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A Theory-Based Method for Correlation and Prediction of Dense-Fluid Transport Properties[1]

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Dense-fluid transport property data for a wide range of compounds have been successfully correlated on the basis of universal curves for the reduced diffusion coefficient, D^*, the reduced viscosity, η^*, and the reduced thermal conductivity, λ^*, against the reduced volume V/V_0, where V is the molar volume, and V_0 is a characteristic volume equal to the volume of close packing for a system of hard spheres. The reduced transport properties, X^*, are defined in terms of the low-density hard-sphere values by $(X/X_0)(V/V_0)^{2/3}$, where X is η, λ, or the product of the number density and the diffusion coefficient. To provide a theoretical justification for this approach, extensive computer simulation results for these transport properties, given in the literature for a system of Lennard-Jones (12–6) molecules, have been considered. It is found that the reduced transport properties for different temperatures are superimposable upon the results for any reference isotherm when plotted versus log V, as found previously for real fluids. However, to reproduce this density dependence at any given temperature on the basis of the universal curves, the characteristic volume for self-diffusion must be greater than that for viscosity or thermal conductivity.

KEY WORDS: correlation; dense fluids; diffusion; Dymond–Assael equation; Enskog theory; thermal conductivity; transport properties; viscosity.

1. INTRODUCTION

It is not yet possible to give a rigorous theoretical interpretation of the transport properties of dense fluids because of the problem of accounting successfully for many-body interactions and, also, because of the lack of detailed information on the pair interaction potential energy function for all but the simplest of molecules. At the present time, the most satisfactory

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approach for correlating dense-fluid transport properties is based on consideration of the hard-sphere model. The model is reasonably realistic since, at high density, greater than the critical density, the molecular trajectory in real systems is determined predominantly by repulsive interactions, and although real intermolecular repulsive interactions are not as hard as that of the hard-sphere system, the interaction curve is very steep. The advantage of this hard-sphere model is that exact values can be calculated for self-diffusion D, viscosity η, and thermal conductivity λ from the approximate Enskog theory, together with the computed corrections [1, 2], for specific values of the reduced volume, V/V_o, where V_o is the volume of close packing of spheres of diameter σ given by $N_A\sigma^3/2^{1/2}$.

This model is most conveniently applied to the correlation of dense fluid transport properties by consideration of reduced properties D^*, η^*, and λ^*, which are independent of choice of core size. They are defined as follows [3]:

$$D^* = (nD/n_o D_o)(V/V_o)^{2/3} \tag{1}$$

$$\eta^* = (\eta/\eta_o)(V/V_o)^{2/3} \tag{2}$$

$$\lambda^* = (\lambda/\lambda_o)(V/V_o)^{2/3} \tag{3}$$

where n is the number density and subscript o refers to the low-density hard-sphere values.

These reduced properties can also be calculated from experimental data, on the assumption that a real fluid is behaving like an assembly of hard spheres, since on substitution for the hardsphere expressions (see, e.g., Ref. 3), Eqs. (1)–(3) become

$$D^* = 5.030\times10^8(M/RT)^{1/2}\,DV^{-1/3} = F_D(V/V_o) \tag{4}$$

$$\eta^* = 6.035\times10^8(1/MRT)^{1/2}\,\eta V^{2/3} = F_\eta(V/V_o) \tag{5}$$

$$\lambda^* = 1.936\times10^7(M/RT)^{1/2}\,\lambda V^{2/3} = F_\lambda(V/V_o) \tag{6}$$

where M is the molar mass, T is the absolute temperature, R is the gas constant, and all quantities are expressed as SI units.

The density dependence of each of these reduced transport properties for monatomic fluids at a constant temperature is very similar to that exhibited by a system of hard spheres. This is clearly demonstrated [3] by comparing plots of the reduced transport property for hard spheres versus $\log(V/V_o)$ with corresponding plots of the reduced transport property versus $\log V$ for the real fluid. The horizontal shift required to produce coincidence of these curves leads to a value for the characteristic volume V_o

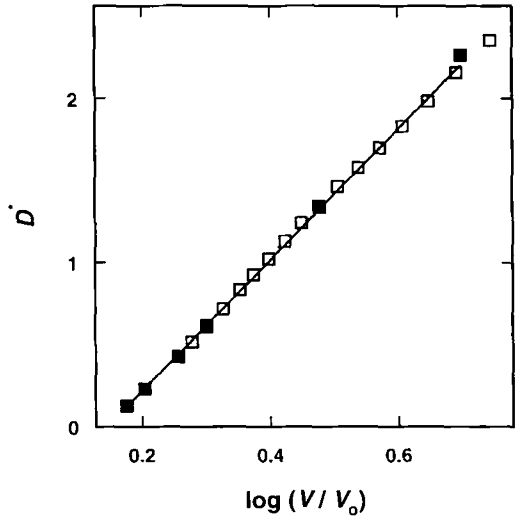

Fig. 1. Reduced self-diffusion for neon versus logarithm of reduced volume: □, experimental data [4]; ■, exact hard-sphere theory; solid line, Eq. (7).

at the given temperature. This is illustrated in Fig. 1, where diffusion measurements for xenon at 298 K [4] have been fitted to hard-sphere theory. The solid line is given by the following simple relationship, which reproduces closely (within 5%) the exact hardsphere results for D^* values down to 0.13 and covers the range $1.5 \leqslant V/V_0 \leqslant 5$:

$$F_D = 3.98\{\log(V/V_0) - 0.145\} \tag{7}$$

The experimental data are fitted within 2.5% over the extended density range down to one-half the critical density with V_0 equal to $24.7 \times 10^{-6}\ \mathrm{m^3 \cdot mol^{-1}}$ at 298 K.

Expressions have been given [5] for the functionals F_D (at higher reduced densities), F_η, and F_λ in Eqs. (4)-(6), based on the hard-sphere results but also taking into account the density dependence of the reduced transport properties of real fluids at higher reduced densities.

For pseudo-spherical molecular fluids and nonspherical molecular fluids, where there is the possibility of translational-rotational coupling, a roughness parameter has been introduced. It has been shown in the case of alkanes [5], aromatic hydrocarbons [6] and other simple molecular fluids

[7], and refrigerants [8] that the transport properties X can be very satisfactorily reproduced on the assumption that

$$X^* = R_x F_x \tag{8}$$

where R_x is the roughness parameter, which is found for these compounds to be both temperature and density independent. Values for R_x and V_0 are simply derived from the vertical and horizontal shifts necessary to superimpose plots of $\log X^*$ versus $\log V$ from experiment and $\log X^*$ versus $\log(V/V_0)$ given by the functions F_x. In accordance with the basic model, the V_0 values have been taken to be identical at a given temperature for all three properties. As expected, these V_0 values for a given compound decrease as the temperature is raised in reflection of the soft repulsive interaction potential of real fluids.

On this basis, a very successful correlation scheme for dense fluid transport properties has been developed. Since, for the transport property of any fluid at constant temperature, a plot of $\log X^*$ versus $\log V$ is superimposable upon the curve given by $\log F_x$ versus $\log(V/V_0)$, it follows that different experimental isotherms will be superimposable upon a given reference isotherm simply by lateral movement—without reference to F_x. This is an extremely useful test of the accuracy of high-density transport property data. From the shifts, ratios of the characteristic volumes are derived which should exhibit a smooth variation with temperature. Once a reference isotherm has been established, accurate prediction of that transport property at other temperatures and densities can be made from knowledge of the property under one set of conditions, for example, at atmospheric pressure.

To place this correlation method on a more sound theoretical basis, an analysis has been made of transport property data which have been computed for the more realistic Lennard-Jones (12–6) intermolecular potential energy function.

2. LENNARD-JONES (12–6) FLUID

Extensive computations of the transport properties of systems of Lennard-Jones (12–6) molecules have been performed by Heyes [9–11] at reduced temperatures (equal to T divided by the attractive well depth) from 0.72 to 10 over a wide range of reduced density.

In view of the agreement found between transport property data for real fluids and the functionals F_x, as described above, it is to be expected that the data for Lennard-Jones (12–6) molecules should be successfully correlated in a similar way. Values for the reduced transport properties

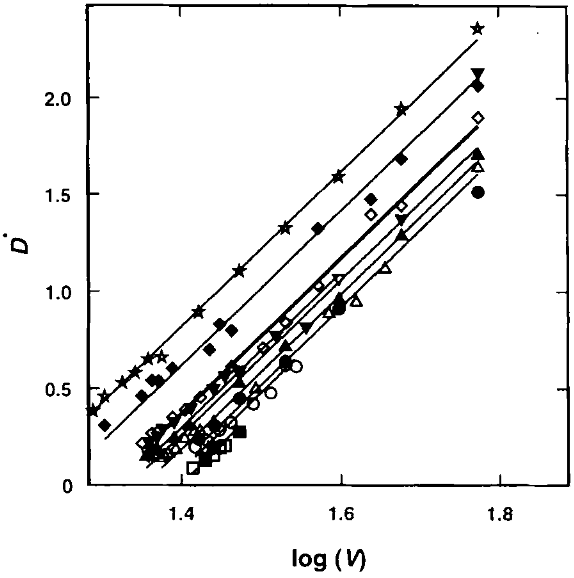

Fig. 2. Reduced self-diffusion for Lennard-Jones (12-6) molecules versus logarithm of volume (in 10^{-6} $m^3 \cdot mol^{-1}$) at different reduced temperatures: □, 0.72; ■, 0.81; , 1.06; ●, 1.35; △, 1.4562; ▲, 1.8627; ▽, 2.0; ▼, 2.5138; ◇, 2.6974; ◆, 6.0; ☆, 10.0.

were calculated for Lennard-Jones "argon" from the literature values [11], with the energy and size parameters given therein, using Eqs. (4)-(6). For diffusion, plots of D^* versus log V are practically linear, as shown in Fig. 2. The solid lines are given by Eq. (7), with values of V_0 summarized in Table I. A comparison of the computed values for 108, 256, and 512 particle systems leads to an estimated uncertainty of 7% in some values, and

Table I. Values of V_0 (in 10^{-6} $m^3 \cdot mol^{-1}$) for Lennard-Jones (12-6) "Argon"

	T (K)						
	97.04	126.7	174.4	223.1	323.1	718	1098
V_0 (diffusion)	17.8	17.2	16.2	15.5	14.5	12.6	11.2
V_0 (viscosity)	17.2	16.2	15.4	14.6	13.5	11.3	10.1
$V_0(D)/V_0(\eta)$	1.04	1.06	1.05	1.06	1.07	1.11	1.11

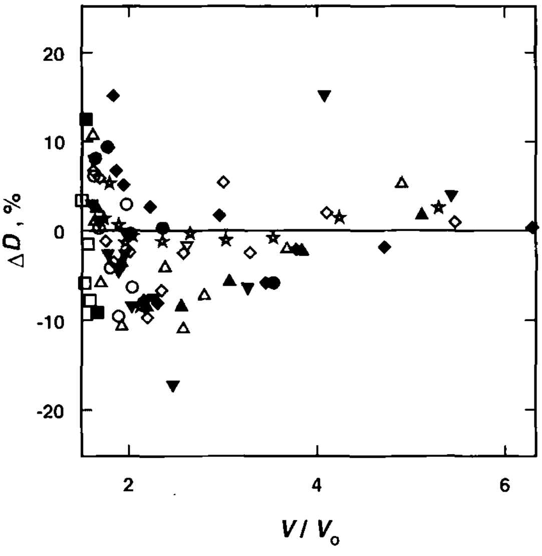

Fig. 3. Deviation plot for diffusion versus reduced volume. $\Delta D = 100(D_{LJ} - D_{eqn})/D_{eqn}$. Key as for Fig. 2.

the erratic deviation of certain points from the lines can be taken as an indication of the uncertainty in these computations. At the highest densities, there is some evidence that the calculated values become higher than values given by the equation, but for the range $1.6 \leqslant V/V_0 \leqslant 6$, the equation gives a very satisfactory fit to the Lennard-Jones results. This is illustrated in Fig. 3.

For viscosity, curves for different isotherms were superimposed on the curve for a reduced temperature of 1.8627, which was taken as the reference curve. The results, shown in Fig. 4, give an excellent correlation of these "experimental" data over this reduced temperature range, which is very much wider than the range of measurements on any real fluid.

The solid line corresponds to Eq. (5) with F_η from Ref. 5, for $V_0 = 14.64 \times 10^{-6}\ \mathrm{m^3 \cdot mol^{-1}}$ at 223 K. The deviations of the computed Lennard-Jones values from the universal function are illustrated in Fig. 5. In view of the fact that at a reduced temperature of 1.8627, the viscosity increases by a factor of 16 over the density range considered, the fit is very satisfactory. Deviations can be attributable partly to computational errors. Although there is now much closer agreement between the results of calculations by equilibrium molecular dynamics and those by nonequilibrium molecular dynamics, there are still uncertainties of a few percent in these values.

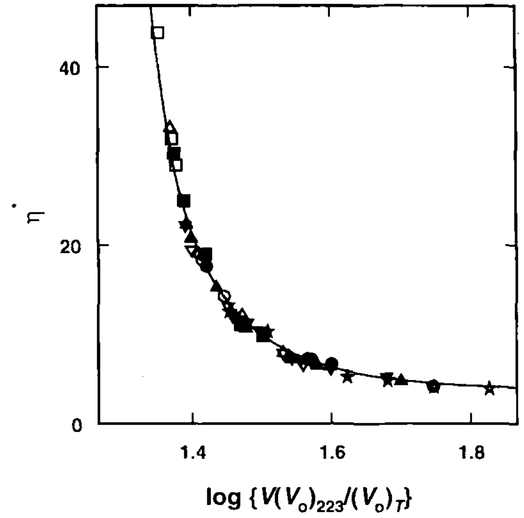

Fig. 4. Reduced viscosity for Lennard Jones (12-6) molecules versus logarithm of volume (in 10^{-6} $m^3 \cdot mol^{-1}$) at different reduced temperatures adjusted to superimpose on the curve for the 223 K isoterm. Key as for Fig. 2; solid line, F_η [5].

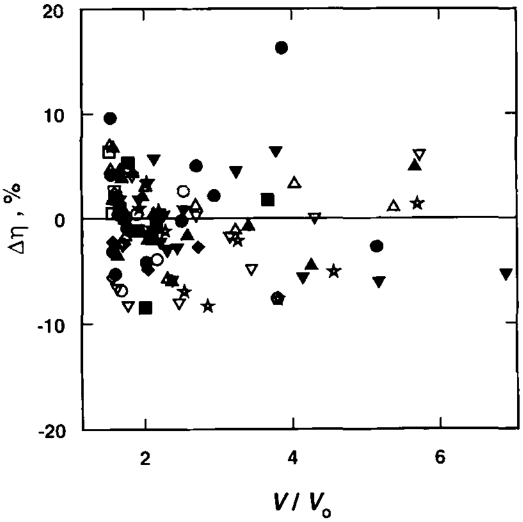

Fig. 5. Deviation plot for viscosity versus reduced volume. $\Delta\eta = 100(\eta_{\mathrm{LJ}} - \eta_{\mathrm{eqn}})/\eta_{\mathrm{eqn}}$. Key as for Fig. 2.

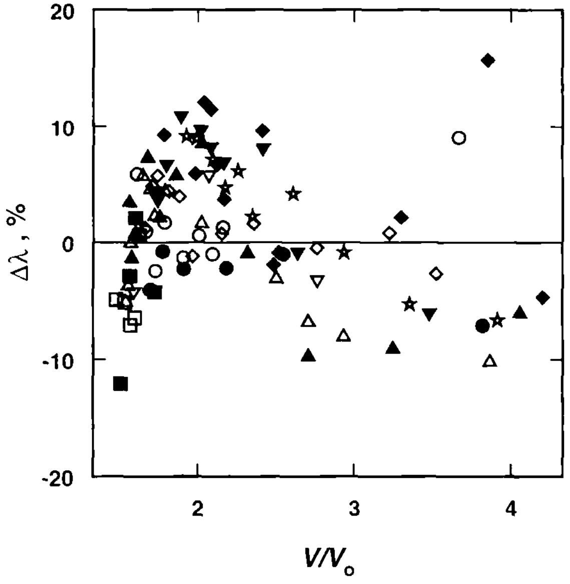

Fig. 6. Deviation plot for thermal conductivity versus reduced volume. $\Delta\lambda = 100(\lambda_{LJ} - \lambda_{eqn})/\lambda_{eqn}$. Key as for Fig. 2.

The V_0 values are summarized in Table I. For Lennard-Jones argon, a direct comparison can be made of the V_0 values for diffusion and viscosity for the equivalent hard-sphere system at corresponding temperatures. It is found that these are not identical but that V_0 for diffusion is about 5% greater than V_0 for viscosity at the same temperature, except at very high temperatures where there is an increase in this ratio.

In the case of the reduced thermal conductivity data fit, it is found that the V_0 values can be taken as identical to those for viscosity at the same temperatures. Figure 6 shows the deviations of the computed values from those given by Eq. (6) with F_λ from Ref. 5. These deviations are greater than those found for viscosity (Fig. 5), but this is as expected in view of the larger variations in the number dependence of the computed results for this property.

3. APPLICATIONS

An important consequence for correlating transport property data for dense fluids using the functions F_X based on the hard-sphere model is that, although a hard-sphere system will have the same core size for all properties, analysis of the Lennard-Jones (12–6) results demonstrates that the equivalent core size for self-diffusion should be larger by about 5% than that for viscosity and thermal conductivity at a given temperature. This is interesting in view of the earlier observation [3, 12] that for methane, a pseudo-spherical molecule, the roughness factor for viscosity was 1 —indicative of smooth hard-sphere behavior—but for self-diffusion, it was about 0.9. This was interpreted as evidence of translational–rotational coupling. In that treatment it had been assumed, in the absence of any evidence to the contrary, that V_0 was identical for the two properties at the same temperature. However, it is not unreasonable that the effective hard-sphere core sizes for diffusion, on one hand, and thermal conductivity and viscosity, on the other, should differ for systems of real molecules. It has previously been found for a dilute gas that, in the case of particles interacting with an inverse-power potential [13], and with the Lennard–Jones (m–6) potentials [14], the equivalent hard-sphere collision cross section for a given temperature was smaller for diffusion than for viscosity or thermal conductivity. Here, at high densities, the opposite effect is observed.

If R_D is put equal to 1, as for a smooth hard-sphere system, methane self-diffusion data [15, 16] show a linear variation of D^* with log V, for volumes up to 1.6 times the critical volume, which is well represented by Eq. (7). Values derived for V_0 are compared in Table II with results obtained from fitting the viscosity data [5]. It is found that the results for diffusion are larger at a given temperature, and the ratios are similar to those obtained for Lennard–Jones (12–6) "argon" (Table I), with remarkably close agreement above the critical temperature. It thus appears that both diffusion and viscosity data for methane can be interpreted on the basis of a smooth hard-sphere model for this molecule.

It would be useful confirmation to have accurate diffusion and viscosity data for one of the rare gases over a wide density range at the same temperature. For xenon, there are data for these properties at 323 K [4, 17] but over a somewhat limited density range. The derived V_0 values

Table II. Values of V_0 (in $10^{-6}\,\text{m}^3 \cdot \text{mol}^{-1}$) for Methane

	T (K)					
	110	140	160	223	298	323
V_0 (diffusion)	22.2	21.3	20.8	19.7	18.8	18.6
V_0 (viscosity)	22.0	20.8	20.1	18.7	17.9	17.7
$V_0(D)/V_0(\eta)$	1.01	1.02	1.03	1.06	1.05	1.05

for diffusion and viscosity are 24.3×10^{-6} and $23.6 \times 10^{-6}\ \mathrm{m^3 \cdot mol^{-1}}$ respectively, giving a ratio of 1.03, which is in general agreement with the results of analysis of the Lennard–Jones (12–6) results.

4. CONCLUSIONS

Consideration of the Lennard–Jones (12–6) transport properties has demonstrated that the correlation method whereby plots of reduced transport properties versus log V are superimposed upon a given reference isotherm has a sound theoretical basis. The density dependence is mimicked very closely by the hard-sphere model, but to fit the data, the V_0 for diffusion must be about 5% larger than the corresponding value for viscosity or thermal conductivity at the same temperature.

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