region when  $\omega'_1 \rightarrow 1/\tau_1$ . This and the fact that the short-time behaviour is exactly taken care of in our model reveal that the model determines an overestimated contribution to shear viscosity from the long-time behaviour of  $\hat{S}(t)$ . However, this contribution at long times is not enough to explain the results of shear viscosity for a very dense fluid or for the glassy phase. For example, our result for  $\eta^*$  at the triple point ( $T^* = 0.73$  and  $n^* = 0.84$ ) is  $2.61$ , compared with a simulation value of  $3.03$ . This may be due to non-inclusion of mode coupling effects, which is quite important at high densities. The overestimation of the long-time effects by our model essentially explains the slight overestimations of the shear viscosity calculated using the model as is depicted in figure 1. However, for  $T^* = 6.0$  and  $10.0$  the reason for the underestimation of shear viscosity may lie in the use of two different simulation data generated using different methods. For example, on comparing two simulation data at  $T^* = 3.5$  and  $6.0$  for the same density, say at  $n^* = 0.5$ , we find that the result for shear viscosity is higher at  $T^* = 6.0$  by about a factor of  $2$ , which is generally not expected. Here it may be noted that the information theory with the use of theoretical sum rules provided an estimate of shear viscosity in very close agreement with the results of our model used here.



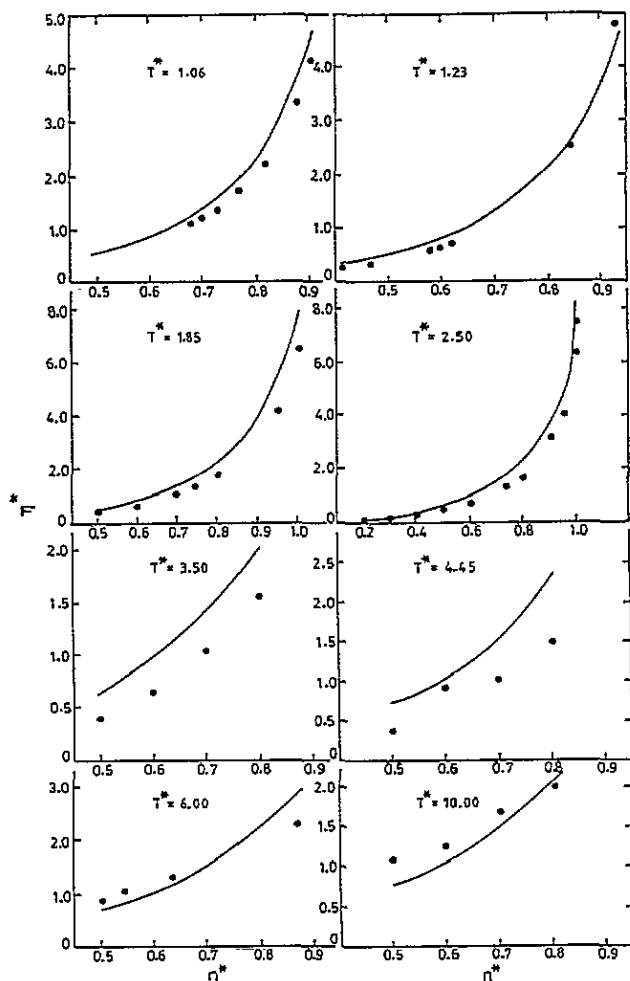


Figure 1. Variation in the shear viscosity  $\eta^*$  with density. Full curves are the results obtained from equation (24), whereas MD results of Heyes are represented by full circles.

### 3.3. Thermal conductivity

For the calculation of thermal conductivity,  $\omega_1$  and  $\tau_1$  are evaluated by using tabulated data [4] for the frequency sum rules of the energy current density autocorrelation function for various densities and temperatures of the LJ fluids. It has been found that for a given temperature  $\tau_1$  decreases with increase in density whereas  $\omega_1'$  increases with increase in density. For a given density, it has been found that  $\tau_1$  decreases whereas  $\omega_1$  increases with increase in temperature. We also note that, like  $S(t)$ , the ECDAC function also does not show any negative region in its time development, which is in agreement with the available simulation results. These values of  $\omega_1'$  and  $\tau_1$  are used in expression (24) with  $K = n/k_B^2 T$  to calculate thermal conductivity  $\lambda^* = \lambda(\sigma^2/k_B)(m/\varepsilon)^{1/2}$ . The results obtained are shown as full curves in figure 2. The non-equilibrium molecular dynamics results of Heyes [2] are also shown there as full circles. The crosses are the results obtained by Heyes [2] for a comparable fit to experimental data on argon. From figure 2 it can be seen that our model successfully explains the density dependence of thermal conductivity, yielding

a good agreement with simulation/experimental results except for densities greater than the triple-point density and at the highest temperature investigated here. However, results at  $T^* = 3.5$  are closer to the fitted data of experiments on argon. The maximum deviation from simulation data is found at  $T^* = 1.85$  at density  $n^* = 1.024$ . The deviation from the simulation results may be attributed to the non-inclusion of correct long-time behaviour, as has been discussed above for shear viscosity. Here, it may also be noted that results of information theory and of our model for thermal conductivity are in very close agreement.

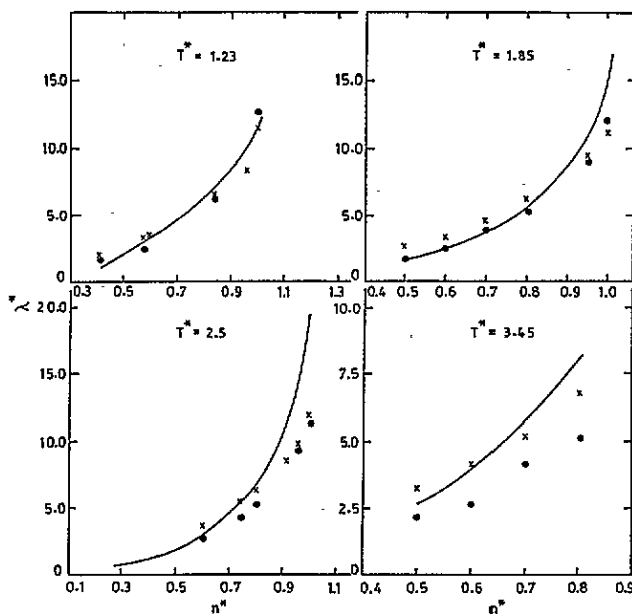


Figure 2. Variation in the thermal conductivity  $\lambda^*$  with density. Full curves are results obtained from equation (24), full circles are MD results of Heyes, and crosses are the results of an equation fitted to experimental results on argon.

#### 4. Conclusion

In this paper we have used the values of the theoretical sum rules needed in the information theory of Heyes and Powles and found that there is no improvement in the results for the diffusion coefficient over those obtained by them using an indirect method of evaluation of sum rules, as was expected by them. We have also proposed a phenomenological form for the TCF itself to estimate the self-diffusion, shear viscosity and thermal conductivity of an LJ fluid over wide ranges of density and temperature. It has been found that this model provides a reasonable estimate of transport coefficients for the whole fluid range. The agreement is found to be good for the self-diffusion coefficients and thermal conductivity as judged from their comparison with simulation results. On comparing the results of this model for shear viscosity and thermal conductivity with the information theory, it is found that both are in very close agreement. On the other hand, for the self-diffusion coefficients our model predicts better results than the information theory for dense fluids.

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