

Note

Correlation and Prediction of Dense Fluid Transport Coefficients. IV. A Note on Diffusion

M. J. Assael,¹ J. H. Dymond,² and P. M. Patterson²

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Recent accurate calculations of the corrections to Enskog theory for hard-sphere diffusion have resulted in a revision of the hard-sphere based correlation for dense fluid transport coefficients. The expression previously given for the reduced diffusion coefficient in terms of reduced volume is adjusted in line with these values. No changes are required to the characteristic volumes but the roughness factors are reduced. Of particular note is the fact that methane now corresponds to a rough hard-sphere system.

KEY WORDS: diffusion; hard-sphere theory; molecular dynamics.

1. INTRODUCTION

In recent years, a scheme has been developed [1, 2] for the successful correlation of the transport coefficients of dense gases and liquids over a wide range of temperatures and pressures. To date, it has been applied to *n*-alkanes [2] and to other simple organic molecular liquids [3] and has been extended to *n*-alkane mixtures [4]. It has been demonstrated that this method can lead to an accurate ($\pm 6\%$) estimation of transport coefficients.

The basis of the method is the exact hard-sphere theory, by which the transport coefficients for dense fluids are expressed [5] in terms of the reduced volume V/V_0 , where V_0 is the volume of close packing of hard-spheres. These values were then corrected for effects of correlated molecular motions by using the results of computer simulation studies [6, 7]. They also depend only on V/V_0 and thus there is just the one molecular parameter, V_0 , to consider. V_0 is assumed to decrease in value with an

¹ Chemical Engineering Department, Aristotle University, GR-54006 Thessaloniki, Greece.

² Chemistry Department, University of Glasgow, Glasgow G12 8QQ, United Kingdom.

increase in temperature in accordance with the soft repulsive interaction potential energy function for real molecules.

Unfortunately, as there are insufficient accurate experimental transport coefficient measurements for the dense rare gas fluids, it is necessary to turn to simple molecular fluids. A further consideration in applying this model to molecular fluids is that there is now the possibility of coupling between translational and rotational motion. Following Chandler [8], the transport coefficients for such rough hard-sphere fluids are taken to be directly proportional to the smooth hard-sphere values. For each property there exists a roughness factor which is generally assumed to be both temperature and pressure independent.

The simplest molecular fluid for which extensive accurate self-diffusion coefficient measurements are available is methane [9, 10]. It has been generally assumed [2, 9, 11] that this can be considered as a smooth hard-sphere molecule, with a roughness factor equal to 1.0. In applying this model it was necessary to take into account the differences between two sets of molecular dynamics results then available for the correction to Enskog theory for diffusion: those of Alder et al. [6] and those of Eastal et al. [7]. The experimental diffusion coefficient data for methane were found to show the same density dependence at constant temperature as a smooth hard-sphere system if the molecular dynamics calculations of the latter were employed. On the basis of these results, a universal curve for the reduced diffusion coefficient as a function of V/V_0 was developed for the successful correlation scheme [2].

However, a recent study by Erpenbeck and Wood [12] showed the importance of including long-time contributions to the Green-Kubo integral in the calculation of the hard-sphere diffusion coefficient. This leads to results for the correction to the Enskog diffusion coefficient in excellent agreement with the earlier values given by Alder et al. [6].

2. THE REVISED SCHEME

As a result of this change in the accepted corrections to the Enskog theory for diffusion, it is necessary to modify the equation given previously [2] for the reduced diffusion coefficient, D^* , as a function of reduced volume. All that is required is a change to the numerical term, so that the expression becomes

$$\begin{aligned} \log(D^*) = & 3.33076 - 31.74261/V_r + 133.0472/V_r^2 - 285.1914/V_r^3 \\ & + 298.1413/V_r^4 - 125.2472/V_r^5 \end{aligned} \quad (1)$$

where $V_r = V/V_0$ and D^* is related to the experimental self-diffusion coefficient of a compound with relative molar mass M at a given temperature T by the equation

$$D^* = \frac{D_{\text{exp}}^*}{R_D} = 5.038 \times 10^8 \left[\frac{M}{RT} \right]^{1/2} \frac{DV^{-1/3}}{R_D} \quad (2)$$

R_D is the roughness factor for diffusion, with values expected to be less than or equal to one [8].

Values for D/D_E were then calculated for different reduced volumes using D^* values from Eq. (1) using

$$D/D_E = D^*(V_0/V)^{2/3} g(\sigma) \quad (3)$$

where $g(\sigma) = (1 - 0.5\zeta)/(1 - \zeta)^3$ and $\zeta = 0.74048(V_0/V)$. Table I presents these D/D_E values in comparison with the molecular dynamics values for the self-diffusion of the hard-sphere fluid relative to the Enskog value, in the first approximation, obtained by Alder et al. [6] and by Erpenbeck and Wood [12]. Erpenbeck and Wood [12] used the D_E value obtained in the ninth Enskog approximation and therefore all their results were multiplied by 1.01896 in comparing with others. Figure 1 also shows this comparison as a function of reduced density, V_0/V . As can readily be seen, the agreement is very satisfactory in this reduced density range. Figure 1 clearly illustrates the difference between the present results and those given by the empirical equation of Speedy [13], which is based on the molecular dynamics results of Easteal et al. [7]. At lower densities, there are differences between the values derived from the reduced diffusion curve and the

Table I. Molecular Dynamics Results for the Self-Diffusion Coefficient of the Hard-Sphere Fluid Relative to the Enskog Value, in the First Approximation, from the Present Study, Alder et al. [6], and Erpenbeck and Wood [12]

V/V_0	ζ	$g(\sigma)$	D/D_E		
			This study	Ref. 6	Ref. 12
1.5	0.4937	5.8016	0.6995	0.58	—
1.6	0.4628	4.9578	0.8787	0.84	0.859
1.7	0.4356	4.3502	1.018	—	1.029
1.8	0.4114	3.8948	1.126	1.15	1.150
2.0	0.3702	3.2626	1.274	1.27	1.273
3.0	0.2468	2.0517	1.348	1.34	1.345

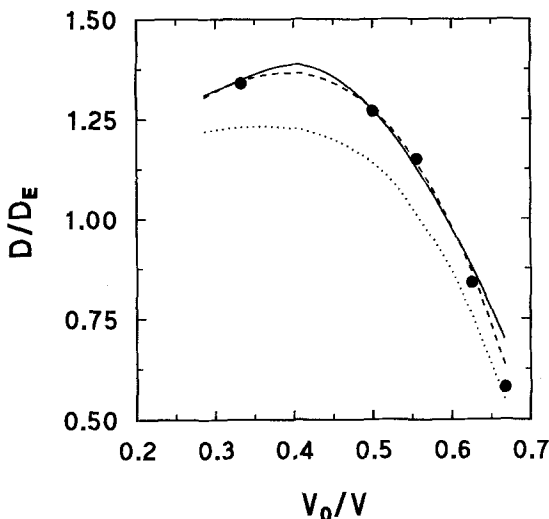


Fig. 1. Corrections to Enskog theory for self-diffusion as a function of reduced density. The solid line represents the present study, while the filled circles are from Alder et al. [6]. The dashed line shows the results of Erpenbeck and Wood [12], Eq. (23), multiplied by 1.01896. The dotted line represents the empirical expression of Speedy [13].

computer calculations because of the effects of attractive forces, which become important with real fluids. At $V/V_0 < 1.5$ the diffusion coefficient for real liquids at constant temperature falls off less rapidly with an increase in density than that expected from the Speedy equation [14].

When Eq. (1) is applied to the methane diffusion measurements, it is found that it is no longer correct to consider methane as a smooth hard-sphere molecule. A comparison of the experimental data, in reduced form as described previously [2], shows that the roughness factor, R_D , for methane is 0.90. The V_0 values remain unchanged.

Values for the roughness factor for diffusion for other molecular fluids must also be adjusted. For n -alkanes

$$R_D = 0.7445 + 0.2357C^{0.5} - 0.075C \quad (4)$$

and the corrected values for other miscellaneous molecular fluids are listed in Table II. In all cases the V_0 values are unchanged and the quality of the prediction of transport properties is maintained.

As the roughness factor for diffusion of simple molecular fluids such as methane now no longer equals 1.0, there is no reason why the roughness

Table II. Revised R_D Values for Simple Molecular Fluids

Compound	R_D
C_2H_4	0.892
CS_2	0.765
C_6H_{12}	1.035
CCl_4	0.750
CH_3CN	0.610
$CHCl_3$	0.709

factor for viscosity, R_η , should have the value 1.0. However, in view of the much larger uncertainty in the corrections to Enskog theory for this property, it is not considered appropriate at this time to make adjustments to the universal curve for the reduced viscosity coefficient or to the roughness factors previously given for viscosity.

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