TRANSPORT PROPERTIES IN DENSE FLUIDS AND THEIR BINARY MIXTURES

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ABSTRACT

A critical appraisal of the ability of the effective diameter hard-sphere theory (EDHST) for predicting thermal conductivities, and shear and bulk viscosities of fluids interacting through the Lennard-Jones potential is presented. This method relies on the use of the kinetic theory of hard-spheres and the 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. In the dense regime this procedure, using a variational scheme to obtain the effective hard-sphere diameters makes predictions with an average global deviation of 37% for the shear viscosity, 32 % for the bulk viscosity, and 10 % for the thermal conductivity. However, in certain regions of the phase diagram the predictions are better. All other schemes give worse results than the variational scheme, except in the case of the shear viscosity in certain regions of the phase diagram (for this case we include the low density regions), where the Verlet and Weis scheme gives better results. For mixtures, we calculated the transport properties of mixtures using the equivalent one-fluid approximation, and comparisons with molecular dynamics calculations previously reported were performed. Our results are quite satisfactory. In addition, we made comparisons with actual fluids and extended our procedure to fluids of nonspherical molecules.

INTRODUCTION

The Lennard-Jones (LJ) potential is known to be inaccurate as a representation of the actual intermolecular potential for inert gases, but it is sufficiently close to reality for providing a convenient starting point to deal with transport properties (TP's) of actual fluids.

The main purpose of this paper is to show the usefulness of a procedure to predict TP's of LJ fluids and their binary mixtures. In addition, we will show that this method can give good results for actual fluids, and it can be generalized to non-spherical LJ potentials. This procedure relies 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 potential. We call this approach the EDHST. We will show that it gives good estimates for shear and bulk viscosities, and for thermal conductivities of the LJ fluids and their mixtures, in wide ranges of densities and temperatures.

This procedure has been used with success to predict TP's of actual pure fluids (Karkheck et al.,1981,1989; Castillo et al.,1988-1990) and their mixtures (Castillo et al.,1986-1990). The underlying assumptions are: (1) The particles in the fluid can be modeled 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, hence hard-sphere expressions for TP's can give reliable 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 there has been a lot of work done to determine if this type of procedures is appropriate, it has not been subjected to a stringent test. This test can be done now since enough molecular dynamics (MD) data for LJ systems have appeared recently.

THEORY

Until now, there is no formal kinetic theory to handle TP's of LJ fluids and their mixtures, and the few attempts to deal with the problem of predicting thermal conductivities (λ), shear (η) and bulk (κ) viscosities of these systems from rigorous, fundamental molecular theories, have proven to be very difficult (Karkheck et al.,1981,1982,1988; Stell et al.,1983; Sung et al.,1984; Castillo et al.,1989). Here, one line of approach although approximate, to deal with pure fluids has been the kinetic variational theories (KVT's), and the kinetic reference theories (KRT's), both dealing with model potentials given by a hard-sphere core and a soft attractive tail. For the mentioned TP's, KVT (hard core plus an attractive tail (Karkheck and Stell,1981; Stell et al.,1983) and KVTI(Karkheck et al.,1982) (hard core plus an attractive tail in the Kac limit) give the same results as in the Enskog theory (Dorfman and van Beijeren,1977). The KVTII and KVTIII generate the same expressions as in the Enskog theory, however, with the provision that the reference hard-sphere structure is replaced by the structure of the real system (Stell et al.,1983; Sung and Dahler,1984; Karkheck et al.,1988,1989), except for the case of bulk viscosity (van Beijeren et al., 1988). The transport coefficients of the KRT versions are the same as in the Enskog equations, but corrected by density-dependent factors obtained from MD.

For mixtures the problem of obtaining TP's is not as developed as in pure fluids. On one hand, the KVTII presents several unsolved problems (Castillo et al.,1986,1989) and the KVTIII has not been explored. On the other hand, the KVTI gives the TP's of our interest here as in the revised Enskog theory (RET) (Karkheck et al., 1982). In addition, there is nothing analogue to Dymond's correction in mixtures, hence there are no KRT versions for mixtures.

In order to make the discussion with the most simplified theory, our starting point will be the equations for the hard-sphere fluid given in the RET (van Beijeren and Ernst,1973). Here, the expressions for pure fluids are the following:

$$\eta = \frac{1}{\chi^c} \left[1 + \frac{4}{5}\left(\frac{2}{3}\pi n \sigma^3 \chi^c\right) + 0.7615\left(\frac{2}{3}\pi n \sigma^3 \chi^c\right)^2 \right]\eta_o \tag{1a}$$

$$\kappa = 1.002\left(\frac{2}{3}\pi n \sigma^3 \chi^c\right)^2 \eta_o / \chi^c \tag{1b}$$

$$\lambda = \frac{1}{\chi^c}\left[1 + \frac{6}{5}\left(\frac{2}{3}\pi n\sigma^3\chi^c\right) + 0.7575\left(\frac{2}{3}\pi n\sigma^3\chi^c\right)^2\right]\lambda_o \qquad (1c)$$

where

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

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

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

The evaluation of equations 1 requires the knowledge of χ^c. We used the approximate expression of Carnahan and Starling for pure fluids and its generalization for the binary mixture (Mansoori et al.,1971).

MD calculations have proven that Enskog's expressions for pure fluids are not exact, since these do not take into account velocity correlations in the dense regime. Correction multiplicative factors to the Enskog expressions have been given by Dymond (1976) for shear viscosity and thermal conductivity, although for the case of shear viscosity van der Gulik and Trappeniers (1986) have modified these expressions on the basis of the computations given by Michels and Trappeniers (1980). For bulk viscosity we used the correction given in the paper of Heyes (1987). The correction factors are:

$$C_\eta = 1.02 + 10.61(n^* - 0.495)^3 + 247.49\,(n^* - 0.813)^3 \qquad n^* > 0.813$$

$$= 1.02 + 10.61(n^* - 0.495)^3 \qquad 0.593 > n^* > 0.813$$

$$= 1.02 \qquad 0.593 > n^*$$

$$(2a)$$

$$C_\kappa = 0.9881 + 0.2710\,n^* - 1.8394\,n^{*2} + 4.1881\,n^{*3} - 2.5960\,n^{*4} \qquad 0.8839 > n^*$$

$$= 1.0982 - 8.4584\,(n^* - 0.8839) \qquad n^* > 0.8839$$

$$(2b)$$

$$C_\lambda = 0.99 + 0.1597\,n^* - 0.7464\,n^{*2} + 1.2115\,n^{*3} - 0.5583\,n^{*4}. \qquad (2c)$$

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

In order to obtain the molecular and collisional contribution for the TP's given in eqs. 1 and 2, we need a prescription to obtain 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 given by some appropriate mathematical technique to the first few terms, expressions in terms of a hard-sphere fluid of effective diameter $\sigma(n\sigma_o^3, kT/\epsilon_o)$ are obtained. Here, σ_o and ϵ_o are the LJ parameters. The most widely used schemes from a first order perturbation theory are those given by

Barker and Henderson (1967) (BH), by Weeks, Chandler and Andersen (1971) (WCA), by Verlet and Weis (1972) (VW). Quite recently, a new algorithm for calculating the effective hard-sphere diameter in the WCA scheme was given by Song and Mason (1989) (SM). From the schemes using a variational theory, we have chosen those given by Mansoori and Canfield (1969), and Rasaiah and Stell (1970) (MC/RS). All these schemes give a hard-sphere diameter depending on both temperature and density, except those given by BH and SM which are temperature dependent only. For our calculations in pure fluids, we followed the explicit procedures given by Verlet and Weis (1972) and Rasaiah and Stell (1970).

While successful attempts have been made in the prediction of equilibrium thermodynamic properties for pure fluids by the methods using hard-sphere diameters just mentioned, the theory for mixtures needs much more improvement because of additional difficulties. One of these difficulties has been the lack of a satisfactory way to define mixture rules for the cross interaction in the model potential (LJ). Hence, we calculated the TP's of the binary mixture through defining an equivalent one-fluid, with the following mixture rules for the equivalent one-fluid interaction parameters:

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

Therefore, we assume that the TP's of the binary mixture can be equated to that of the equivalent one fluid, and the equivalent one-fluid TP's can be evaluated as in the pure fluid case, just described above.

THE MOLECULAR DYNAMICS DATA

In order to make our comparisons, TP's of LJ systems obtained by MD experiments given by several authors were used. For the thermal conductivity, we used 65 states (Borgelt et al.,1990; Hoheisel,1990), all of these in the dense regime. For the case of shear viscosity we used 105 states, 36 in the dilute regime, below the critical density, and the remainder states are in the dense regime. For the bulk viscosity we used 45 states all in the dense regime (Borgelt et al.,1990).

A natural extension of the present investigation to binary fluids is quite difficult because of the scarce MD data for TP's in binary LJ fluids. The first extensive MD work, as far as we know, which addresses this problem has been done by Vogelsang and Hoheisel (1988) using the Green-Kubo method. MacGowan and Evans (1986) used non-equilibrium molecular dynamics to evaluate TP's, but for one thermodynamic state only. We will compare our calculation with the former.

RESULTS AND DISCUSSION

We evaluated the TP's under discussion, and made several comparisons between our results and the MD data using different prescriptions to obtain effective diameters as discussed above. Our results for for the case of shear viscosity are displayed in tables 1 and 2. Here, we present each of the states studied using the MC/RS scheme to obtain the effective diameters (under the heading EDHST), a note of the thermodynamic states, the MD results

TABLE 1

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

n^*	T^*	MD	EDHST	δMC/RS	δVW
0.050	1.300	0.157	0.231	47.324	32.462
0.050	1.499	0.185	0.252	36.199	22.001
0.050	2.000	0.240	0.301	25.492	11.120
0.050	3.000	0.320	0.392	22.416	5.517
0.050	5.000	0.465	0.560	20.439	-2.406
0.050	10.000	0.721	0.950	31.734	-6.910
0.100	1.300	0.179	0.238	33.066	22.213
0.100	1.499	0.208	0.259	24.451	13.986
0.100	2.000	0.270	0.308	14.100	3.467
0.100	3.000	0.339	0.399	17.588	3.943
0.100	5.000	0.485	0.565	16.487	-2.754
0.100	10.000	0.746	0.939	25.868	-6.871
0.150	1.300	0.217	0.250	15.207	8.441
0.150	1.499	0.244	0.272	11.339	4.299
0.150	2.000	0.313	0.322	2.828	-4.612
0.150	3.000	0.383	0.412	7.677	-2.245
0.150	5.000	0.534	0.577	8.010	-6.743
0.150	10.000	0.797	0.937	17.567	-8.527
0.200	1.300	0.258	0.271	4.911	0.950
0.200	1.499	0.284	0.290	2.237	-1.739
0.200	2.000	0.352	0.342	-2.979	-7.925
0.200	3.000	0.435	0.434	-0.217	-6.888
0.200	5.000	0.572	0.596	4.276	-6.604
0.200	10.000	0.854	0.946	10.757	-9.172
0.250	1.300	0.300	0.294	-1.909	-3.160
0.250	1.499	0.317	0.317	-0.022	-1.506
0.250	2.000	0.387	0.370	-4.372	-6.548
0.250	3.000	0.475	0.464	-2.404	-6.148
0.250	5.000	0.610	0.626	2.620	-4.594
0.250	10.000	0.901	0.966	7.164	-7.158
0.300	1.300	0.351	0.328	-6.622	-5.339
0.300	1.499	0.383	0.352	-7.999	-7.127
0.300	2.000	0.447	0.406	-9.061	-8.551
0.300	3.000	0.528	0.502	-4.930	-5.588
0.300	5.000	0.700	0.664	-5.090	-8.122
0.300	10.000	0.983	0.998	1.529	-7.050

MD data from Michels and Trappeniers (1985)

of several authors, and the percent deviations between these
calculations and MD data ($\delta\xi = 100 \ [\xi^{EDHST} - \xi^{DM}]/ \ \xi^{DM}$). There too,
the percent deviations between our calculations using only one of
the perturbative schemes (VW) and MD data are presented.

In table 3, the root-mean-square of the percent deviations
($\delta_{RMS} = \{1/N \ \Sigma \ \delta\xi^2\}^{1/2}$) are presented for the schemes studied in
this work. This table gives a global idea about the capability of
the EDHST for predicting TP's of pure fluids.

Of all the transport properties discussed here, thermal
conductivity is the best predicted by EDHST. Table 3 shows that,
predictions of thermal conductivity of dense fluid using the MC/RS
scheme have a δ_{RMS} of 10.4, in the direction of overestimation.
Calculations for TP's using the other schemes lie far above from
the MD values. Calculations with BH, WCA and VW schemes behave in

TABLE 2

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

n*	T*	MD	ref	EDHST	δMC/RS	δVW
0.401	2.470	0.500	c	0.566	13.189	19.627
0.500	3.460	0.710	c	0.832	17.140	30.736
0.600	1.280	0.860	c	0.835	-2.948	10.703
0.625	1.162	0.660	a	0.896	35.707	55.731
0.625	1.200	0.830	c	0.909	8.742	24.970
0.720	1.000	1.310	c	1.291	-1.425	16.981
0.720	1.009	1.250	b	1.293	3.307	22.596
0.731	1.005	1.420	a	1.358	-4.347	14.157
0.731	1.050	1.340	b	1.368	2.098	13.696
0.731	1.050	1.440	c	1.368	-4.992	22.181
0.749	2.560	1.450	c	1.687	16.345	44.526
0.781	0.664	2.037	f	1.547	-24.049	-5.259
0.781	0.848	1.960	f	1.689	-14.129	9.623
0.781	0.854	1.860	f	1.685	-9.406	3.879
0.781	1.038	1.915	f	1.747	-9.901	10.694
0.781	1.098	1.783	f	1.755	-2.568	20.168
0.781	1.199	1.639	f	1.755	7.079	32.769
0.781	1.329	1.694	f	1.780	5.049	31.019
0.781	1.515	1.771	f	1.812	2.316	28.309
0.781	1.632	1.794	f	1.839	2.156	28.360
0.781	1.850	1.694	f	1.869	10.336	39.035
0.781	2.130	1.583	f	1.912	21.057	50.552
0.781	2.295	1.628	f	2.049	19.344	50.734
0.781	2.715	1.738	f	2.012	15.754	45.734
0.801	0.937	2.030	a	1.881	-7.345	14.371
0.801	0.940	1.980	c	1.882	-4.955	17.329
0.801	1.900	1.900	c	2.059	8.371	37.886
0.842	0.674	2.845	f	2.196	-22.817	-2.075
0.842	0.761	2.812	f	2.291	-18.516	1.322
0.842	0.820	2.591	f	2.304	-12.072	11.405
0.842	0.839	2.978	f	2.307	-22.529	1.696
0.842	0.852	2.646	f	2.310	-12.697	9.796
0.842	0.997	2.701	f	2.339	-13.418	10.302
0.842	1.029	2.602	f	2.344	-9.935	14.951
0.842	1.172	2.469	f	2.371	-3.967	23.605
0.842	1.306	2.391	f	2.397	0.226	29.614
0.842	1.492	2.502	f	2.429	-2.926	26.170
0.842	1.697	2.292	f	2.479	7.916	40.103
0.842	1.876	2.248	f	2.510	11.648	44.948
0.842	2.054	2.203	f	2.539	15.269	49.830
0.842	2.218	2.292	f	2.566	11.952	45.642
0.842	2.398	2.115	f	2.594	22.624	59.703
0.842	2.484	2.314	f	2.606	12.632	46.769
0.844	0.722	3.345	d	2.305	-31.205	-14.545
0.844	0.750	3.030	b	2.310	-23.761	-5.412
0.844	0.730	3.190	c	2.310	-27.585	-10.213
0.844	0.730	3.189	e	2.310	-27.562	-10.185
0.844	2.370	2.130	e	2.615	22.777	60.068
0.859	0.680	3.650	c	2.362	-35.282	-17.832
0.884	0.679	3.532	f	2.910	-17.598	6.017
0.884	0.831	3.399	f	2.985	-12.185	13.735
0.884	0.872	3.598	f	2.999	-16.673	8.???
0.884	1.008	2.845	f	3.016	6.002	39.366
0.884	1.059	3.609	f	3.024	-16.220	10.449
0.884	1.179	3.288	f	3.048	-7.292	22.844
0.884	1.205	2.812	f	3.059	8.576	43.994
0.884	1.334	2.768	f	3.079	11.226	47.945
0.884	1.376	3.266	f	3.087	-5.496	25.811
0.884	1.517	2.658	f	3.112	21.666	53.338
0.884	1.725	2.758	f	3.149	15.129	53.950
0.884	1.821	2.735	f	3.165	17.192	56.830
0.884	1.985	2.690	f	3.199	18.696	59.006
0.884	2.217	2.491	f	3.231	29.719	73.952
0.884	2.537	2.635	f	3.281	24.535	67.261
0.909	4.420	2.690	c	4.145	53.712	113.663
1.000	2.470	4.580	e	6.418	83.806	177.319
1.940	2.510	5.370	c	13.522	135.300	256.811
1.119	2.840	7.970	c	26.014	226.399	434.605

MD data form [a] Gosling, McDonald and Singer (1973); [b] Heyes (1983); [c] Schoen and Hoheisel (1985); [d] Erpenbeck (1988); [e] Hoheisel (1990); [f] Borgelt, Hoheisel and Stell (1990)

the same way, although the best fit was obtained with the VW. Calculations with the SM scheme are globally better than those using the other perturbative methods, but with a very bad trend, underestimation at low temperatures and large overestimation at high temperatures.

For the case of shear viscosity, in the low density region, table 3 shows that calculations with all prescriptions give a δRMS around 10%, except when the variational method is used. In this case calculations are in error by around 17%. A closer view of the data (see table 1) reveals that, in the density range between $0.2 <$ $n^* < 0.3$, when the variational method is used a better fit is obtained, since the δRMS's are in general less than 10%. In the temperature range $1.3 < T^* < 5$ these deviations are less than 5%. It is 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

TABLE 3

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

	MC/RS	BH	VW	WCA	SM
		LOW DENSITY			
η	17.2	9.9	9.8	9.8	12.4
		HIGH DENSITY			
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

same order of deviation. In general, in the range of $1 < T^* < 2$,
deviations using perturbative schemes go from underestimation
($\sim$5-8%) at reduced densities around 0.3, to overestimation
($\sim$20-35%) at densities around 0.05. WCA and VW give almost the
same numbers, and the SM is the worst for this task. At high
temperatures ($T^* \geq 5$), the use of perturbative prescriptions gives
good results, a few percent below the MD data in all the dilute
regime, probably reflecting their origin as high temperature
perturbative expansions. This does not occur when the variational
scheme is used. For this scheme, overestimation is the rule at
densities below 0.2, but it is better at higher densities. The
failure of EDHST at low densities, and in particular at low
temperatures, no matter whichever procedure is used to obtain
effective diameters, only reflects the inability of this procedure
to deal with fluids in thermodynamic states where attractive forces
have an important role.

For shear viscosity in the dense regime, table 3 shows that
better predictive results are obtained when the variational method
is used to obtain effective diameters. A closer view of the data
in this dense regime shows that, at constant density as the
temperature increases in the range $0.8 < T^* < 2.7$ calculations go
progressively from underestimating to overestimating the η's, no
matter what scheme is used. Calculations with BH, WCA and VW
schemes start at around zero percent and go to more than 50% above
the MD results, in this range of temperature. Calculations with
these schemes behave in almost the same way although, with WCA
there is an additional overestimate 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% deviations. The variational scheme in this range of
temperature is the best option, since calculations differ from
around -15% to around 25%. In addition, it is easy to see that,
with the variational scheme, deviations are centered around zero.
This is not true when the WCA scheme is used. Another general
behavior of EDHST is that at the very high densities ($n^* > 0.9$), no
matter what scheme is used to obtain the effective diameters, we
have a very important overestimation. For the perturbative
schemes, this overestimation trend begins at lower densities.
Better results are obtained again, with variational scheme,
although with a very important overestimation. Probably, this
behavior is due to the failure of the Carnahan-Starling
approximation to obtain the χ^c.

For the case of bulk viscosity table 3 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. They go progressively from a underestimation in the range of -60% at temperatures about $T \cong$ 0.66, to an overestimation of the order of 20% at temperatures about $T \cong 2.7$. Perturbative schemes show this behavior, but they can overestimate by more than a 30%, at high temperatures. EDHST using the variational method can predict bulk viscosities with 20% of error when temperature is above $T = 1.3$. This is not true for the perturbative schemes in particular for the better option of the VW, this percent of error occurs in the temperature range of $1.2 < T < 2.2$, only. Therefore, the use of the variational scheme is a better option to predict bulk viscosities, mainly when the temperature is above 1.2 or 1.3.

The results for mixtures using the equivalent one-fluid are presented in table 4. Following Vogelsang and Hoheisel (1988), we characterize the LJ binary mixture by a vector containing four quantities,

$$(\mu, \nu, \mu_{12}, \nu_{12}),$$

where μ and ν are defined by

$$\sigma_{22} = \mu \, \sigma_{11} \quad \text{and} \quad \varepsilon_{22} = \nu \, \varepsilon_{11}, \tag{4}$$

and μ_{12} and ν_{12} give are defined by

$$\sigma_{12} = \mu_{12} \, (\sigma_{11} + \sigma_{22})/2 \quad \text{and} \quad \varepsilon_{12} = \nu_{12} \, (\varepsilon_{11} + \varepsilon_{22})/2. \tag{5}$$

For table 4, the magnitudes of ε_{11} and σ_{11} are unimportant, since reduced units are used. In order to compare with the MD data given by Vogelsang and Hoheisel (1988), we made our calculation for equimolar mixtures with the same parameters and values for μ and ν given by these authors:

for systems A1-A5 $\mu = 1$, $\nu = 2$

for systems B1-B5 $\mu = 1.4$, $\nu = 1$.

TABLE 4

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

	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

The results with 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 the MD calculations is less than 10%. 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 (eq.5), no matter how the energy cross interaction changes, the use of the variational scheme gives better results. On the other hand, if there is no additivity, i.e. $\mu_{12} \neq 1$, the use of perturbative schemes is a better option than the variational scheme. For bulk viscosity, from table 2 we can see that no matter how the parameters are varied in general the use of the variational scheme is better.

ACTUAL FLUIDS AND EXTENSIONS

The above discussion can be applied when EDHST is compared with actual fluids like argon. In figure 1, percent deviations
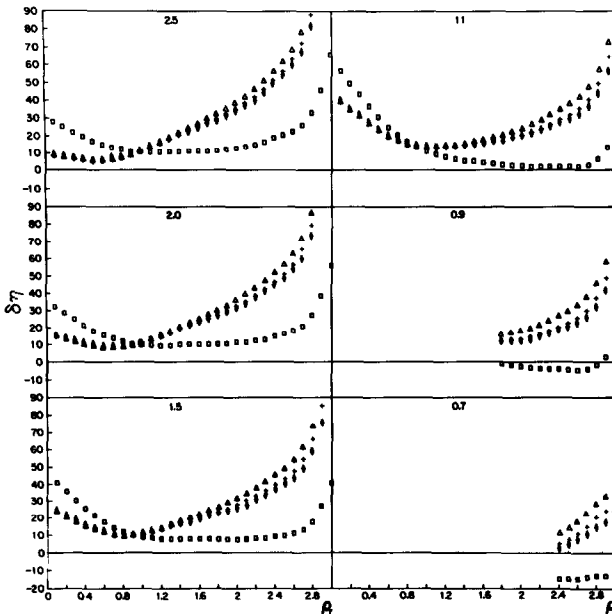
Fig. 1. Percent deviation of predicted η's from experimental data, versus reduced density, for six different reduced temperatures, and several prescriptions to obtain the state-dependent hard-sphere diameters.(□) MC/RS; (+) BH; (◊) VW; (Δ) WCA.

effective diameter. As expected, for thermal conductivity the percent deviations are less than for the shear viscosity when the MC/RS scheme is used (similar deviation charts for λ can be seen in Castillo and Orozco, 1990).

The effective-diameter hard-sphere theory can be extended to deal with fluids interacting through the gaussian overlap potential (Berne and Pechukas, 1972). The effective diameter is obtained through the perturbation expansion method for nonspherical fluids given by Mo and Gubbins (1975). Figure 2 shows our calculations for a fluid with an anisotropy parameter of 1.5, for several reduced densities at $T^* = 1.5$. A thorough evaluation of this method is presently under way. Variational method can be generalized too. Here, the free energy of a fluid interacting through the gaussian overlap potential is developed in terms of a hard-nonspherical fluid. An effective diameter to deal with this fluid can be obtained. The results will be published shortly.
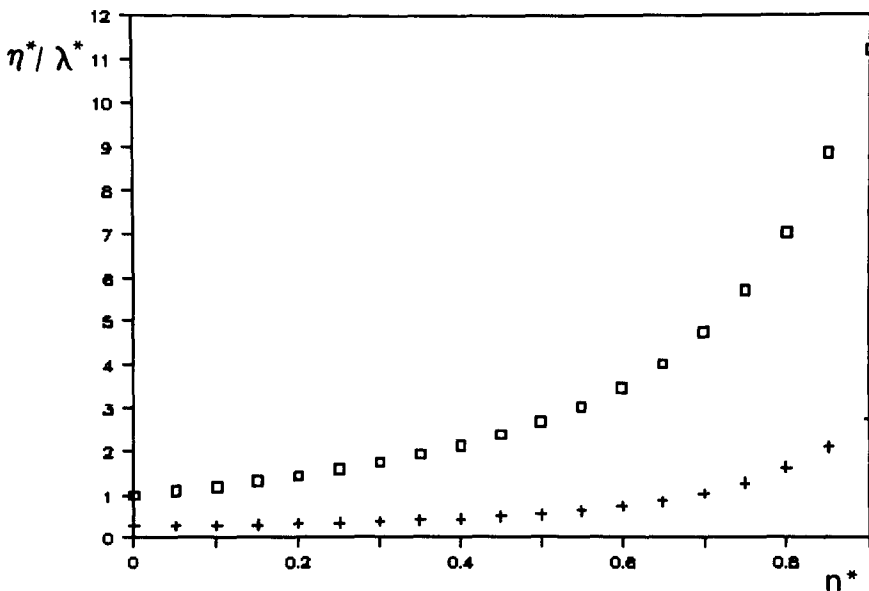
Fig. 2. Reduced shear viscosities (+) and reduced thermal conductivities (□) for a fluid with an anisotropy parameter of 1.5 at several states. The effective diameters were evaluated according to Mo and Gubbins (1975).

CONCLUDING REMARKS

In this work we found that the EDHST can estimate the transport properties of Lennard-Jones fluids, actual fluids, and their mixtures, if we are in the dense regime and use the variational scheme (MC/RS) to obtain the effective diameters. Generally speaking, this is true for the thermal conductivity, the shear viscosity, and for the case of the bulk viscosity, if we are above $T^*=1.2$. At the very high densities, $n^* > 1$, the EDHST can not be used. At low densities, EDHST with VW diameters can be used to estimate shear viscosities at reduced densities between 0.05 and 0.15. At higher densities it is better to use the variational diameters.

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