Prediction of transport properties for Lennard-Jones fluids and their binary mixtures using the effective-diameter hard-sphere kinetic theory

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We present a critical appraisal of the ability of effective diameter hard sphere theory to predict thermal conductivities and shear and bulk viscosities of fluids interacting through the Lennard-Jones potential. This method relies on the use of the kinetic theory of hard spheres and on state dependent effective diameters given by the equilibrium liquid state theory. Predictions using this method are compared with molecular dynamics data given by several authors for pure fluids in many states (65 states for the thermal conductivity, 105 for the shear viscosity, and 45 for the bulk viscosity). In the dense regime, this procedure makes predictions with an average global deviation of 37% for the shear viscosity, 32% for the bulk viscosity, and 10% for the thermal conductivity when a variational scheme is used to give the effective hard sphere diameters. In specific regions of the phase diagram, however, the predictions are much better. All other schemes give worse results, although shear viscosity in certain regions of the phase diagram (for this case we include the low density regions), is better predicted by one of the perturbative methods. For mixtures, we extend the effective diameter hard sphere theory to binary systems with the standard hard sphere cross interaction. In addition, we calculate the transport properties of mixtures using the equivalent one-fluid approximation. Comparisons are also made with molecular dynamics calculations previously reported in 10 states for mixtures. Our results are satisfactory, mainly when the one-fluid approximation is used.

1. Introduction

The Lennard-Jones (LJ) fluid has been studied by several authors, most of them quite recently, in order to obtain accurate estimates of transport properties (TPs) using molecular dynamics (MD) calculations [1–18]. Although the LJ model is known to be inaccurate as a representation of the actual intermolecular potential for inert gases, it is sufficiently close to reality to provide a convenient starting point for dealing with actual fluids. In contrast, the problem of developing a kinetic theory for LJ fluids and their mixtures has not been solved, in particular for the dense regime, although several approximate approaches have been developed with some success [19–30]. Here we will show how a procedure relying on the kinetic theory of hard spheres, combined with a prescription to obtain effective state-dependent hard-sphere diameters given in terms of the parameters associated with the LJ potential, can give good estimates both for shear and bulk viscosities as well as for thermal conductivities of LJ fluids and their mixtures over wide ranges of density and temperature. This approach has been used successfully to predict TPs of actual pure fluids [19, 24, 27, 29, 30] and their mixtures [25–30]. The diffusion coefficient is not discussed in this paper since kinetic theory for LJ mixtures has fundamental problems not yet solved, but we will discuss this issue in a forthcoming paper.

The approach, which is not really new, has been suggested by other researchers in order to model actual fluids. Examples include the work of Enskog through the so called modified Enskog theory [31] quite recently generalized to mixtures [32], the semiempirical curve fitting approach of Dymond for pure fluids [33, 34] and the procedure based on prescriptions coming from the equilibrium liquid state theory to obtain state dependent effective diameters [19, 24–30]. The underlying assumptions in all these procedures are quite similar. (1) The particles in the fluid can be modelled by the LJ potential. (2) In the high density regime, the dynamics of the fluid is mainly determined by the repulsive part of the interaction potential. Hard sphere expressions for TPs can thus give confident results if some way to obtain state dependent effective diameters is used in order to reflect the somewhat soft repulsive part of the model potential. Although much work has been done to determine if this type of procedure is appropriate, it has not been subjected to a stringent test. Such tests can now be performed since enough MD data have appeared recently [8–18].

The main purpose of this paper is to show the usefulness of the procedure just mentioned to predict TPs of LJ fluids and their binary mixtures. The principal questions are: Which of the prescriptions to obtain state dependent diameters is best suited to predict TPs of LJ fluids? In what region of the phase diagram of the pure fluid does our procedure give better results? Can we extend this procedure to mixtures with some confidence, and is it better to handle these as mixtures or as equivalent one-fluid systems?

The paper is organized as follows. In section 2 we review the procedure to obtain transport coefficients through hard sphere kinetic theory where the diameters are evaluated according to some prescription. In section 3 we comment on the MD data used, and in section 4 the numerical results are presented and compared with the MD data. Here a critical discussion is also presented. Finally, in section 5 we make some concluding remarks.

2. Theory

2.1. *Introductory remarks*

Until now, there has been no formal kinetic theory to handle TPs of LJ fluids and their mixtures, and the few attempts to predict thermal conductivities (λ), shear (η) and bulk (κ) viscosities of these systems from rigorous, fundamental molecular theories have proven that the problem is very difficult [19–23, 35]. One line of approach, albeit approximate, to treat pure fluids has employed kinetic variational theories (KVTs) and kinetic reference theories (KRTs), both of which use model potentials given by a hard sphere core and a soft attractive tail. For the TPs, KVT (hard core plus an attractive tail [19, 20]) and KVTI (hard core plus an attractive tail in the Kac limit [35]) give the same results as Enskog theory [31]. KVTII and KVTIII also can generate the same expressions as Enskog theory, with the provision, however, that the reference hard sphere structure be replaced by the structure of the real system [20–22, 24], except for the case of bulk viscosity [36]. The transport coefficients of KRT versions are the same as in the Enskog equations, but corrected by density dependence factors obtained from MD [37–39] (for details see [19–24]).

For mixtures, the problem of obtaining TPs is not as developed as for pure fluids. On the one hand, KVTII presents several unsolved problems [23, 26] and KVTIII has not even been explored; on the other hand, KVTI does give TPs of interest here, as does the revised Enskog theory (RET). There is no analogue of Dymond's correction in mixtures, however, and hence there are no KRT versions for mixtures.

2.2. *Explicit formulae for the TPs*

We will frame the discussion in terms of the most simplified theory, since for the TPs of interest here the more sophisticated of the above-mentioned theories will make little difference. Our starting point will be the set of coupled nonlinear integro-differential equations for the hard sphere single particle distribution function given in RET, first derived by van Beijeren and Ernst [40]. Here the two hard sphere radial distribution functions are the same functionals of the number densities as the radial distribution function of a mixture in nonuniform equilibrium. The RET equations can be solved by use of the Chapman–Enskog method. The molecular fluxes and the transport coefficients for dense hard-sphere mixtures, up to the Navier–Stokes level, can be directly obtained on the basis of the procedure used in [41]. Here we only present the final expressions to obtain the TPs. The expressions for pure fluids are:

$$\eta = \frac{1}{\chi^c} [1 + \tfrac{4}{5}(\tfrac{2}{3}\pi n\sigma^3 \chi^c) + 0{\cdot}7615(\tfrac{2}{3}\pi n\sigma^3 \chi^c)^2]\eta_0, \qquad (1\,a)$$

$$\kappa = 1{\cdot}002(\tfrac{2}{3}\pi n\sigma^3 \chi^c)^2 \eta_0/\chi^c, \qquad (1\,b)$$

$$\lambda = \frac{1}{\chi^c} [1 + \tfrac{6}{5}(\tfrac{2}{3}\pi n\sigma^3 \chi^c) + 0{\cdot}7575(\tfrac{2}{3}\pi n\sigma^3 \chi^c)^2]\lambda_0, \qquad (1\,c)$$

where

$$\eta_0 = \frac{5k}{16\pi\sigma^2}(\pi mkT)^{1/2}, \qquad (1\,d)$$

$$\lambda_0 = \frac{75k}{64\pi\sigma^2}\left(\frac{\pi kT}{m}\right)^{1/2}. \qquad (1\,e)$$

In these expressions, n is the number density, σ the hard sphere diameter, m the mass of the particle, χ^c the pair distribution at contact, T the absolute temperature, and k Boltzmann's constant. The expressions for binary mixtures are:

$$\eta = \frac{1}{2}\sum_{i=1}^{n}\left(1 + \frac{4}{5}\sum_{j=1}^{n}\rho b_{ij}M_{ji}\chi_{ij}^c\right)\frac{n_i}{n}kTb_0^{(i)}$$
$$+ \frac{4}{15}\sum_{i=1}^{n}\sum_{j=1}^{n}\left(\frac{2\pi m_i m_j kT}{m_i + m_j}\right)^{1/2} n_i n_j \sigma_{ij}^4 \chi_{ij}^c, \qquad (2\,a)$$

$$\kappa = \frac{4}{9}\sum_{i=1}^{n}\sum_{j=1}^{n}\left(\frac{2\pi m_i m_j kT}{m_i + m_j}\right)^{1/2} n_i n_j \sigma_{ij}^4 \chi_{ij}^c + 2kT\sum_{i=1}^{n}\frac{n_i}{n}\left(\sum_{j=1}^{n}\rho b_{ij}M_{ji}\chi_{ij}^c\right)h_1^{(i)}, \quad (2\,b)$$

$$\lambda_\infty = \frac{5k}{4n}\sum_{i=1}^{n}n_i\left(1 + \frac{12}{5}\sum_{j=1}^{n}\rho b_{ij}M_{ij}M_{ji}\chi_{ij}^c\right)\left(a_1^{(i)} - \sum_{k=1}^{n}(d_{i,1}^{(k)} - d_{i,1}^{(l)})d_k^{\text{th}}\right)$$
$$+ \frac{4}{3}k\sum_{i=1}^{n}\sum_{j=1}^{n}\left(\frac{2\pi m_i m_j kT}{m_i + m_j}\right)^{1/2}\frac{n_i n_j \sigma_{ij}^4 \chi_{ij}^c}{m_i + m_j}. \qquad (2\,c)$$

Here $\rho b_{ij} = 2/3\pi n_j \sigma_{ij}^3$, $M_{ij} = m_i/(m_i + m_j)$, where m_i is the mass of the hard sphere of diameter σ_i, n_i the number density of component i, and χ_{ij}^c the pair distribution function at contact. $a_1^{(i)}$, $b_0^{(i)}$, $d_{i,1}^{(k)}$ and $h_1^{(i)}$ are the coefficients that appear in the Sonine polynomial expansion of the one-particle distribution function, in the so called Nth Enskog approximation, i.e., when the first $N - 1$ Sonine polynomials are taken into

account in the expansion. The $a_1^{(i)}$, $b_0^{(i)}$, $d_{i,1}^{(k)}$ and $h_1^{(i)}$ are determined from a set of linear equations (for details see [41]). Here we have used up to the 10th Enskog approximation.

Evaluation of (1) and (2) requires knowledge of χ^c. We use the approximate expression of Carnahan and Starling for pure fluids and its generalization for the binary mixture [42], since it appears to be quite accurate when compared to molecular dynamics data.

MD calculations have proven that Enskog's expressions for a pure fluid are not exact, since these do not take into account velocity correlations in the dense regime. Multiplicative correction factors to the Enskog expressions have been given by Dymond [37] (Dymond's correction) for shear viscosity and thermal conductivity, although for the case of shear viscosity, van der Gulik and Trappeniers [38] have further modified these expressions on the basis of computations reported by Michels and Trappeniers [43]. For bulk viscosity we use the correction given by Heyes [39]. The correction factors are

$$
\begin{aligned}
C_\eta &= 1{\cdot}02 + 10{\cdot}61\,(n^* - 0{\cdot}495)^3 \\
&\quad + 247{\cdot}49\,(n^* - 0{\cdot}813)^3, \qquad n^* > 0{\cdot}813, \\
&= 1{\cdot}02 + 10{\cdot}61\,(n^* - 0{\cdot}495)^3, \qquad 0{\cdot}593 > n^* > 0{\cdot}813, \\
&= 1{\cdot}02, \qquad\qquad\qquad\qquad\qquad 0{\cdot}593 > n^*, \qquad\qquad (3\,a)
\end{aligned}
$$

$$
\begin{aligned}
C_\kappa &= 0{\cdot}9881 + 0{\cdot}2710 n^* - 1{\cdot}8394 n^{*2} \\
&\quad + 4{\cdot}1881 n^{*3} - 2{\cdot}5960 n^{*4}, \qquad 0{\cdot}8839 > n^* \\
&= 1{\cdot}0982 - 8{\cdot}4584\,(n^* - 0{\cdot}8839), \qquad n^* > 0{\cdot}8839, \qquad (3\,b)
\end{aligned}
$$

$$
C_\lambda = 0{\cdot}99 + 0{\cdot}1597 n^* - 0{\cdot}7464 n^{*2} + 1{\cdot}2115 n^{*3} - 0{\cdot}5583 n^{*4}. \qquad (3\,c)
$$

In all the above equations $n^* = n\sigma^3$.

2.3. *Effective diameters*

To obtain the molecular and collisional contribution for the TPs given in (1)–(3), we need a prescription for a state dependent hard sphere diameter in terms of the parameters associated with the LJ potential.

Effective diameters can be obtained by several schemes well established in equilibrium liquid state theory for the case of pure fluids. Here expansions of the properties of the system around some reference system are made, and after truncation to the first few terms (given by some appropriate mathematical technique), expressions in terms of a hard sphere fluid of effective diameter σ ($n\sigma_0^3$, kT/ε_0) are obtained. σ_0 and ε_0 are the LJ parameters. The most widely used schemes coming from a first order perturbation theory are those given by Barker and Henderson [44] (BH), by Weeks, Chandler and Andersen [45] (WCA), and by Verlet and Weiss [46] (VW). The latter is a corrected version of the WCA scheme. Quite recently, a new algorithm for calculating the effective hard sphere diameter in the WCA scheme was given by Song and Mason [47] (SM). Of the schemes coming from a variational theory, we have those by Mansoori and Canfield [48], and Rasaiah and Stell [49] (MC/RS). All these techniques give a hard sphere diameter that depends on both temperature and density, except that the method given by BH is temperature dependent only. For our calculations in pure fluids, we follow the explicit procedures given in [46] and [49].

While successful attempts to predict equilibrium thermodynamic properties for pure fluids have been made by methods using hard sphere diameters, the theory for mixtures needs improvement. One difficulty has been the lack of a satisfactory way to define mixture rules for the cross interaction in the model potential (LJ). Hence we implement here two approaches in order to deal with TPs of binary mixtures. In the first, we calculate the TPs of the binary mixture by defining an equivalent one-fluid system with the following mixture rule for the equivalent one-fluid interaction parameters:

$$\sigma_x^3 = \sum_{i,j}^{2} \sigma_{ij}^3 x_i x_j, \qquad \varepsilon_x \sigma_x^3 = \sum_{i,j}^{2} \sigma_{ij}^3 \varepsilon_{ij} x_i x_j. \tag{4}$$

We, therefore, assume that the TPs of the binary mixture can be equated to those of the equivalent one-fluid, and the equivalent one-fluid TPs can be evaluated as in the pure fluid case, just described above.

In the second approach to binary mixtures, the diameter of each component σ_{ii} in the mixture is calculated independently, that is, by considering each component in the mixture as a pure fluid at the temperature T, the temperature of the mixture, and at the number density n_i, the number density of component i in the mixture. This corresponds to the simplest approximation in the first order perturbation theory of mixtures [50]. Explicit calculations are done according to [46] and [49]. For the cross interaction, we assume it to be that of a hard sphere mixture in order to be consistent with this approach, namely,

$$\sigma_{12} = \tfrac{1}{2}(\sigma_{11} + \sigma_{22}) \tag{5}$$

3. The molecular dynamics sources

3.1. *Pure fluids*

As a source of MD data, we use the TPs given in [1–18], which were obtained from computer simulation experiments. In these references we can see that earlier works were devoted to the study of the states in the immediate neighbourhood of the triple point, through the use of the Green–Kubo formalism. After this period, the non-equilibrium molecular dynamical (NEMD) method was developed, and around the mid-eighties we can see MD data using both techniques in several regions of the LJ phase diagram. Only in the last two years, though, have consistent sets of MD data appeared, mainly those given by Hoheisel and his collaborators.

One problem with using MD data to test theory is the reliability of the experimental data. In most cases the authors estimate their error at around 5–10%, although in a few instances they do not give this information. There are substantial differences, however. In particular, results coming from the NEMD method devised by Heyes lie systematically below the Green–Kubo MD data, probably because this method does not correctly account for the fluxes. For this reason we include only few points from this author. In addition, several sources of systematic error have not been properly evaluated, although there is some consensus that they affect the MD values by only a few per cent, as is the case for contributions due to the truncated LJ and to the long tails. A discussion related to these points can be found for the case of shear viscosity in [14].

In order to make our comparisons for the thermal conductivity, we use 65 states, coming mainly from [15] and [16], all of these in the dense regime. For the case of

shear viscosity we use 105 states, 36 in the dilute regime, i.e. below the critical density, and the remainder states are in the dense regime; the data are mainly from [9] and [16]. For the bulk viscosity we use 45 states, all in the dense regime, from [16].

3.2. *Binary mixtures*

A natural extension of the present investigation to binary fluids is quite difficult because of the scarce MD data for TPs in binary LJ fluids. The first extensive MD work, as far as we know, addressing this problem has been done by Vogelsang and Hoheisel [17] using the Green–Kubo method. MacGowan and Evans [18] used nonequilibrium molecular dynamics to evaluate TPs, but in one thermodynamic state only. We will compare our calculation with the former. In that work the authors argue that their MD results have an estimated error of the order of 5% for η and κ, and 1% for λ.

Here we must comment on the thermal conductivity. Diffusion and heat conduction in a fluid mixture become inextricably coupled. In a uniform mixture, as time progress over the course of an experimental determination, concentration gradients appear in the mixture and they themselves provide driving forces for opposing fluxes. Eventually, in a steady state, thermal diffusive flux is exactly balanced by this back diffusive flux, so that there is no net molecular flow. To stress this fact, experimentalists define two λ coefficients. The first one, λ_0, is the thermal conductivity of a uniform mixture (no concentration gradients), while the second, λ_∞, is the thermal conductivity corresponding to a fluid in the steady state (no mass fluxes). The work of Vogelsang and Hoheisel [17] does not mention what kind of λ was obtained within their MD experiments. Hence since many accurate experiments actually measure λ_∞, we decided to calculate this quality. The formal definition of λ_∞ for a binary mixture is given by

$$j_q = \lambda_\infty \partial T / \partial r \qquad j_1 = 0, \tag{6}$$

where j_i is the mass flux of component i, and λ_∞ is given by expression (2 c) In any case, if in [17] they do not evaluate this coefficient the error would amount only to a few percent.

4. Results and discussion

4.1. *Pure fluids*

The different prescriptions for obtaining effective diameters and the procedure for calculating TPs, given in section 2, enable us to evaluate the coefficients under discussion, and several comparisons between our results and the MD data have been made. Our results using the variational method (MC/RS) to obtain the effective diameters, using the heading EDHST, the thermodynamic states, the MD results of several authors, and the percent deviations between our calculations and MD data ($\delta\xi = [(\xi^{EHST} - \xi^{DM})/\xi^{DM}] \times 100$) appear in tables 1 to 4. There, too, the percent deviations of our calculations using only one of the perturbative methods (VW) are tabulated.

In table 5, the root mean square of the percent deviations ($\delta_{RMS} = [(1/N) \Sigma \delta\xi^2]^{1/2}$) for the schemes studied in this work are presented. This table gives a global idea about the capability of the EDHST for predicting TPs of pure fluids. In addition, deviations between our calculations using the MC/RS and the VW schemes are given in figures 1–4.

Table 1. Comparison between thermal conductivities obtained with MD and with EDHST

n^*	T^*	MD	Reference	EDHST	$\delta_{MC/RS}$	δ_{VW}
0·650	1·270	3·720	[13]	4·061	9·170	25·610
0·650	1·588	4·140	[15]	4·288	3·574	20·215
0·650	1·851	4·460	[15]	4·455	−0·119	16·525
0·650	3·564	5·300	[15]	5·346	0·859	19·172
0·715	0·940	5·010	[13]	4·806	−4·074	11·837
0·750	1·008	4·720	[15]	5·541	17·402	39·852
0·750	1·330	5·640	[15]	5·810	3·010	24·557
0·750	2·017	6·060	[15]	6·292	3·828	27·037
0·750	2·913	7·020	[15]	6·854	−2·367	19·494
0·781	0·664	5·880	[16]	5·555	−5·528	16·453
0·781	0·854	5·460	[16]	6·064	11·060	24·859
0·781	0·848	5·806	[16]	6·058	4·336	32·979
0·781	1·038	6·422	[16]	6·237	−2·881	17·907
0·781	1·098	5·753	[16]	6·289	9·310	33·162
0·781	1·193	5·992	[16]	6·367	6·260	30·037
0·781	1·329	6·000	[16]	6·474	7·905	32·711
0·781	1·515	6·550	[16]	6·614	0·983	24·771
0·781	1·632	6·507	[16]	6·700	2·964	27·460
0·781	1·850	6·800	[16]	6·855	0·815	25·055
0·781	2·130	6·359	[16]	7·050	10·868	37·614
0·781	2·295	6·130	[16]	7·163	16·847	44·989
0·781	2·715	6·380	[16]	7·444	16·675	44·452
0·842	0·674	6·391	[16]	7·233	13·168	42·029
0·842	0·761	6·917	[16]	7·553	9·198	34·421
0·842	0·820	6·125	[16]	7·607	24·192	53·952
0·842	0·839	7·986	[16]	7·623	−4·540	18·574
0·842	0·852	7·140	[16]	7·635	6·929	32·996
0·842	0·997	7·853	[16]	7·755	−1·242	24·301
0·842	1·023	6·508	[16]	7·776	19·491	50·643
0·842	1·172	6·959	[16]	7·895	13·448	44·067
0·842	1·306	7·374	[16]	8·000	8·491	38·325
0·842	1·492	7·916	[16]	8·146	2·908	31·571
0·842	1·697	7·470	[16]	8·308	11·219	42·265
0·842	1·876	8·230	[16]	8·447	2·641	31·199
0·842	2·054	7·799	[16]	8·566	9·839	40·500
0·842	2·218	7·709	[16]	8·672	12·490	43·969
0·842	2·398	7·895	[16]	8·784	11·256	42·468
0·842	2·484	7·714	[16]	8·836	14·541	46·715
0·844	0·715	7·100	[12]	7·513	5·818	30·563
0·844	0·730	6·760	[13]	7·582	12·165	37·688
0·844	0·733	7·100	[12]	7·585	6·834	31·199
0·850	0·745	7·660	[15]	7·774	1·494	25·369
0·850	0·908	7·180	[15]	7·914	10·218	38·579
0·850	1·033	7·340	[15]	8·014	9·179	38·494
0·850	1·318	8·030	[15]	8·238	2·589	31·501
0·850	1·503	8·190	[15]	8·384	2·374	31·514
0·850	1·976	8·080	[15]	8·734	8·092	38·991
0·850	2·905	8·460	[15]	9·295	9·865	41·714
0·884	0·673	7·156	[16]	8·660	21·012	54·144
0·884	0·831	6·938	[16]	8·917	28·522	64·590
0·884	0·879	8·039	[16]	8·951	11·343	43·259
0·884	0·959	8·000	[16]	9·008	12·602	45·791
0·884	1·008	8·129	[16]	9·044	11·255	44·483
0·884	1·053	8·969	[16]	9·077	1·207	31·739
0·884	1·179	8·469	[16]	9·173	8·318	41·629

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Table 1 (*continued*).

n^*	T^*	MD	Reference	EDHST	$\delta_{MC/RS}$	δ_{VW}
0·884	1·205	7·847	[16]	9·194	17·163	53·289
0·884	1·334	8·618	[16]	9·293	7·831	41·405
0·884	1·376	9·065	[16]	9·323	2·843	34·961
0·884	1·517	9·123	[16]	9·421	3·268	35·762
0·884	1·725	9·400	[16]	9·562	1·719	33·925
0·884	1·821	8·810	[16]	9·625	9·246	34·895
0·884	1·985	8·746	[16]	9·730	11·246	46·603
0·884	2·217	9·054	[16]	9·873	9·043	43·776
0·884	2·537	8·921	[16]	10·061	12·778	48·812
0·962	2·725	11·800	[12]	12·756	8·105	51·644

Table 2. Comparison between shear viscosity obtained with MD and with EDHST, at low densities.

n^*	T^*	MD	Reference	EDHST	$\delta_{MC/RS}$	δ_{VW}
0·050	1·300	0·157	[9]	0·231	47·324	32·462
0·050	1·499	0·185	[9]	0·252	36·199	22·001
0·050	2·000	0·240	[9]	0·301	25·492	11·120
0·050	3·000	0·320	[9]	0·392	22·416	5·517
0·050	5·000	0·465	[9]	0·560	20·439	−2·406
0·050	10·000	0·721	[9]	0·950	31·734	−6·910
0·100	1·300	0·179	[9]	0·238	33·066	22·213
0·100	1·499	0·208	[9]	0·259	24·451	13·986
0·100	2·000	0·270	[9]	0·308	14·100	3·467
0·100	3·000	0·339	[9]	0·399	17·588	3·943
0·100	5·000	0·485	[9]	0·565	16·487	−2·754
0·100	10·000	0·746	[9]	0·939	25·868	−6·871
0·150	1·300	0·217	[9]	0·250	15·207	8·441
0·150	1·499	0·244	[9]	0·272	11·339	4·299
0·150	2·000	0·313	[9]	0·322	2·828	−4·612
0·150	3·000	0·383	[9]	0·412	7·677	−2·245
0·150	5·000	0·534	[9]	0·577	8·010	−6·743
0·150	10·000	0·797	[9]	0·937	17·567	−8·527
0·200	1·316	0·258	[9]	0·271	4·911	0·950
0·200	1·499	0·284	[9]	0·290	2·237	−1·739
0·200	2·000	0·352	[9]	0·342	−2·979	−7·925
0·200	3·000	0·435	[9]	0·434	−0·217	−6·888
0·200	5·000	0·572	[9]	0·596	4·276	−6·604
0·200	10·000	0·854	[9]	0·946	10·757	−9·172
0·250	1·300	0·300	[9]	0·294	−1·909	−3·160
0·250	1·499	0·317	[9]	0·317	−0·022	−1·506
0·250	2·000	0·387	[9]	0·370	−4·372	−6·548
0·250	3·000	0·475	[9]	0·464	−2·404	−6·148
0·250	5·000	0·610	[9]	0·626	2·620	−4·594
0·250	10·000	0·901	[9]	0·966	7·164	−7·158
0·300	1·300	0·351	[9]	0·328	−6·622	−5·339
0·300	1·499	0·383	[9]	0·352	−7·999	−7·127
0·300	2·000	0·447	[9]	0·406	−9·061	−8·551
0·300	3·000	0·528	[9]	0·502	−4·930	−5·588
0·300	5·000	0·700	[9]	0·664	−5·090	−8·122
0·300	10·000	0·983	[9]	0·998	1·529	−7·050

Table 3. Comparison between shear viscosity obtained with MD and with EDHST, at high densities.

n^*	T^*	MD	Reference	EDHST	$\delta_{MC/RS}$	δ_{VW}
0·401	2·470	0·500	[8]	0·566	13·189	19·627
0·500	3·460	0·710	[8]	0·832	17·140	30·736
0·600	1·280	0·860	[8]	0·835	−2·948	10·703
0·625	1·162	0·660	[2]	0·896	35·707	55·731
0·625	1·200	0·830	[8]	0·909	8·742	24·970
0·720	1·000	1·310	[8]	1·291	−1·425	16·981
0·720	1·000	1·250	[6]	1·291	3·307	22·596
0·731	1·005	1·420	[2]	1·358	−4·347	14·167
0·731	1·050	1·340	[6]	1·368	2·098	13·696
0·731	1·050	1·440	[8]	1·368	−4·992	22·181
0·749	2·560	1·450	[8]	1·687	16·345	44·526
0·781	0·664	2·037	[16]	1·547	−24·049	−5·259
0·781	0·848	1·960	[16]	1·689	−14·129	9·623
0·781	0·854	1·860	[16]	1·685	−9·406	3·879
0·781	1·038	1·915	[16]	1·725	−9·901	10·694
0·781	1·098	1·783	[16]	1·737	−2·568	20·168
0·781	1·199	1·639	[16]	1·755	7·079	32·769
0·781	1·329	1·694	[16]	1·780	5·049	31·019
0·781	1·515	1·771	[16]	1·812	2·316	28·309
0·781	1·632	1·794	[16]	1·839	2·156	28·360
0·781	1·850	1·694	[16]	1·869	10·336	39·035
0·781	2·130	1·583	[16]	1·916	21·057	52·676
0·781	2·295	1·628	[16]	1·949	19·344	50·552
0·781	2·715	1·738	[16]	2·012	15·754	45·734
0·801	0·937	2·030	[2]	1·881	−7·345	14·371
0·801	0·940	1·980	[8]	1·882	−4·955	17·329
0·801	1·900	1·900	[8]	2·059	8·371	37·886
0·842	0·674	2·845	[16]	2·196	−22·817	−2·075
0·842	0·761	2·812	[16]	2·291	−18·516	1·322
0·842	0·820	2·591	[16]	2·304	−11·072	11·405
0·842	0·839	2·978	[16]	2·307	−22·529	−2·696
0·842	0·852	2·646	[16]	2·310	−12·697	9·796
0·842	0·997	2·701	[16]	2·339	−13·418	10·302
0·842	1·029	2·602	[16]	2·344	−9·935	14·951
0·842	1·172	2·469	[16]	2·371	−3·967	23·605
0·842	1·306	2·391	[16]	2·397	0·236	29·614
0·842	1·492	2·502	[16]	2·439	−2·755	26·170
0·842	1·697	2·292	[16]	2·479	7·916	40·193
0·842	1·876	2·248	[16]	2·510	11·648	44·948
0·842	2·054	2·203	[16]	2·539	15·269	49·830
0·842	2·218	2·292	[16]	2·566	11·952	45·642
0·842	2·398	2·115	[16]	2·594	22·624	59·703
0·842	2·484	2·314	[16]	2·606	12·632	46·769
0·844	0·722	3·345	[14]	2·301	−31·205	−14·545
0·844	0·730	3·030	[6]	2·310	−23·761	−5·472
0·844	0·730	3·190	[8]	2·310	−27·585	−10·213
0·844	0·730	3·189	[15]	2·310	−27·562	−10·185
0·844	2·370	2·130	[15]	2·615	22·777	60·068
0·859	0·680	3·650	[8]	2·362	−35·282	−17·832
0·884	0·679	3·532	[16]	2·910	−17·598	6·017
0·884	0·831	3·399	[16]	2·985	−12·179	13·735
0·884	0·879	3·598	[16]	2·999	−16·812	8·275
0·884	0·959	3·078	[16]	3·007	−2·310	28·016
0·884	1·008	2·845	[16]	3·016	6·002	39·366

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Table 3 *(continued)*.

n^*	T^*	MD	Reference	EDHST	$\delta_{MC/RS}$	δ_{VW}
0·884	1·059	3·609	[16]	3·024	−16·220	10·449
0·884	1·179	3·288	[16]	3·048	−7·292	22·844
0·884	1·205	2·812	[16]	3·059	8·576	43·994
0·884	1·334	2·768	[16]	3·079	11·226	47·945
0·884	1·376	3·266	[16]	3·087	−5·496	25·811
0·884	1·517	2·558	[16]	3·112	21·666	62·338
0·884	1·725	2·735	[16]	3·149	15·129	53·960
0·884	1·821	2·701	[16]	3·165	17·192	56·830
0·884	1·985	2·690	[16]	3·199	18·696	59·006
0·884	2·217	2·491	[16]	3·231	29·719	73·952
0·884	2·537	2·635	[16]	3·281	24·535	67·261
0·909	4·420	2·690	[8]	4·135	53·712	113·663
1·000	2·470	4·580	[15]	8·418	83·806	177·319
1·040	2·510	5·370	[8]	12·529	133·306	256·811
1·119	2·840	7·970	[8]	26·014	226·399	434·605

Thermal conductivity, of all the transport properties discussed here, is the best predicted by EDHST. Table 5 shows that predictions of thermal conductivity, using the MC/RS scheme in the dense regime, have a δ_{RMS} of 10·4, and table 1 shows that, for the most part of all deviations, they are in the direction of overestimation. In the range of density and temperature studied ($0·650 < n^* < 0·962$ and $0·664 < T^* < 3·564$), it is not possible to discern any special trend for the behaviour of the λ deviations. If there is any trend, it is masked by the statistical error in the MD calculations.

Calculations with the other schemes lie far above the MD values. Calculations using the BH, WCA, and VW schemes behave in the same way, although the best fit is obtained with VW. Calculations with the SM scheme are globally better than those using the other perturbative methods, but with a very bad trend, i.e. underestimation at low temperatures and large overestimation at high temperatures. For the low density regime, it is not yet possible to make comparisons, since as far as we know, there is not enough MD information. Some idea, though, can be obtained from our comparisons made with accurate experimental data of argon and presented in [30].

For the case of shear viscosity in the low density regime, table 5 shows that calculations with all prescriptions give a δ_{RMS} around 10%, except when the variational method is used. In this case the figures are around 17%. A closer view of the data (see table 2 and figures 1 to 4) reveals that, in the density range between $0·2 < n^* < 0·3$, a better fit is obtained when the variational method is used, since the δ_{RMS}s are in general less than 10%. In the temperature range $1·3 < T^* < 5$ these deviations are less than 5%. It is at around $n^* = 0·2$ that calculations using perturbative schemes give a better fit to MD data. Calculations using BH, VW and WCA prescriptions are closer to the MD data when $n^* < 0·2$, and with the same order of deviation. In general, in the range of $1 < T^* < 2$, deviations using perturbative schemes go from underestimation ($\sim 5 - 8\%$) at densities around 0·3, to overestimation ($\sim 20-35\%$) at densities around 0·05. WCA and VW almost give the same numbers, and the SM is the worst for this task. At high temperatures ($T^* \geqslant 5$), the use of perturbative prescriptions gives good results a few percent below the MD data in all of the dilute regime, probably reflecting their origin as high temperature

Table 4. Comparison between bulk viscosity obtained with MD and with EDHST.

n^*	T^*	MD	Reference	EDHST	$\delta_{MC/RS}$	δ_{VW}
0·781	0·664	1·207	[16]	0·426	−64·691	−60·723
0·781	0·854	0·985	[16]	0·473	−51·937	−47·161
0·781	0·848	0·974	[16]	0·472	−51·495	−46·701
0·781	1·038	0·753	[16]	0·502	−33·338	−25·898
0·781	1·098	0·931	[16]	0·510	−45·237	−38·877
0·781	1·193	0·753	[16]	0·523	−30·593	−22·230
0·781	1·329	0·711	[16]	0·538	−24·278	−14·550
0·781	1·515	0·689	[16]	0·559	−18·860	−7·862
0·781	1·632	0·771	[16]	0·571	−25·958	−15·606
0·781	1·850	0·603	[16]	0·592	−1·901	12·440
0·781	2·130	0·692	[16]	0·616	−10·962	2·575
0·781	2·295	0·531	[16]	0·629	18·444	36·945
0·781	2·715	0·630	[16]	0·661	4·987	21·874
0·842	0·674	1·251	[16]	0·500	−60·032	−55·825
0·842	0·761	1·174	[16]	0·527	−55·147	−50·746
0·842	0·820	0·897	[16]	0·538	−39·979	−33·747
0·842	0·839	0·897	[16]	0·542	−39·540	−33·193
0·842	0·852	0·930	[16]	0·544	−41·474	−35·203
0·842	0·997	0·853	[16]	0·571	−33·075	−25·275
0·842	1·023	0·897	[16]	0·575	−35·919	−28·295
0·842	1·172	0·620	[16]	0·598	−3·480	8·757
0·842	1·306	0·830	[16]	0·618	−25·529	−15·706
0·842	1·492	0·731	[16]	0·643	−12·077	0·082
0·842	1·696	0·720	[16]	0·667	−7·316	6·008
0·842	1·876	0·642	[16]	0·688	7·164	22·876
0·842	2·054	0·686	[16]	0·706	2·873	18·435
0·842	2·218	0·786	[16]	0·721	−8·212	5·972
0·842	2·398	0·642	[16]	0·737	14·829	33·057
0·842	2·484	0·720	[16]	0·744	3·346	20·002
0·884	0·673	1·528	[16]	0·545	−64·314	−60·592
0·884	0·831	0·908	[16]	0·586	−35·503	−28·310
0·884	0·879	1·129	[16]	0·595	−47·257	−41·163
0·884	0·959	1·096	[16]	0·611	−44·232	−37·479
0·884	1·008	0·963	[16]	0·621	−35·507	−27·583
0·884	1·053	0·974	[16]	0·629	−35·427	−27·298
0·884	1·179	0·974	[16]	0·651	−33·204	−24·401
0·884	1·205	0·930	[16]	0·655	−29·621	−20·231
0·884	1·334	0·819	[16]	0·675	−17·558	−6·240
0·884	1·376	0·686	[16]	0·681	−0·714	13·111
0·884	1·517	0·742	[16]	0·701	−5·554	8·035
0·884	1·725	0·620	[16]	0·727	17·316	34·889
0·884	1·821	0·720	[16]	0·739	2·663	18·231
0·884	1·985	0·775	[16]	0·757	−2·337	12·968
0·884	2·217	0·554	[16]	0·781	41·064	63·798
0·884	2·537	0·675	[16]	0·812	20·297	40·427

perturbative expansions. This does not occur, however, when the variational scheme is used, where overestimation is the rule at densities below 0·2, but is quite better after this density. The failure of EDHST at low densities, and in particular at low temperatures, no matter which procedure is used to obtain effective diameters, only reflects the inability of EDHST to deal with fluids in thermodynamic states where
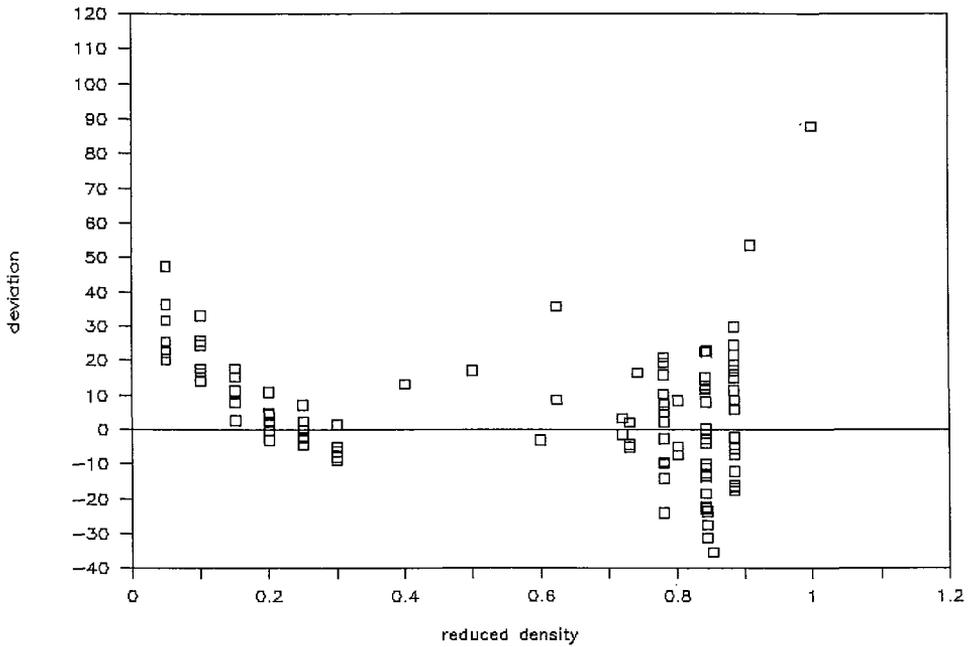
Figure 1. Percent deviations for the shear viscosity calculations (EDHST using the MC/RS scheme) and MD plotted against the reduced density.
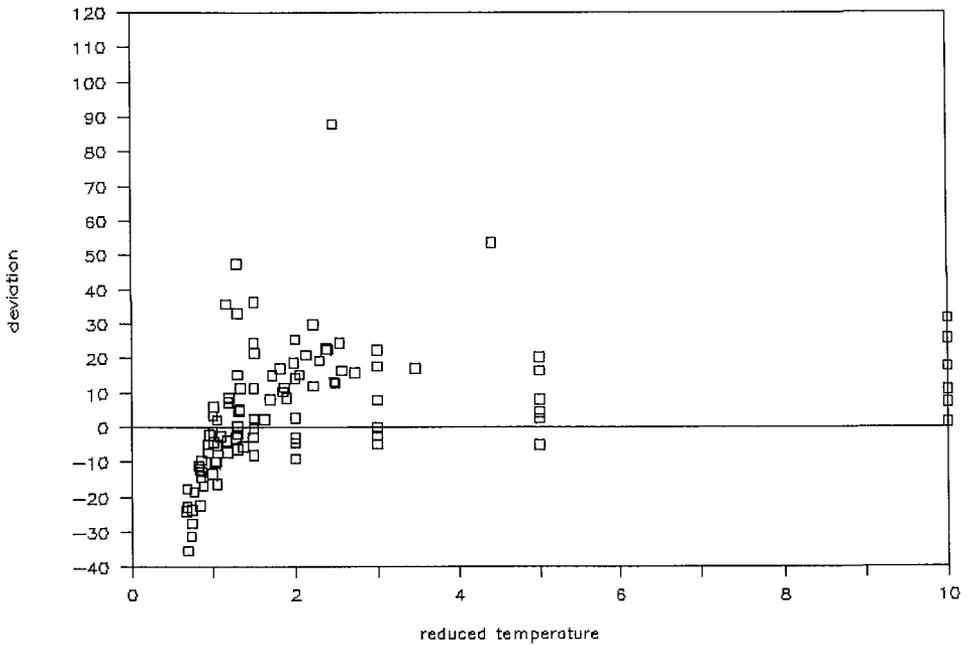
Figure 2. Percent deviations for the shear viscosity calculations (EDHST using the MC/RS scheme) and MD plotted against the reduced temperature.
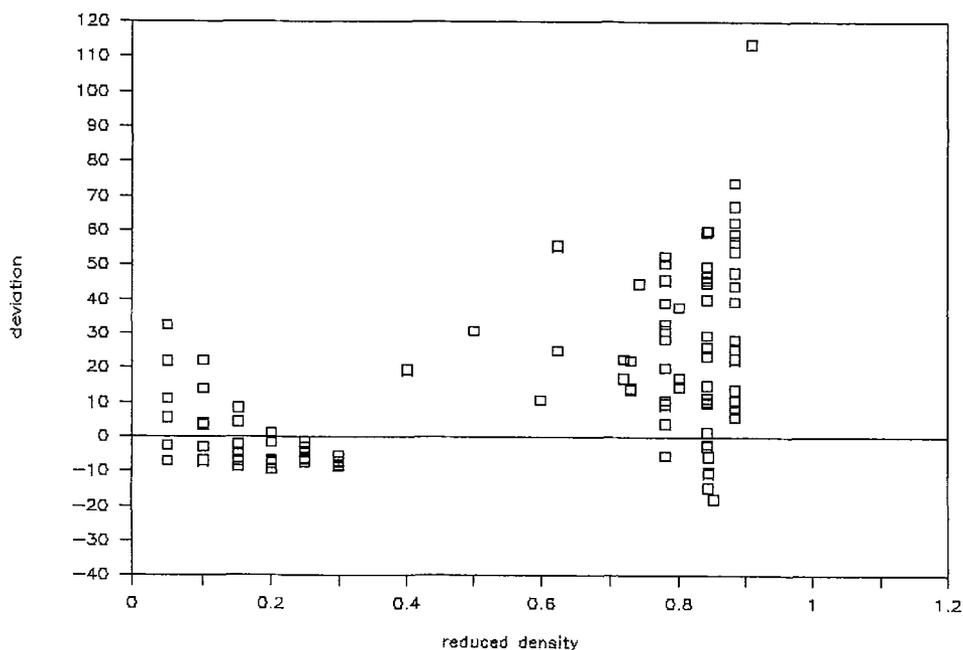
Figure 3. Percent deviations for the shear viscosity calculations (EDHST using the VW scheme) and MD plotted against the reduced density.
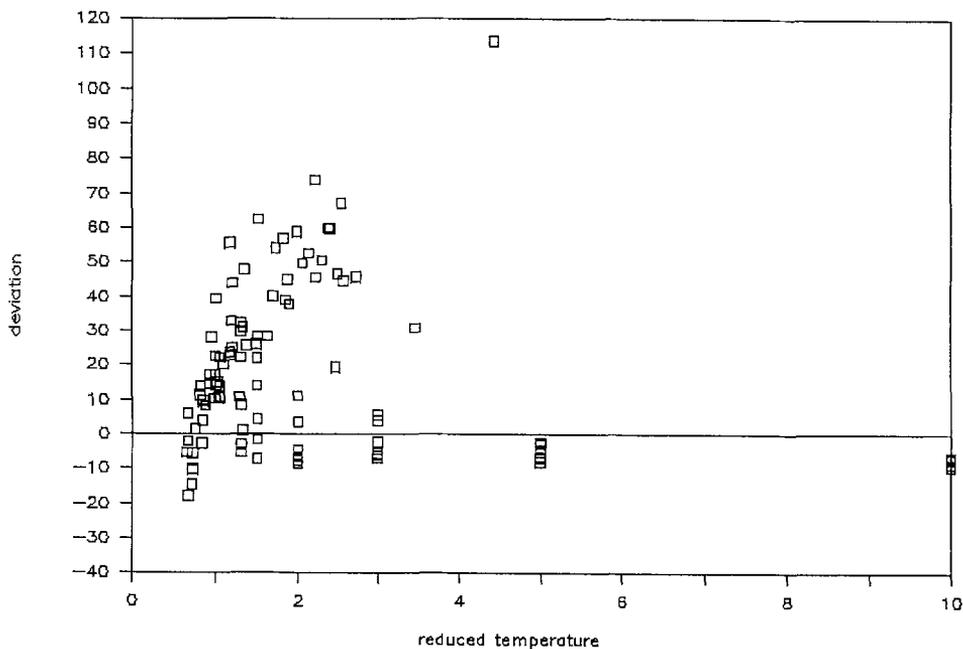
Figure 4. Percent deviations for the shear viscosity calculations (EDHST using the VW scheme) and MD plotted against reduced temperature.

Table 5. Global deviation (δ_{RMS}) between MD data and EDHST using different effective diameters.

	MC/RS	BH	Low density VW	WCA	SM
η	17·2	9·9	9·8	9·8	12·4
	MC/RS	BH	High density VW	WCA	SM
λ	10·4	41·7	37·3	48·6	29·4
η	37·4	84·1	73·8	87·9	97·3
κ	32·6	31·6	31·4	31·5	36·1

attractive forces have an important role. The described behaviour agrees with our findings when experimental data are used instead of MD results [28–30].

For shear viscosity in the dense regime, table 5 shows that better predictive results are obtained when the variational method is used to obtain effective diameters. Table 3 represents the deviations between our results and MD data, when MC/RS and VW schemes are used. A closer view of the data in this dense regime shows that, as the temperature increases in the range $0.8 < T^* < 2.7$, calculations go progressively from underestimating to overestimating the ηs, no matter what scheme is used. This is not easy to see in figure 2 for the MC/RS scheme, and in figure 4 for the VW scheme, since the low density data are shown there too. Calculations with BH, WCA, and VW schemes start from a few percent around zero and go to more than 50% above the MD results in this range of temperatures. Calculations with these schemes behave almost in the same way, although with WCA there is an additional overestimation of around 10% over the other two. Apparently, calculations with the SM scheme are the most critically dependent on the temperature, since they go from -30% to more than 70% of deviation. In this range of temperature, the variational scheme is the best option, since calculations go from around -15% to around 25%. In addition, from figure 1 it is easy to see that, with the variational scheme, deviations are centred around zero, while this is not true when the VW scheme is used (figure 3). Another general behaviour of EDHST is that at very high densities ($n^* > 0.9$), no matter what scheme is used to obtain the effective diameters, we have a very significant over-estimation (some of these points are not presented in figures 1 to 4, since they are quite out of scale). For the perturbative schemes, this overestimation trend begins at lesser densities. Again, with the variational scheme better results are obtained, although with a very important overestimation (see table 3 and figures 1 to 4), This behaviour probably is due to the failure of the Carnahan–Starling approximation to obtain χ^c. At very high densities this quantity is less than the actual MD values, and, through (1 a), larger viscosity values are obtained.

Bulk viscosity results are presented in table 4, where we tabulate the deviations when the MC/RS and the VW schemes are used. Table 5 shows that with all schemes to obtain the diameter, we have about the same predictive capability. The most important feature of bulk viscosity calculations with EDHST is the failure of this procedure to give good results at low temperatures. In figure 5, we give the deviations when the variational scheme is used, irrespective of the density. They go progressively from an underestimation in the range of -60% at temperatures about $T^* \simeq 0.66$, to an overestimation on the order of 20% at temperatures about $T^* \simeq 2.7$. Per-turbative schemes also show this behaviour, but they can overestimate by more than
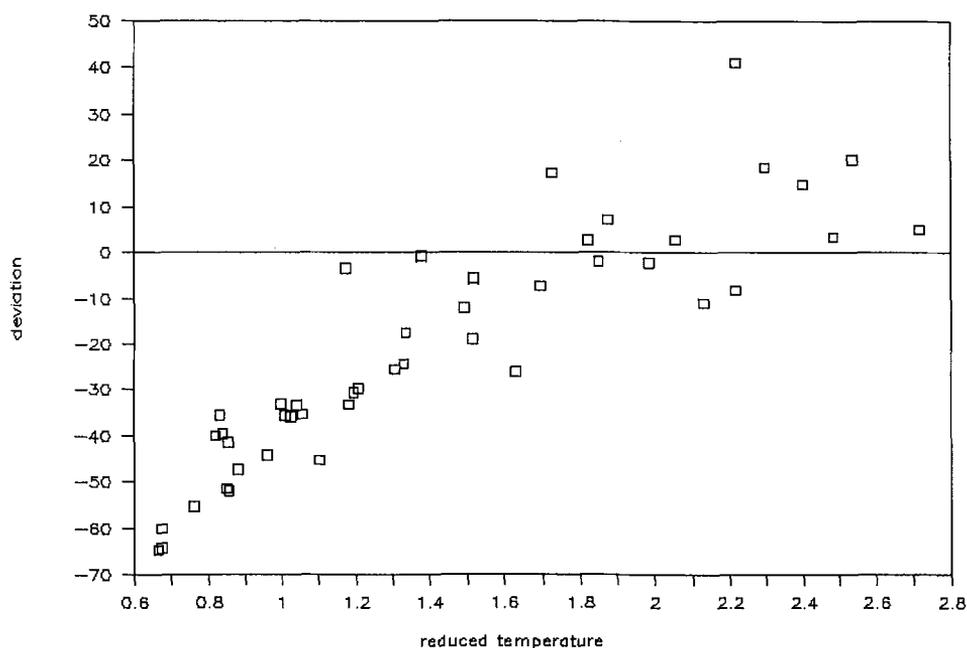
Figure 5. Percent deviations for the bulk viscosity calculations (EDHST using the MC/RS scheme) and MD plotted against the reduced temperature.

30% at high temperatures. As we can see from that figure, EDHST using the variational method can predict bulk viscosities with a 20% error when the temperature is above $T^* = 1.3$. This is not true for the perturbative schemes; in particular, for the better option (i.e. the VW), this percent of error occurs in the temperature range of $1.2 < T^* < 2.2$ only. The use of the variational scheme is, therefore, a better option to predict bulk viscosities, mainly when the temperature is above 1·2 or 1·3.

4.2. *Mixtures*

As mentioned above, TPs of LJ mixtures were obtained in two different ways. The results using the equivalent one-fluid are displayed in table 6. Results where diameters

Table 6. Deviation between EDHST in the equivalent one-fluid approximation and MD.

System	ρ	T	μ_{12}	ν_1	$\delta\eta_{MC/RS}$	$\delta\eta_{VW}$	$\delta\kappa_{MC/RS}$	$\delta\kappa_{VW}$	$\delta\lambda_{MC/RS}$	$\delta\lambda_{VW}$
A1	1·74	128·25	1	0·8	−8·7	9·7	−36·7	−31·6	8·0	28·2
A2	1·74	135·38	1	0·9	−1·2	18·7	31·9	42·6		
A3	1·74	142·50	1	1·0	−10·7	7·2	68·3	81·9	8·7	28·9
A4	1·74	149·63	1	1·1	−7·6	11·0	74·0	88·0		
A5	1·74	156·75	1	1·2	−5·4	13·6	40·0	51·3	6·7	26·6
B1	1·92	134·38	0·90	1	−17·0	−0·3	7·9	16·6	1·6	20·6
B2	1·79	134·38	0·95	1	−18·8	−2·4	80·9	95·5		
B3	1·67	134·38	1·00	1	−15·7	1·3	72·5	86·5	5·4	25·0
B4	1·55	134·38	1·05	1	−18·4	−2·0	34·0	44·8		
B5	1·44	134·38	1·10	1	−5·3	13·7	8·3	17·1	7·0	27·0

Table 7. Deviation between EDHST and MD diameters evaluated in an independent way and cross interaction given by (5).

System	ρ	T	μ_{12}	v_1	$\delta\eta_{MC/RS}$	$\delta\eta_{VW}$	$\delta\kappa_{MC/RS}$	$\delta\kappa_{VW}$	$\delta\lambda_{MC/RS}$	$\delta\lambda_{VW}$
A1	1·74	128·25	1	0·8	−16·3	4·9	−46·2	−28·9	8·3	33·8
A2	1·74	135·38	1	0·9	−10·6	11·9	10·7	45·6		
A3	1·74	142·50	1	1·0	−20·2	−0·4	38·4	82·6	6·4	31·0
A4	1·74	149·63	1	1·1	−18·6	1·8	40·3	85·6		
A5	1·74	156·75	1	1·2	−17·9	2·8	10·8	47·0	1·6	25·4
B1	1·92	134·38	0·90	1	18·9	55·7	70·2	130·5	54·6	100·2
B2	1·79	134·38	0·95	1	−4·7	21·5	125·7	198·6		
B3	1·67	134·38	1·00	1	−17·8	2·4	71·4	123·0	11·5	37·1
B4	1·55	134·38	1·05	1	−32·9	−18·1	6·7	37·2		
B5	1·44	134·38	1·10	1	−33·2	−20·0	−30·2	−11·1	−16·2	−1·0

are evaluated in an independent way, and with cross interaction given by (5), are presented in table 7. Following Vogelsang and Hoheisel [17], we characterize the LJ binary mixture by a vector containing four quantities,

$$(\mu, v, \mu_{12}, v_{12}),$$

where μ and v are defined by

$$\sigma_{22} = \mu\sigma_{11} \quad \text{and} \quad \varepsilon_{22} = v\varepsilon_{11},$$

and μ_{12} and v_{12} are defined by

$$\sigma_{12} = \mu_{12}(\sigma_{11} + \sigma_{22})/2 \quad \text{and} \quad \varepsilon_{12} = v_{12}(\varepsilon_{11} + \varepsilon_{22})/2.$$

For table 6, the magnitudes of ε_{11} and σ_{11} are unimportant, since reduced units are used. For table 7, we use the parameters given in [17]. In order to compare with the MD data of [17], we make the calculation for all the equimolar mixtures with the same values for μ and v given therein:

for systems A1–A5 $\quad \mu = 1, \quad v = 2$

for systems B1–B5 $\quad \mu = 1·4, \quad v = 1.$

The results using the equivalent one-fluid approximation are quite good when the variational scheme is used to obtain the equivalent one-fluid diameter. In particular for the thermal conductivity, no matter how the cross interactions are varied, or the ratio between the pure component LJ parameters, the deviation from MD calculations is less than 10%. In figure 6, we present λ for systems B1, B3 and B5, and the results using the perturbative schemes. As we can see there, better results are obtained with the variational scheme. In the case of the shear viscosity calculations, they reveal a very high sensitivity to the cross interactions. If $\mu_{12} = 1$, i.e. when the cross interaction is that of a hard sphere mixture (5), no matter how the energy cross interaction changes, the use of the variational scheme gives better results. This is the real motivation for the second way to obtain TPs in mixtures to be discussed below. On the contrary, if there is no additivity, i.e. $\mu_{12} \neq 1$, the use of perturbative schemes is a better option than the variational scheme, as can be observed in figure 7. For bulk viscosity, from table 6 we see that no matter how the parameters are varied, in general the use of the variational scheme is better although still with a very significant error.
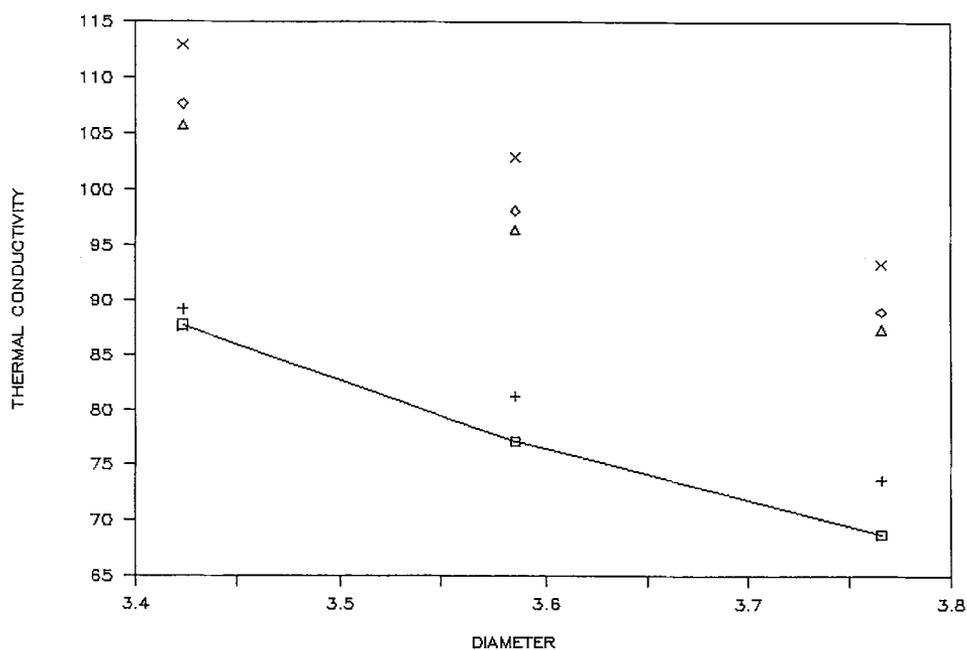
Figure 6. Thermal conductivity ($\mathrm{J\,m^{-1}\,s^{-1}\,K^{-1}}$) predictions for LJ mixtures with different cross interaction σ_{12} (Å) given by EDHST using different schemes ($\square$ MD, $+$ MC/RS, $\diamond$ BH, $\triangle$ VW, $\times$ WCA) and in the equivalent one-fluid approximation. Full line is only to aid visualization.
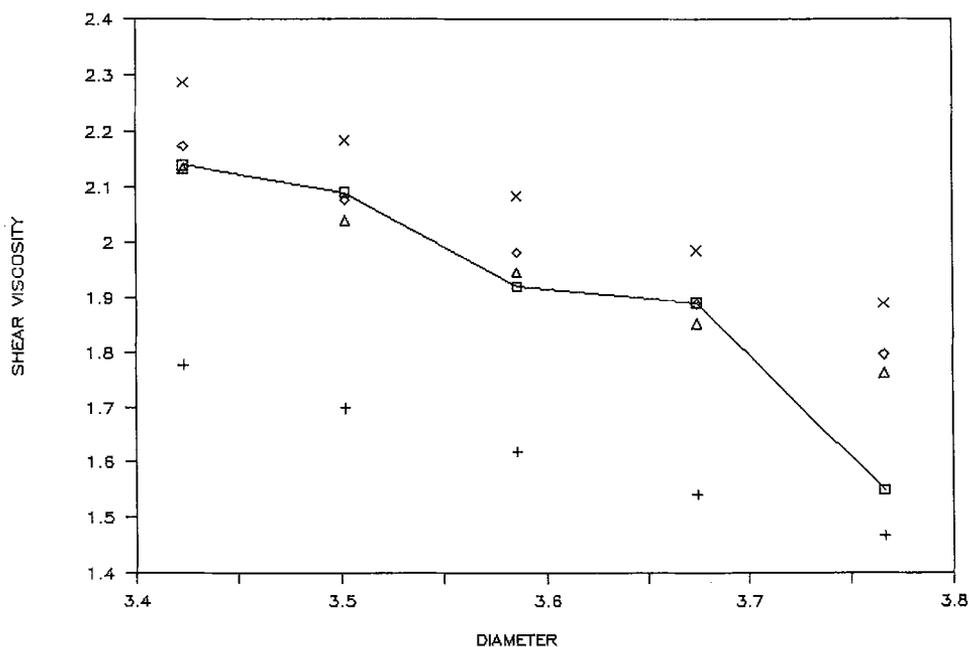
Figure 7. Shear viscosity (Pas) predictions for LJ mixtures with different cross interaction σ_{12} (Å) given by EDHST using different schemes ($\square$ MD, $+$ MC/RS, $\diamond$ BH, $\triangle$ VW, $\times$ WCA), and in the equivalent one-fluid approximation. Full line is only to aid visualization.
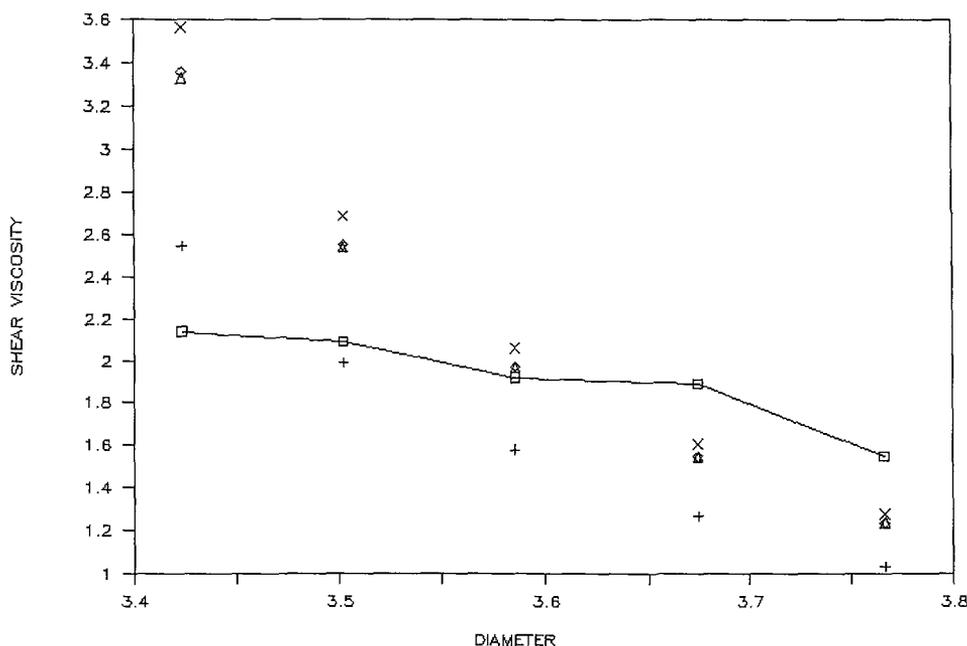
Figure 8.   Shear viscosity (Pas) predictions for LJ mixtures with different cross interaction σ_{12} (Å) given by EDHST using different schemes ($\square$ MD, + MC/RS, $\diamond$ BH, $\triangle$ VW, $\times$ WCA). Here, the diameters are evaluated in an independent way, and the cross interaction is given by (5). Full line is only to aid visualization.

It is important to note that all our calculations and all the MD results are for the same reduced thermodynamic state through the mixing rules given in (4), i.e. $T^* = 0.95$ and $n^* = 0.75$. Although there is no MD data for pure fluids at this specific point, the results of table 7 agree in general with these MD results, except for the case of the bulk viscosity. This makes us suspicious about the MD bulk viscosity values in mixtures or about some conceptual failure of the equivalent one-fluid approach for the bulk viscosity.

With the second approach to obtain TPs, we need be cautious since it cannot be used to obtain definite answers due to the lack of a correction for velocity correlations, i.e. Dymond's correction. If this correction is in the direction of increasing the TPs, as it usually is, table 6 shows that this approach to evaluating the diameters can give good estimates of shear viscosity and thermal conductivity when the cross interaction σ_{12} is additive and when the variational scheme is used to obtain the independent diameters. When the cross interaction σ_{12} is not additive, this procedure is not appropriate for thermal conductivity calculations. For bulk viscosity, our calculations with the second procedure are quite far from MD data. Use of the other perturbative schemes (BH, WCA and SM) to obtain the hard sphere diameters in the mixture gives worse results, and in some cases with a bad trend. As an example, in figure 8 the shear viscosity calculations for different cross interaction, σ_{12}, are presented, using all schemes to obtain the independent diameters.

5. Concluding remarks

The main aim of addressing the usefulness of EDHST for predicting transport properties of LJ fluids and their mixtures has been reached, to some extent. Now it is clear that although this procedure captures the main qualitative aspects in the dense regime, it is quite far from being a quantitative technique. Some lines of research must be developed in the near future to obtain more quantitative theories to deal with pure fluids, and to improve our understanding of TPs of fluid mixtures. In particular we can mention: (a) MD experients for hard sphere binary mixtures in order to determine the velocity correlation correction to RETs transport properties. (b) MD experiments for LJ mixtures in several regions of the binary phase diagram, in order to have a critical evaluation of the procedures given here, and in a general way. (c) New approaches for developing kinetic theories which can deal with realistic potentials directly.

References

[1] LEVESQUE, D., VERLET, L., and KURKIJARVI, J., 1973, *Phys. Rev. A*, **7**, 1690.
[2] GOSLING, E. M., McDONALD, I. R., and SINGER, K., 1973, *Molec. Phys.*, **26**, 1475.
[3] ASHURT, W. T., and HOOVER, W. G., 1975, *Phys. Rev. A*, **11**, 658.
[4] HOOVER, W. G., EVANS, D. J., HICKMAN, R. B., LADD, A. J. C., and MORAN, B., 1980, *Phys. Rev. A*, **22**, 1690.
[5] EVANS, D., 1982, *Phys. Lett.*, **91A**, 475.
[6] HEYES, D. M., 1983, *J. Chem. Soc. Faraday Trans. 2*, **79**, 1741.
[7] HEYES, D. M., 1984, *J. Chem. Soc. Faraday Trans. 2*, **80**, 1363.
[8] SCHOEN, M., and HOHEISEL, C., 1985, *Molec. Phys.*, **56**, 653.
[9] MICHELS, J. P. J., and TRAPPENIERS, N. J., 1985, *Physica*, **133A**, 281.
[10] PAOLINI, G. V., CICOTTI, G., and MASSOBRIO, C., 1986, *Phys. Rev. A.*, **34**, 1355.
[11] HOHEISEL, C., 1987, *J. chem. Phys.*, **86**, 2328.
[12] LEVESQUE, D., and VERLET, L., 1987, *Molec. Phys.*, **61**, 143.
[13] VOGELSANG, R., and HOHEISEL, C., 1987, *J. chem. Phys.*, **86**, 6371.
[14] ERPENBECK, J., 1988, *Phys. Rev. A.*, **38**, 6255.
[15] HOHEISEL, C., 1990, *Comput. Phys. Rep.*, **12**, 29.
[16] BORGELT, P., HOHEISEL, C., and STELL, G., 1990, *Phys. Rev. A.*, **42**, 789.
[17] VOGELSANG, R., and HOHEISEL, C., 1988, *Phys. Rev. A.*, **38**, 6296.
[18] MACGOWAN, D., and EVANS, D. J., 1986, *Phys. Rev. A.*, **34**, 2133.
[19] KARKHECK, J., and STELL, G., 1981, *J. chem. Phys.*, **75**, 1475.
[20] STELL, G., KARKHECK, J., and VAN BEIJEREN, G. H., 1983, *J. chem. Phys.*, **79**, 3166.
[21] SUNG, W., and DAHLER, J. S., 1984, *J. chem. Phys.*, **80**, 3025.
[22] KARKHECK, J., STELL, G., and XU, J., 1988, *J. chem. Phys.*, **89**, 5829.
[23] CASTILLO, R., MARTINA, E., LOPEZ DE HARO, M., KARKHECK, J., and STELL, G., 1989, *Phys. Rev. A.*, **39**, 3106.
[24] KARKHECK, J., STELL, G., and YU, J., 1989, *Int. J. Thermophys.* **10**, 113.
[25] CASTILLO, R., LOPEZ DE HARO, M., and MARTINA, E., 1986, *Int. J. Thermophys.*, **7**, 851.
[26] CASTILLO, R., MARTINA, E., and LOPEZ DE HARO, M., 1986, *KINAM*, **7**, 61.
[27] CASTILLO, R., and CASTAÑEDA, S., 1988, *Int. J. Thermophys.*, **9**, 383.
[28] CASTILLO, R., and CASTAÑEDA, S., 1989, *J. Non-Equil. Thermodyn.*, **14**, 69.
[29] CASTILLO, R., and OROZCO, J. V., 1989, *Int. J. Thermophys.*, **11**, 1025.
[30] CASTILLO, R., and OROZCO, J. V., 1990, *Physica A*, **166**, 505.
[31] DORFMAN, J. R., and VAN BEIJEREN, H., 1977, *Statistical Mechanics. Part B*, edited by B. J. Berne (Plenum) Chap. 3.
[32] KINCAID, J. M., PEREZ, S., and COHEN, E. G. D., 1985, *Phys. Rev. A*, **38**, 3628.

[33] DYMOND, J. H., 1985, *Q. Rev. Chem. Soc.*, **3**, 317.
[34] DYMOND, J. H., 1974, *Physics*, **75**, 100.
[35] KARKHECK, J., MARTINA, E., and STELL, G., 1982, *Phys. Rev. A*, **25**, 3328.
[36] VAN BEIJEREN, H., KARKHECK, J., and SENGERS, J. V., 1988, *Phys. Rev. A*, **37**, 2247.
[37] DYMOND, J. H., 1976, *Physica*, **85A**, 175.
[38] VAN DER GULIK, P. S., and TRAPPENIERS, N. J., 1986, *Physica*, **135A**, 1.
[39] HEYES, D. M., 1987, *Physica*, **146A**, 341.
[40] VAN BEIJEREN, H., and ERNST, M. H., 1973, *Physica (Utrecht)*, **68**, 437.
[41] LOPEZ DE HARO, M., COHEN, E. G. D., and KINCAID, J. M., 1983, *J. chem. Phys.*, **78**, 2746.
[42] MANSOORI, G. A., CARNAHAN, N. F., STARLING, K. E., and LELAND, T. W., 1971, *J. chem. Phys.*, **54**, 1523.
[43] MICHELS, J. P. J., and TRAPPENIERS, N. J., 1980, *Physica*, **104A**, 243.
[44] BARKER, J. A., and HENDERSON, D., 1967, *J. chem. Phys.*, **47**, 4714.
[45] WEEKS, J. D., CHANDLER, D., and ANDERSEN, H. C., 1971, *J. chem. Phys.*, **54**, 5237.
[46] VERLET, L., and WEIS, J. J., 1972, *Phys. Rev. A*, **5**, 939.
[47] SONG, Y., and MASON, E. A., 1989, *J. chem. Phys.*, **91**, 7840.
[48] MANSOORI, G. A., and CANFIELD, F. B., 1969, *J. chem. Phys.*, **51**, 4958.
[49] RASAIAH, J., and STELL, G., 1970, *Molec. Phys.*, **18**, 249.
[50] BOUBLIK, T., NEZBEDA, I., and HLAVATY, K., 1980, *Statistical Thermodynamics of Simple Liquids and Their Mixtures*. (Elsevier).