Hard-sphere Theories of Transport Properties

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1 Introduction

A detailed study of transport properties of fluids and fluid mixtures is important not only for the solution of problems involving heat and mass transfer but also for the development of our understanding of molecular motions and interactions in such systems. For monatomic gases at low densities, the coefficients of viscosity, thermal conductivity, and diffusion can be accurately calculated at any temperature using exact kinetic theory expressions based on the work of Boltzmann, Enskog, and Chapman (see *ref.* 1) and methods have been devised[2,3] for the direct determination of the pair potential energy functions of these substances from experimental transport data. However, such methods cannot be applied to monatomic fluids at high densities or to polyatomic fluids because there is at present no formal theory which allows an exact evaluation of transport properties in terms of a realistic description of the molecular interactions.

An alternative approach, which has led to significant progress towards a successful molecular theory of transport properties in dense fluids, is the use of the computer simulation method of molecular dynamics.[4,5] This can be applied in different ways. Firstly, in an attempt to simulate real fluids under given conditions of temperature and density, transport coefficients are evaluated for a system of molecules interacting with a specified form of potential energy function. The function most widely used is the well-known Lennard-Jones (12—6) potential which relates the interaction energy to the separation of a pair of molecules according to equation 1:

$$U(r) = 4\varepsilon[(\sigma/r)^{12} - (\sigma/r)^{6}] \tag{1}$$

where parameters ε and σ represent the depth of the attractive well and the separation at zero energy. The self-diffusion coefficient of a fluid is then calculated from the integration of the velocity autocorrelation function:

$$D = \frac{1}{3}\int_0^t < \vec{v_i}(0)\cdot\vec{v_i}(t) > \mathrm{d}t \tag{2}$$

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[1] G. C. Maitland, M. Rigby, E. B. Smith, and W. A. Wakeham, 'Intermolecular Forces', Clarendon Press, Oxford, 1981.

[2] J. H. Dymond, *J. Chem. Phys.*, 1968, **49**, 3673.

[3] D. W. Gough, G. C. Maitland, and E. B. Smith, *Mol. Phys.*, 1972, **24**, 151.

[4] B. J. Alder and T. E. Wainwright, *J. Chem. Phys.*, 1959, **31**, 459.

[5] A. Rahman, *Phys. Rev.*, 1964, **136**, A405.

where the average is over all particles over a set of initial times, or from the mean-square displacement using the Einstein expression:

$$D = \lim_{i \to \infty} \frac{1}{6t} < \left[\vec{r_i}(t) - \vec{r_i}(0) \right]^2 > \tag{3}$$

Calculation of the self-diffusion of argon, the simplest atomic fluid, has been made[5–7] in this way for a number of different temperatures and densities. For molecular fluids the (12—6) potential function is used to represent the interactions between the nuclei in neighbouring molecules as in the 'two-centres' computations of the self-diffusion coefficient fluorine, chlorine, bromine, and carbon dioxide[8] and of nitrogen,[9] and the 'three-centres' calculations of the self-diffusion coefficient for carbon disulphide.[10]

The shear viscosity and thermal conductivity coefficient may also be calculated by a steady-state molecular dynamics method[11,12] by expressing these coefficients in either the Einstein form or in terms of an autocorrelation function. The problem is the significantly greater computing time required for the evaluation of these transport coefficients, which are properties of the system as a whole, compared with the self-diffusion coefficient for which the diffusion of each individual molecule can be determined and the average taken. Thus, for a similar precision in the results, the molecular dynamics computations need to be carried out for about N times as long, where N is the number of particles considered. As an indication of accuracy, calculated viscosity coefficients of simulated argon[12] had a statistical error of 15 per cent. Transport coefficients can also be calculated by non-equilibrium molecular dynamics methods.[13] Recent studies[14,15] indicate that this is a more economic way of computing liquid viscosities, but the uncertainty in the reported results is still about 10 per cent.

As a result of such computational studies, it is possible, by suitable choice of molecular parameters, to obtain a reasonably satisfactory fit to the experimental data, considering the uncertainties in the experimental measurements and in these computations. However, there are disadvantages to this general approach. It is expensive of computer time because of the necessity to evaluate numerically the transport coefficients for each substance considered [for homonuclear diatomics, for example, there is an additional (dimensionless) parameter, the ratio of the bond-length to the diameter of each 'atom'] for several temperatures and densities in order to determine the molecular parameters and the dependence of the transport coefficients on the experimental variables. Furthermore, it should be noted that,

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[6] D. Levesque and L. Verlet, *Phys. Rev. A*, 1970, **2**, 2514.

[7] D. M. Heyes, *J. Chem. Soc., Faraday Trans. 2*, 1983, **79**, 1741.

[8] K. Singer, J. V. L. Singer, and A. J. Taylor, *Mol. Phys.*, 1979, **37**, 1239.

[9] P. S. Y. Cheung and J. G. Powles, *Mol. Phys.*, 1975, **30**, 921.

[10] D. J. Tildesley, *Mol. Phys.*, 1983, **48**, 129.

[11] B. J. Alder, D. M. Gass, and T. E. Wainwright, *J. Chem. Phys.*, 1970, **53**, 3813.

[12] E. M. Gosling, I. R. McDonald, and K. Singer, *Mol. Phys.*, 1973, **26**, 1475.

[13] W. T. Ashurst and W. G. Hoover, *Phys. Rev. A*, 1975, **11**, 658.

[14] D. J. Evans, *Phys. Rev. A*, 1981, **23**, 1988.

[15] D. Fincham and D. M. Heyes, *Chem. Phys.*, 1983, **78**, 425.

even if exact agreement was obtained with experimental data over a wide range of experimental conditions, it would not necessarily follow that the assumed form of potential energy function accurately represented the interactions of the real molecules.

The second general application of the molecular dynamics method is the simulation of assemblies of molecules interacting with somewhat over-simplified forms of potential energy function in order to establish a sound physical basis for the development of a successful theory of transport properties in dense fluids. For example, the computations of Alder and Einwohner[16,17] on the free-path distribution for hard-spheres, which interact according to

$$\begin{aligned} U(r) &= 0 \quad && r > \sigma \\ U(r) &= \infty \quad && r \leqslant \sigma \end{aligned} \tag{4}$$

and square-well molecules, for which the interaction potential is

$$\begin{aligned} U(r) &= 0 \quad && r \geqslant R\sigma \\ U(r) &= -\varepsilon \quad && \sigma < r < R\sigma \\ U(r) &= \infty \quad && r \leqslant \sigma \end{aligned} \tag{5}$$

showed that molecular motion proceeds by a succession of small diffusive steps and not by a relatively small number of jumps whose length is approximately equal to the intermolecular spacing, as is implicit in the activation model of Eyring.[18] Furthermore, they showed[17] that the Brownian motion approximation, which postulates that the molecules undergo many 'collisions' involving the attractive part of the potential (soft collisions) between successive repulsive interactions (hard collisions) and which was used by Rice and co-workers[19] as a basis for a theory of transport properties, is unsatisfactory even at a high pressure and at low temperature.

What is required is a theory based on a reasonably realistic description of the trajectory of the molecules which can be used as a physically motivated and accurate approximation to the more formal theories. Such a theory is the van der Waals theory, which has served well for equilibrium properties. The van der Waals model of a fluid is of an assembly of molecules having a weak long-range attractive energy and a hard-core repulsive energy, as illustrated in Figure 1(a).

For real systems, the dependence of the pair interaction potential energy on molecular separation has the familiar shape shown in Figure 1(b). The potential does have a steep repulsive part and the range of the attractive part can be considered large relative to the interparticle spacing at densities greater than the critical density. The attractive energy then forms a uniform attractive energy surface, and the molecules will move in straight lines between core collisions. This

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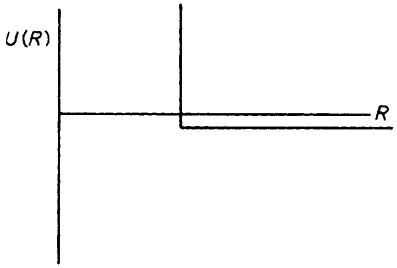
[16] B. J. Alder and T. Einwohner, *J. Chem. Phys.*, 1965, **43**, 3399.

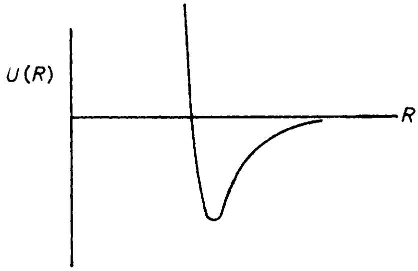
[17] T. Einwohner and B. J. Alder, *J. Chem. Phys.*, 1968, **49**, 1458.

[18] S. Glasstone, K. J. Laidler, and H. Eyring, 'The Theory of Rate Processes', McGraw-Hill Book Co. Inc., New York, 1941.

[19] S. A. Rice and A. R. Allnatt, *J. Chem. Phys.*, 1961, **34**, 2144.



(a) Van der Waals Model



(b) Realistic Pair Potential Function

Figure 1 *Comparison of a realistic pair potential energy curve with that given by the van der Waals model*
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description of the molecular motion is expected to be correct at temperatures greater than the attractive energy well-depth or, approximately, the critical temperature, when the kinetic energy will exceed the attractive potential energy.

An extremely important consequence for the van der Waals theory of transport properties is that it is equivalent to the hard-sphere theory, providing that the core sizes are allowed to decrease as the temperature increases to reflect the somewhat soft repulsive energy of real systems. This is the justification of the present widely-accepted method of interpreting transport coefficient data on the basis of the hard-sphere model.

In the first part of this paper, the expressions are given for the transport coefficients of dense assemblies of smooth hard-spheres and of rough hard-spheres. In the following sections, these hard-sphere theories are applied to the rare gases, to metals, to molecular fluids, and to mixtures. Although the shear viscosity and thermal conductivity coefficients are of greater significance from the chemical engineering point of view, theoretically it is the diffusion coefficient which has proved the most important in the development of theories in dense fluids. This arises because it is the simplest transport property to treat theoretically and also because of the greater accuracy with which it can be calculated for a given intermolecular potential energy function.

2 Transport Coefficients for a Dense Hard-sphere Fluid

A kinetic theory for transport coefficients of a dense hard-sphere system has been given by Enskog.[20] In a dense system, the collision rate is higher than in a dilute system because the diameter of the molecule is no longer negligible compared with the interparticle distance. The Enskog theory of diffusion assumes that the high density system behaves exactly as a low density system except that the collision frequency in increased by a factor of $g(\sigma)$, where $g(\sigma)$ is the radial distribution function at contact for spheres of diameter σ. The solution of the Boltzmann equation valid at low density is merely scaled in time to give the ratio of the diffusion coefficient D_E at high number density n relative to that at low density, subscript zero:

$$nD_E/n_0D_0 = 1/g(\sigma) \tag{6}$$

$g(\sigma)$ is obtained from computer simulation studies and is given by the Carnahan-Starling equation:[21]

$$g(\sigma) = (1 - 0.5\xi)/(1 - \xi)^3 \tag{7}$$

where $\xi = b/4V$ for a molar volume V, and $b = 2\pi N\sigma^3/3$. D_0 is related to the number density n_0 at temperature T by the expression

$$D_0 = (3/8n_0\pi\sigma^2)(\pi kT/m)^{\frac{1}{2}} \tag{8}$$

where m is the molecular mass and k is the Boltzmann constant.

For diffusion the particles themselves must move, but for viscosity and thermal conductivity there is the additional mechanism of collisional transfer whereby momentum and energy can be passed to another molecule upon collision. The Enskog theory for the viscosity η_E and the thermal conductivity λ_E in terms of the low density coefficients accordingly contains additional terms:

$$\eta_E/\eta_0 = [1/g(\sigma) + 0.8b/V + 0.761g(\sigma)(b/V)^2] \tag{9}$$

$$\lambda_E/\lambda_0 = [1/g(\sigma) + 1.2b/V + 0.755g(\sigma)(b/V)^2] \tag{10}$$

where the low density coefficients are given to first-order approximation by

$$\eta_0 = (5/16\pi\sigma^2)(\pi mkT)^{\frac{1}{2}} \tag{11}$$

$$\lambda_0 = (25C_V/32\pi\sigma^2)(\pi kT/m)^{\frac{1}{2}} \tag{12}$$

where C_V is the molecular heat capacity at constant volume.

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[20] D. Enskog, *Kungl. Svenska. Vet.-Ak. Handl.*, 1922, **63**, No. 4.

[21] N. F. Carnahan and K. E. Starling, *J. Chem. Phys.*, 1969, **51**, 635.

In order to apply equations 6, 9, and 10 for the calculation of dense gas transport coefficients, it is necessary to assign a value to the core size. In the original application of this method,[22] values for σ for the rare gases were obtained by fitting pVT data to the van der Waals equation of state. It was found that the calculated high density transport coefficients differed by less than 10 per cent from the experimental values.

Now the Enskog theory is based on the molecular chaos approximation. A sphere is considered as always colliding with other spheres approaching from random directions with random velocities from a Maxwell–Boltzmann distribution for the appropriate temperature. However, molecular dynamics calculations[23,24] have shown that there are correlated molecular motions in hard-sphere systems. At high densities, the principal correlation effect is back-scattering, whereby a sphere closely surrounded by a shell of surrounding spheres is most likely to have its velocity reversed on collision with its neighbours and this leads to a decreased diffusion coefficient. At intermediate densities, there is a different correlation effect associated with an unexpected persistence of velocities which leads to an enhanced diffusion coefficient. The resulting corrections to the Enskog transport coefficients have been computed by Alder, Gass, and Wainwright[11] for systems of 108 and 500 particles, with the diffusion coefficients extrapolated to infinite systems on the basis of hydrodynamic theory. The density dependence of the corrections is illustrated in Figure 2, where V_0, given by $N\sigma^3/\sqrt{2}$, is the volume of close-packing of spheres.

For V_0/V up to about 0.5, corresponding to dense gases at densities up to 2.5-times the critical density, the corrections to Enskog theory for the viscosity and thermal conductivity coefficient are less than 10 per cent, but for diffusion the corrected coefficient is significantly greater than the Enskog value at densities corresponding to 1.5- to 2-times the critical density. At the highest densities, approaching the onset of solidification, the corrections arising from back-scattering result in the exact hard-sphere diffusion coefficient being lower by about 40 per cent, and the viscosity coefficient being higher by a similar amount. To obtain exact expressions for the dense hard-sphere transport coefficients in terms of the low density coefficients, equations 6, 9, and 10 must be multiplied by the appropriate correction factor from Figure 2 at the given reduced volume. With core sizes determined from equilibrium data by extrapolation to infinite temperature, quantitative evidence for the existence of these correlated motions in real systems was obtained by analysis of self-diffusion coefficients of methane[25] and of carbon dioxide.[26]

3 Application of Exact Smooth Hard-sphere Expressions: Self-Diffusion

A. Monatomic Gases and Methane.—It was realised that there were uncertainties

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[22] J. H. Dymond and B. J. Alder, *J. Chem. Phys.*, 1966, **45**, 2061.

[23] B. J. Alder and T. E. Wainwright, 'The Many Body Problem', ed. S. K. Percus, Interscience Publ. Inc., New York, 1963.

[24] B. J. Alder and T. E. Wainwright, *Phys. Rev. Lett.*, 1967, **18**, 988.

[25] J. H. Dymond and B. Alder, *J. Chem. Phys.*, 1968, **48**, 343.

[26] J. H. Dymond and B. J. Alder, *Ber. Bunsenges. Phys. Chem.*, 1971, **75**, 394.

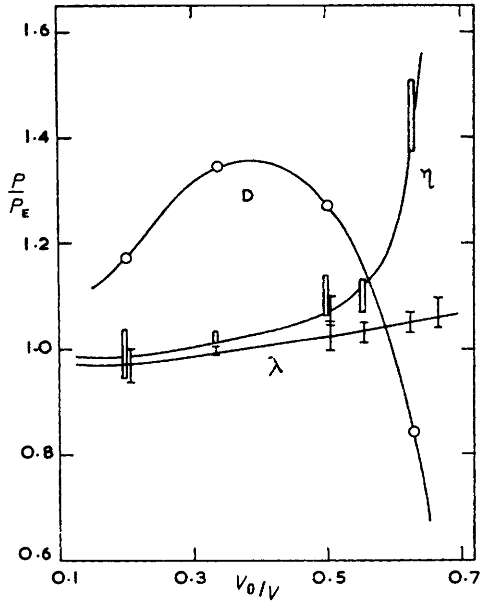

Figure 2 *Ratio of the exact hard-sphere transport coefficients to the Enskog coefficients given by molecular dynamics calculations,* ref. 11
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in determining the core size from equilibrium data and different methods were proposed[27] for comparing calculated and experimental transport coefficients without a prior estimation of core size. A quantity D^* which is independent of molecular diameter was defined according to:

$$D^* = (nD/n_0D_0)(V/V_0)^{\frac{2}{3}} \tag{13}$$

D^* can be calculated from theory by writing

$$D^* = \{1/g(\sigma)\}(D/D_E)(V/V_0)^{\frac{2}{3}} \tag{14}$$

where (D/D_E) is the computed correction to Enskog theory. D^* can also be calculated from experimental data on the assumption that the real fluid is behaving like an assembly of hard spheres, since on substituting for the hard-sphere expressions for n_0D_0 and V_0,

$$D^* = 5.030 \times 10^8\ (M/RT)^{\frac{1}{2}}D/V^{\frac{1}{3}} \tag{15}$$

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[27] J. H. Dymond, *Physica,* 1974, **75**, 100.

From equation (14), D^* is a function of V/V_0; from equation (15), D^* is a function of V for a given substance at a given temperature. To test whether this smooth hard-sphere theory can satisfactorily account for the density dependence of the experimental measurements at a given temperature, D^* from theory, equation (14), is plotted against log (V/V_0) and D^* from experiment, equation (15) is plotted against log (V). If these curves are superimposable laterally then the hard-sphere theory does represent the density dependence of the data, and the range of applicability of the theory can be established. Furthermore, V_0 can be obtained from points where the curves coincide.

In the absence of extensive accurate diffusion coefficient measurements for the rare gases, accurate methane data[28,29] obtained using the n.m.r. spin-echo technique have been used[27–31] to test the applicability of the smooth hard-sphere theory. It was assumed initially, and subsequently confirmed, that methane is a polyatomic molecule to which the rough hard-sphere theory (see Section 4) applies with a coupling factor of unity. It was shown that the experimental points at these temperatures from 1.7-times the critical temperature, T_c, down to 1.2 T_c lie within 5% of the smooth hard-sphere values down to densities about 0.8-times the critical density. A subsequent experimental study was carried out by Harris and Trappeniers[30] on methane at 110, 140, and 160 K. They found the reduced diffusivity D^* isotherms fell on a common curve when plotted against reduced density n^* (equals $n\sigma^3$) with the core sizes given in Table 1, in agreement with the smooth hard-sphere predictions, except at the highest densities ($n^* > 0.86$) where

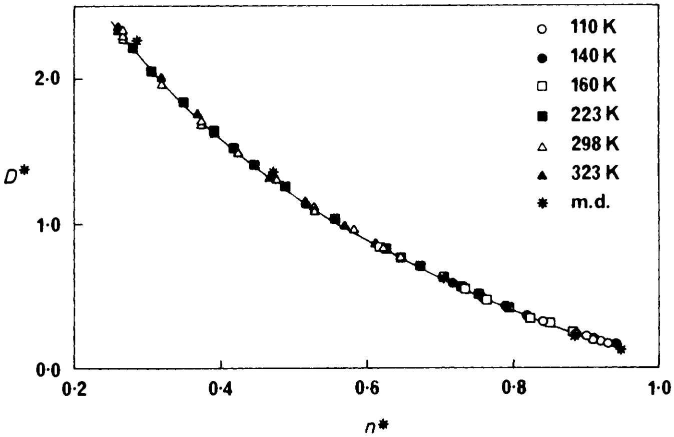

Figure 3 *Reduced diffusion coefficients for methane*
(Reproduced by permission from *Physica*, 1980, **104A**, 268)

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[28] P. H. Oosting and N. J. Trappeniers, *Physica*, 1971, **51**, 418.

[29] K. R. Harris, *Physica*, 1978, **94A**, 448.

[30] K. R. Harris and N. J. Trappeniers, *Physica*, 1980, **104A**, 262.

[31] J. H. Dymond and T. A. Brawn, *Proc. Symp. on Transport Properties of Fluids*, Nat. Eng. Lab., East Kilbride, H.M.S.O., 1979.

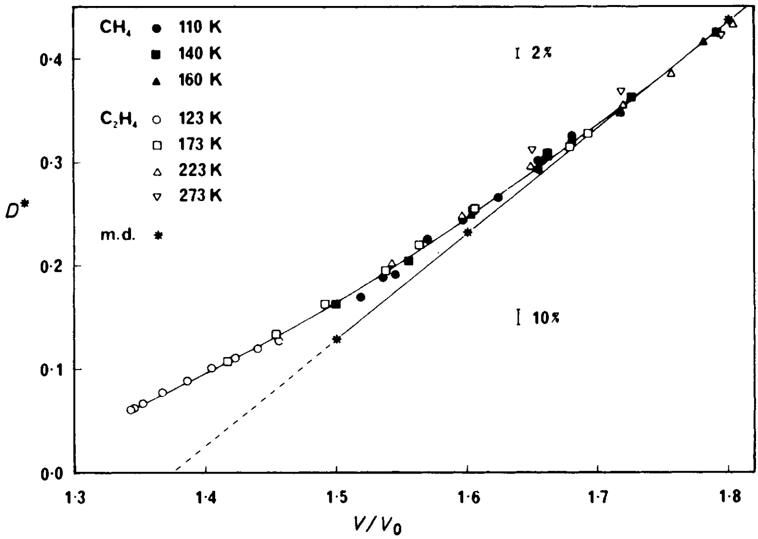

Figure 4 *Reduced diffusion coefficients at high density for methane and ethene*
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the experimental values are significantly higher. A similar conclusion was obtained by analysis of the self diffusion data for ethene obtained by Arends, Prins, and Trappeniers,[32] with the core sizes given in Table 1. This is illustrated in Figures 3 and 4.

This discrepancy at high density casts doubt on the validity of the model. However, recent molecular dynamics studies by Easteal, Woolf, and Jolly[33] of the self diffusion coefficient in a hard-sphere system concluded that although the

Table 1 *Hard-sphere diameters*

CH_4		C_2H_4	
T/K	σ/nm	T/K	σ/nm
110.00	0.3745	123.15	0.4150
140.00	0.3695	173.15	0.4080
160.00	0.3655	223.15	0.4026
223.15	0.3595	273.15	0.3985
298.15	0.3540	298.15	0.3966
323.15	0.3520		

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[32] B. Arends, K. O. Prins, and N. J. Trappeniers, *Physica*, 1981, **107A**, 307.

[33] A. J. Easteal, L. A. Woolf, and D. L. Jolly, *Physica*, 1983, **121A**, 286; *ibid.*, 1984, **127A**, 344.

computed corrections to the Enskog theory were dependent on the number of molecules considered in the calculation, the number dependence was significantly lower than that previously reported by Alder, Gass, and Wainwright.[11] By taking small increments in density, the dependence of (D/D_E) on reduced density was obtained. Their results are compared with previous computations in Figure 5.

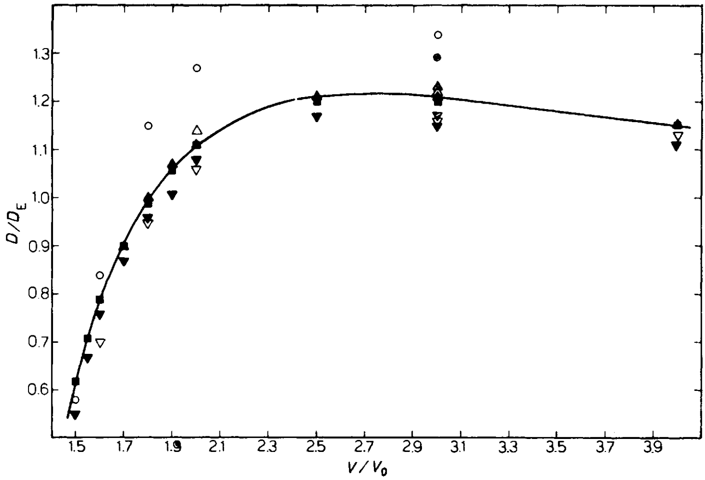

Figure 5 *Density dependence of* D/D_E. *Filled symbols,* ref. 33: ▼, 128 *particles:* ■, 250 *particles:* ▲, 432 *particles. Open symbols,* ref. 11: ▽ 108 *particles:* △, 500 *particles:* ○, *infinite system. Hatched symbols,* ref. 34: ▼, 108 *particles:* ▲, 500 *particles:* Ø, 4 000 *particles*
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The solid line is given by the following equation, where the coefficients have been rounded off to give significant figures only:

$$D/D_E = 0.7144 + 2.878\xi - o.8223\xi^2 - 10.93\xi^3 \qquad (16)$$

Using this correction to Enskog theory, Easteal, Woolf, and Jolly found that D for methane obtained from experiment was in excellent agreement with the smooth hard-sphere predictions over the whole density range, as shown in Figure 6.

The core sizes are given by the following equation, with rounded values for the coefficients,

$$\sigma/\text{nm} = 0.397\,95 - 2.765 \times 10^{-4} T/\text{K} + 3.420 \times 10^{-7} (T/\text{K})^2 \qquad (17)$$

These values are lower than those in Table 3, but they agree to better than 1% with values obtained from the density of methane at the freezing point using the expression for randomly close-packed hard-spheres.[35]

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[34] B. L. Holian and co-workers cited by W. G. Hoover and W. T. Ashurst in 'Theoretical Chemistry', ed. H. Eyring and D. Henderson, Academic Press, New York, 1975, Vol. 1, p. 24.

[35] R. O. Watts and I. J. McGee, 'Liquid State Chemical Physics', Wiley, New York, 1976, 162.

$$\sigma/\mathrm{nm} = 0.1161\,1\,(V/\mathrm{cm}^3\,\mathrm{mol}^{-1})^{\frac{1}{3}} \qquad (18)$$

The smooth hard-sphere model has been used[36] as a basis for the calculation of rare-gas self-diffusion coefficients. Core sizes were derived from densities at the freezing pressure and adjusted at temperatures close to the triple point, as described in Section 6 on viscosity. The calculated values generally agree with the experimental results to within the large experimental uncertainty of the measurements and in fact provide a more reliable estimate of this property for these substances.

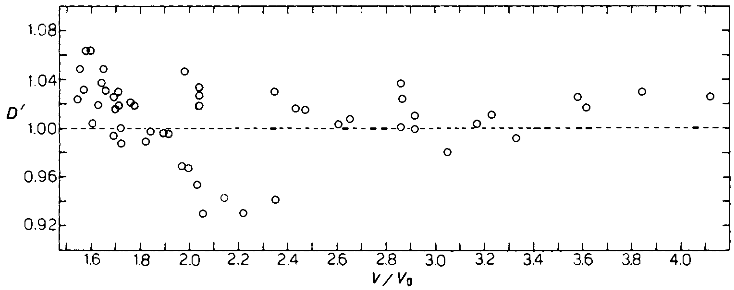

Figure 6 *Comparison of reduced experimental and computed diffusion coefficients for methane. $D' = D\,(calc)/D\,(exp)$*
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B. Liquid Metals.—The applicability of the smooth hard-sphere theory for describing the self-diffusion coefficients of liquid metals was investigated by Protopapas, Andersen, and Parlee.[37] These authors used the correction factors of Alder, Gass, and Wainwright.[11] The core size at the melting point was obtained[38] on the assumption that the packing fraction at the melting point, ξ_m, equal to $\pi n\sigma^3/6$, has the same value of 0.472 for all metals. The temperature dependence of the core diameter was derived from consideration of the average distances of closest approach for repulsive collisions of real molecules. This leads to the expression[38]

$$\sigma/\sigma_m = [1\text{-}B(T/T_m)^{\frac{1}{2}}]/(1\text{-}B) \qquad (19)$$

where subscript m refers to the melting point and B is a constant with a value of 0.112 for all metals.

The predicted self-diffusion coefficients are in close agreement with the measured values as shown in Table 2 for values at the melting point for 13 metals.

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[36] A. J. Easteal and L. A. Woolf, *Physica*, 1984, 124B, 182.

[37] P. Protopapas, H. C. Andersen, and N. A. D. Parlee, *J. Chem. Phys.*, 1973, **59**, 15.

[38] P. Protopapas and N. A. D. Parlee, *High Temp. Sci.*, 1974, **6**, 1.

Table 2 *Comparison of experimental melting point self-diffusion coefficients with the predictions of the hard-sphere theory**

Metal	*Experimental* $D/10^{-9}$ m^2 s^{-1}	*Calculated*
Li	7.00	7.01
Na	4.22	4.24
K	3.82	3.85
Cu	3.96	3.40
Rb	2.62	2.68
Ag	2.55	2.77
Zn	2.05	2.55
Cd	1.78	2.00
Hg	1.17	1.07
Ga	1.72	1.73
In	1.74	1.77
Sn	2.05	1.96
Pb	1.68	1.67

* *Ref.* 37.

The hard-sphere theory also satisfactorily reproduces the temperature dependence of the self-diffusion coefficient as illustrated for liquid sodium in Figure 7, which is based on Figure 3 of *ref.* 37.

4 Rough Hard-sphere Model for Polyatomic Fluids

The motion of a polyatomic molecule in a real liquid has been shown by Chandler[41] to be related to the motion of a particle in a rough hard-sphere fluid. It is assumed that the motion is determined primarily by those parts of the intermolecular potential that are short-ranged and steeply repulsive. This is considered valid at densities above twice the critical density where attractive interactions will play only a minor role. For polyatomic molecules there is the possibility of changes in angular momentum as well as in translational momentum upon collision and Chandler[42] showed that coupling between translational and rotational motions led to the result that the diffusion coefficient for a rough hard-sphere fluid D_{RHS} was related to that for a smooth hard-sphere fluid D_{SHS}:

$$D \approx D_{\mathrm{RHS}} \approx AD_{\mathrm{SHS}} \tag{20}$$

where $0 < A \leqslant 1$.

A was stated to be rigorously independent of density and furthermore assumed to be temperature independent also. There is thus a lowering of the self-diffusion

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[39] R. H. Meyer and N. H. Nachtrieb, *J. Chem. Phys.*, 1955, **23**, 1851.

[40] O. S. Ozelton and R. A. Swalin, *Phil. Mag.*, 1958, **18**, 441.

[41] D. Chandler, *J. Chem. Phys.*, 1974, **60**, 3500.

[42] D. Chandler, *J. Chem. Phys.*, 1975, **62**, 1358.

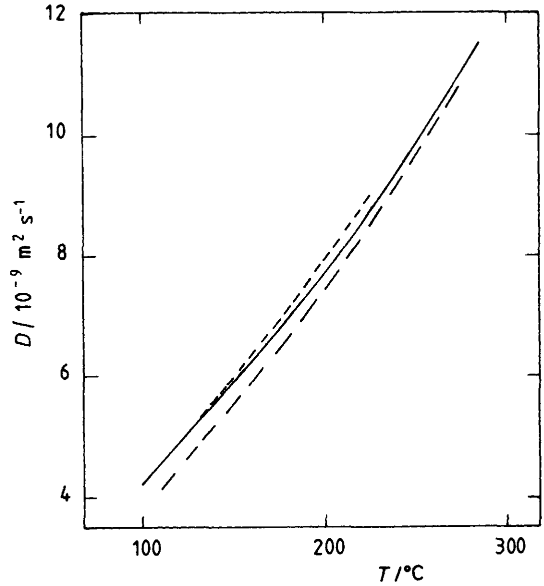

Figure 7 *Comparison of experimental self-diffusion coefficients for sodium with calculated hard-sphere values (solid line). Experimental:* – – –, ref. 39; —— ——, ref. 40

coefficient as coupling produces an additional mechanism for molecular velocity relaxation.

The initial application of this rough hard-sphere theory was to carbon tetrachloride data.[42] The temperature-dependent core size was determined by matching along isotherms the logarithmic derivative of the experimental diffusion coefficient with respect to density with that predicted by the theory. For ease of application, D_E calculated using the Alder, Gass, and Wainwright correction to Enskog[11] was represented by an analytical expression quadratic in reduced density $n\sigma^3$. A satisfactory fit to the high pressure measurements of McCool and Woolf[43] at different temperatures was given with a constant value of A of 0.54 and with core sizes given by:

$$\sigma/\text{nm} = 0.5270[1 - 0.057(T/\text{K} - 283.2/283.2)] \tag{21}$$

Since then accurate measurements of self-diffusion coefficients have been made for several polyatomic fluids by the n.m.r. spin echo technique and the data interpreted in terms of the rough hard-sphere model. In place of the smooth hard-sphere diffusion coefficient expression of Chandler,[42] the simpler relationship given

[43] M. A. McCool and L. A. Woolf, *J. Chem. Soc., Faraday Trans. 1*, 1972, **68**, 1971.

earlier by Dymond[44] has been generally used. Some of the results are collected in Table 3.

Table 3 *Translational–rotational coupling factors, A, for diffusion*

Compound	*T range*/K	*σ range*/nm	*A*	*Ref.*
Methane	110—198	0.372—0.346	1.0	33
Carbon tetrafluoride	235—348	0.451—0.439	1.0	45
Trifluoromethane	168—250	0.398—0.378	0.61 ± 0.04	46
Fluorotrichloromethane	341—460	0.503—0.490	0.64 ± 0.01	47
Chlorotrifluoromethane	303—348	0.460—0.456	0.90 ± 0.02	48
Carbon tetrachloride	283—328	0.527—0.522	0.54	42
Tetramethylsilane	298—373	0.568—0.563	0.59 ± 0.03	49
Benzene	303—433	0.512—0.505	0.77 ± 0.05	49
Perfluorocyclobutane	323—473	0.565—0.554	0.92 ± 0.06	50
Sulphur hexafluoride	240—319	0.487	1.0	45
Sulphur hexafluoride	296—398	0.478—0.472	0.97	51
Cyclohexane	313—383	0.554—0.551	0.78 ± 0.07	52
Methylcyclohexane	203—298	0.578—0.574	0.26—0.52	53
Pyridine	303—423	0.494—0.490	0.62—1.05	54

For the substituted methanes, the extent of translational–rotational coupling is in the order

$$CCl_4 > CHF_3 > CFCl_3 > CF_3Cl > CF_4$$

as might generally be expected from consideration of molecular interlocking which is most evident with carbon tetrachloride and decreases as the chlorine is replaced by fluorine atoms. The coupling factor of trifluoromethane is however difficult to explain since both methane and tetrafluoromethane behave as smooth hard-sphere molecules. For the compounds in Table 3, the factor A is generally temperature independent. However, for trifluoromethane at 142 K, A is found to be 0.38, significantly lower than the value found at higher temperatures. This was attributed to either increased translational–rotational coupling in this dipolar fluid (1.62 *D*) or to the effect of attractive interactions. The temperature variation of A for methylcyclohexane can be explained in terms of the increased departure from spherical shape of the molecules on going from cyclohexane, for which the model

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[44] J. H. Dymond, *J. Chem. Phys.*, 1974, **60**, 969.
[45] J. H. Dymond, *J. Chem. Soc., Faraday Trans. 2*, 1972, **68**, 1789.
[46] F. X. Prielmeier, E. W. Lang, and H.-D. Ludemann, *Mol. Phys.*, 1984, **52**, 1105.
[47] J. DeZwaan and J. Jonas, *J. Chem. Phys.*, 1975, **62**, 4036.
[48] K. R. Harris, *Physica*, 1978, **93A**, 593.
[49] H. J. Parkhurst, Jr. and J. Jonas, *J. Chem. Phys.*, 1975, **63**, 2698.
[50] R. J. Finney, M. Fury, and J. Jonas, *J. Chem. Phys.*, 1977, **66**, 760.
[51] J. DeZwaan and J. Jonas, *J. Chem. Phys.*, 1975, **63**, 4606.
[52] J. Jonas, D. Hasha, and S. G. Huang, *J. Phys. Chem.*, 1980, **84**, 109.
[53] J. Jonas, D. Hasha, and S. G. Huang, *J. Chem. Phys.*, 1979, **71**, 3996.
[54] M. Fury, G. Munie, and J. Jonas, *J. Chem. Phys.*, 1979, **70**, 1260.

works remarkably well, to methylcyclohexane. The results for pyridine can be compared with those for benzene for these molecules have nearly identical shapes and moments of inertia. However, pyridine has a significant dipole moment (2.2 *D*) and the molecules can hydrogen-bond. The effect of these intermolecular interactions will decrease as the temperature is raised, and this is reflected in the increase in A values. At high temperature, A attains the smooth hard-sphere value of 1, which is unexpected by comparison with benzene which has an A value of 0.82.

The predicted density dependence of D for the compounds in Table 3 is in very close agreement with experimental measurements except at high densities corresponding to $V_0/V > 0.66$ where the experimental values are higher than predicted. The failure of the rough hard-sphere theory in this region arises from the fact that the smooth hard-sphere system becomes metastable at these densities.

More recently, Easteal and Woolf[36] have used their values for the corrections to Enskog theory (Figure 5) to determine the dependence of A on density and temperature. The core sizes were determined from molar volumes at the freezing pressure. They found that for carbon tetrachloride, using the data of McCool and Woolf,[43] the factor A is temperature independent, as found by Chandler,[42] but density dependent. This is illustrated in Figure 8. This result is at variance with the postulate of Chandler that A should be rigorously density independent.

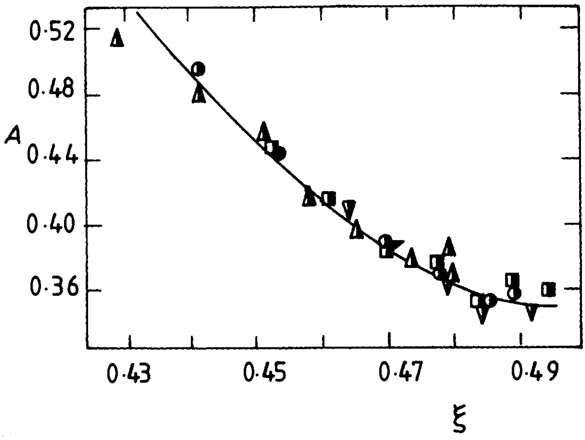

Figure 8 *Density dependence of A for carbon tetrachloride.* ▼, 283.2 K: ◨, 298.2 K: ◑, 313.2 K: ▲, 328.2 K
(Reproduced by permission from *Physica*, 1984, **124B**, 187)

Strong density dependence is also observed[36] for 1,2-dichloroethane, mesitylene, and octamethylcyclotetrasiloxane. For benzene, A is strongly temperature dependent as well as density dependent. However, for carbon disulphide, where the departure from spherical shape is predicted[42] to render the rough hard-sphere model invalid, it is found that the experimental self-diffusion coefficients are in close agreement with values predicted on the basis of this model with a density independent and temperature independent A factor of 0.765 ± 0.02. For the similarly shaped but dipolar acetonitrile, A is temperature dependent, decreasing as the temperature is lowered, but still density independent. A similar result is found for deuteromethanol, where the temperature dependence is significantly greater.

For those molecules where A is found to have a strong density dependence, it might be concluded that the model is invalid. However, another possibility is that the core sizes for transport properties at these low reduced temperatures are not given by equation 18 (see Section 6B). A small variation in the core size leads to a significant change in the density dependence of the calculated diffusion coefficient at high densities. Further studies are required to produce an agreed set of core sizes for these molecules.

5 Diffusion Coefficients in Binary Mixtures

A. Mutual Diffusion Coefficients.—The mutual diffusion coefficient, $(D_{12})_E$, for a binary dense smooth hard-sphere mixture can be calculated by an extension of the Enskog method used for self-diffusion coefficients of dense fluids. At high density, $(D_{12})_E$ is related to the low density coefficient by the unlike pair distribution function at contact $g_{12}(\sigma)$:

$$\frac{(n_1 + n_2)(D_{12})_E}{(n_1 + n_2)_0(D_{12})_0} = \frac{1}{g_{12}(\sigma)} \tag{22}$$

where n_1 and n_2 are the number densities of the particles of molecular masses m_1 and m_2 and with molecular diameters σ_1 and σ_2. The low density mutual diffusion coefficient is given by the expression[55]

$$(D_{12})_0 = [\tfrac{3}{2}(n_1 + n_2)_0(\sigma_1 + \sigma_2)^2][kT(m_1 + m_2)/2\pi m_1 m_2]^{\frac{1}{2}} \tag{23}$$

The initial application of these expressions was to trace gas diffusion in dense gases,[56] using core sizes determined from pVT data and $g_{12}(\sigma)$ values from the approximate expression given by Lebowitz.[57] The qualitative features of the results were that (i) when the trace gas had the higher molecular mass the measured diffusion coefficient was significantly higher than the calculated value but that (ii) when the trace gas had the lower molecular mass the diffusion coefficient was less than predicted. The features were understandable in terms of the correlated events previously described for pure systems, which are neglected in the Enskog theory. The positive deviations arising from a vortex flow pattern are expected to be enhanced by a more massive diffusing particle because of its larger momentum relative to that of the solvent molecule. On the other hand, for a lighter trace gas particle there is an increased probability of back-scattering. These effects were

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[55] S. Chapman and T. G. Cowling, 'The Mathematical Theory of non-uniform Gases', Cambridge University Press, Cambridge, 1970.

[56] J. H. Dymond and B. J. Alder, *J. Chem. Phys.*, 1970, **52**, 923.

[57] J. L. Lebowitz, *Phys. Rev. A*, 1964, **895**, 133.

investigated quantitatively[58,59] by computer simulation studies for systems of a single test particle in a solvent for selected size and mass ratios to give values of the correction factor $(D_{12})_{SHS}/(D_{12})_E$. The exact smooth hard-sphere diffusion coefficient $(D_{12})_{SHS}$ is then given by

$$(D_{12})_{SHS} = \frac{(n_1 + n_2)_0}{(n_1 + n_2)} \frac{(D_{12})_0}{g_{12}(\sigma)} \frac{(D_{12})_{SHS}}{(D_{12})_E} \tag{24}$$

Instead of previous approximate estimates,[57] $g_{12}(\sigma)$ was given by[60]

$$g_{12}(\sigma) = [\sigma_1 g_{22}(\sigma) + \sigma_2 g_{11}(\sigma)]/(\sigma_1 + \sigma_2) \tag{25}$$

where $g_{ii}(\sigma)$ is given by

$$g_{ii}(\sigma) = \frac{1}{1 - \xi} + \frac{3y_i}{2(1 - \xi)^2} + \frac{y_i^2}{2(1 - \xi)^3} \tag{26}$$

where ξ equals $\sum\limits_i n_i\pi\sigma_i^3/6$ and $y_i = (\sigma_i\xi_j + \sigma_j\xi_i)/\sigma_j$.

For application to systems involving polyatomic fluids, effects of translational–rotational coupling are included by expressing the rough hard-sphere mutual diffusion coefficient $(D_{12})_{RHS}$ in terms of the smooth hard-sphere coefficient[61]

$$(D_{12})_{RHS} = A_{12}(D_{12})_{SHS} \tag{27}$$

where A_{12} is the coupling factor between the unlike molecules. For nearly ideal binary liquid mixtures, it was shown by Bertucci and Flygare[61] that the calculated mutual diffusion coefficient was in excellent agreement with experiment over the whole composition range. However, the calculations were based on the assumption that the mass and size ratios were exactly equal to one and the value of $(D_{12})_{SHS}/(D_{12})_E$ obtained for trace amounts of solute was used at all concentrations. To account more precisely for the actual molecular size and mass ratios, Czworniak, Andersen, and Pecora[62] assumed that, in the absence of molecular dynamics calculations at intermediate concentrations, the correction factor in mixtures with mole fraction x_1 of component 1 was given by

$$[(D_{12})_{SHS}/(D_{12})_E] \approx x_1[(D_{12})_{SHS}/(D_{12})_E]_{x_2 \to 0} + x_2[(D_{12})_{SHS}/(D_{12})_E]_{x_1 \to 0}$$

Core sizes for the pure components were derived from self-diffusion coefficient data. They applied this theory to their results obtained from laser light scattering and concluded that the rough hard-sphere theory was accurate for both spherical and

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[58] P. T. Herman and B. J. Alder, *J. Chem. Phys.*, 1972, **56**, 987.

[59] B. J. Alder, W. E. Alley, and J. H. Dymond, *J. Chem. Phys.*, 1974, **61**, 1415.

[60] N. F. Carnahan and K. E. Starling, 'Abstracts of Invited Lectures for the van der Waals Centennial Conference on Statistical Mechanics', North-Holland Publ. Co., Amsterdam, 1973.

[61] S. J. Bertucci and W. H. Flygare, *J. Chem. Phys.*, 1975, **63**, 1.

[62] K. J. Czworniak, H. C. Andersen, and R. Pecora, *Chem. Phys.*, 1975, **11**, 451.

very non-spherical molecules in ideal and moderately ideal solutions. Non-ideality was taken into account by using the relationship

$$D = D_{12}[1 + (\partial \ln y_1/\partial \ln x_1)_{T,P}] \tag{29}$$

where y_1 is the activity coefficient of component 1. D_{12} was determined at any concentration by dividing the experimental mutual diffusion coefficient at that concentration by the thermodynamic factor, for comparison with the calculated $(D_{12})_{SHS}$. Values obtained for A_{12}, assumed to be dependent only on the nature of the components and not on their proportions in the solutions, were in the range 0.5 to 0.65 for C_6H_{12}–$C_6H_5CH_3$, C_6H_6–$C_6H_5CH_3$, C_6H_{12}–CCl_4, C_6H_6–C_6H_{12}, CCl_4–C_6H_6, CCl_4–CS_2, CCl_4–CH_3COCH_3, C_6H_6–CH_3COCH_3 with a value of 0.89 for C_6H_6–n-C_7H_{16}.

In order to provide a more rigorous test of this theory, Dymond and Woolf[63] measured tracer diffusion coefficients for five different solutes in n-hexane at 298 K at pressures up to 400 MPa. These limiting intradiffusion coefficients are theoretically identical to mutual diffusion coefficients at low solute concentration. A comparison with rough hard-sphere values showed remarkable agreement and it was found that the assumption that A_{12} was equal to A for the pure solvent was valid for benzene, toluene, and even carbon disulphide tracers but that for acetonitrile tracer A_{12} was approximately 20% lower than A. For the exact determination of A_{12}, it is essential that values for the correction factor $(D_{12})_{SHS}/(D_{12})_E$ should be obtained at closely spaced mass ratios and size ratios to overcome the errors involved in interpolating the limited computer results. Protapapas and Parlee[64] showed that the results of Alder, Alley, and Dymond[59] could be interpolated quite accurately on the basis of a semilogarithmic plot. Using these correction factors, diffusion coefficients calculated on the basis of the smooth hard-sphere theory for gases diffusing in liquid metals were found to be in good agreement with experiment where the latter were self-consistent. In order to remove this uncertainty of interpolation, Dymond, Easteal, and Woolf[65] have recently studied tracer diffusion of seven solutes in octamethylcyclotetrasiloxane at 323 K at

Table 4 *Core sizes and A_{12} values with OMCTS at* 323 K

		A_{12}		
Tracer	σ/nm	V/V_0 1.607	1.565	1.503
CH_3OH	0.363	0.31	0.27	0.26
CH_3CN	0.410	0.29	0.29	0.28
C_2H_5OH	0.422	0.24	0.21	0.16
CS_2	0.428	0.32	0.30	0.23
CCl_4	0.516	0.26	0.21	0.16
c-C_6H_{12}	0.546	0.23	0.22	0.16
c-C_8H_{16}	0.586	0.22	—	—

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[63] J. H. Dymond and L. A. Woolf, *J. Chem. Soc., Faraday Trans 1*, 1982, **78**, 991.

[64] P. Protapapas and N. A. D. Parlee, *High Temp. Sci.*, 1976, **8**, 141.

[65] J. H. Dymond, A. J. Easteal, and L. A. Woolf, *Chem. Phys.*, submitted.

pressures up to 59 MPa and reported values for the correction factor for the actual size and mass ratios for the individual systems. The derived values for the translational–rotational coupling factors A_{12}, together with the core sizes, are given in Table 4. All the A_{12} values are small, implying considerable rotational–translational momentum transfer between solute and solvent. For the more spherical solute molecules, A_{12} is density dependent.

These results for A_{12} are significantly different from the values obtained for other non-electrolyte systems from measurements of mutual diffusion coefficients. Several studies have been made[66,67,69–74] on different systems using the chromatographic peak-broadening method at atmospheric pressure over a wide range of temperature. The data were in close agreement with the calculated rough hard-sphere values for all the systems studied,[66–73] which included as solutes, rare gases, methane, neopentane, carbon tetrachloride, tetra-alkyl tins (where the alkyl group was methyl, ethyl, n-propyl, n-butyl, or n-decyl) and a variety of solvents including benzene, cyclohexane, n-hexane, n-octane, n-decane, n-tetradecane, acetone, methanol, propan-2-ol, butan-1-ol, and octan-1-ol. The solute core size was determined from the tracer diffusion in one solvent at a given temperature (298 K). A stricter test with measurements for aromatic hydrocarbons in cyclohexane up to its critical temperature concluded[71] that the rough hard-sphere theory was adequate over the whole of this temperature range.

Evans, Tominaga, and Davis[67] considered A_{12} to have different but fixed values for each of the three classes of systems (i) monatomic solute and solvent species for which A_{12} is 1, (ii) monatomic solute and polyatomic solvent species for which A_{12} should be unity, but was found to be 0.78 for an optimum fit of mutual diffusion coefficient data, and (iii) polyatomic solute and solvent species for which they derived a value of 0.7 for A_{12}. These A_{12} values cover the calculated range of molecular roughness with the lower value of 0.7 corresponding to uniform mass distribution throughout the molecule.[74] However, the correction factors were obtained by interpolation of the limited computer results together with some additional simulation values which appear to have a large uncertainty. Furthermore, the core sizes for monatomics were determined from self-diffusion data at temperatures far below the temperature of the actual mutual diffusion measurements, so the A_{12} value should not be taken as exact.

Tracer diffusivity results for small crown ethers in cyclohexane[72] have also been satisfactorily interpreted in terms of the rough hard-sphere theory. The authors suggest that the disk-like shape of the ethers is averaged out by rapid molecular rotation. For larger crown ethers diffusing in n-decane and n-tetradecane, the theory has limited success.[73]

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[66] J. H. Dymond, *J. Phys. Chem.*, 1981, **85**, 3291.

[67] D. F. Evans, T. Tominaga, and H. T. Davis, *J. Chem. Phys.*, 1981, **74**, 1298.

[68] S. H. Chen, H. T. Davis, and D. F. Evans, *J. Chem. Phys.*, 1981, **75**, 1422.

[69] S. H. Chen, H. T. Davis, and D. F. Evans, *J. Chem. Phys.*, 1982, **77**, 2540.

[70] S. H. Chen, D. F. Evans, and H. T. Davis, *AIChE J*, 1983, **29**, 640.

[71] C. K. J. Sun and S. H. Chen, *AIChE J*, in press.

[72] H. C. Chen and S. H. Chen, *Chem. Eng. Sci.*, in press.

[73] H. C. Chen and S. H. Chen, *Ind. Eng. Chem., Fundam.*, in press.

[74] M. Baleiko and H. T. Davis, *J. Phys. Chem.*, 1974, **78**, 1564.

B. Inter- and Intra-diffusion Coefficients away from the Zero Concentration Limit.— The advantage of the rough hard-sphere theory is that it can be applied to intra-(tracer) diffusion and inter-(mutual) diffusion in binary fluid mixtures over the whole composition range. Harris and Woolf[75] calculated tracer diffusion coefficients for each component in five binary liquid mixtures, based on the equation of Sandler and Mason[76]

$$1/(D_i)_j = x_i/D_{ii} + x_j/D_{ij}\,(i,j = 1,2) \qquad (30)$$

It was found generally that the values of the coupling factor obtained by comparison of the calculated tracer diffusion coefficient with the measured coefficient for each of the two components were in close agreement over nearly all the composition range. Furthermore, these values agreed reasonably well with the A_{12} values obtained from limiting diffusion studies in these systems. However, the expression used for $g_{12}(\sigma)$ was incorrect, and the correction factors used to calculate the hard-sphere results were given by the equation of Czworniak, Andersen, and Pecora[62] and based on the assumption that the correction factor for mutual diffusion was a linear function of composition.

For an accurate calculation of all the diffusion coefficients in a binary mixture, computer simulation results are required for the corrections to the Enskog expressions at different compositions. Easteal and Woolf[77] have recently investigated the effects of differing mass ratios (range 1—10) and core size ratios

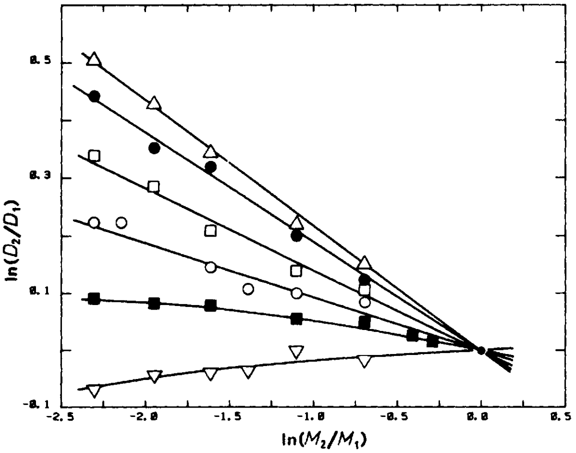

Figure 9 *The mass dependence of the intradiffusion ratio for an equimolar hard-sphere mixture at various reduced volumes, V/V_0.* ▽, 1.5; ■, 1.6; ○, 1.8; □, 2.5; ●, 3.0; △, 4.0 (Reproduced by permission from *Chem. Phys.*, 1984, **88**, 105)

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[75] L. A. Woolf and K. R. Harris, *Chem. Phys.*, 1978, **32**, 349.

[76] S. I. Sandler and E. A. Mason, *J. Chem. Phys.*, 1968, **48**, 2873.

[77] A. J. Easteal and L. A. Woolf, *Chem. Phys.*, 1984, **88**, 101; corrigenda (in press).

(range 1—4) in a V/V_0 range from 1.5 to 4 on the diffusion coefficients in an equimolar mixture. The ratio of the correct smooth hard-sphere intradiffusion coefficient to the Enskog coefficient for component 2 to that for component 1 [denoted by $(D_2/D_1)_c$] is given in Figure 9 for an equimolar mixture with $\sigma_1 = \sigma_2$ to illustrate the mass dependence.

Values at selected reduced volumes are presented in Table 5. The results show that differing size ratios are more important than differing mass ratios.

Table 5 *Predicted intradiffusion ratios in an equimolar mixture*

	$\frac{(D_2)_1/(D_{12})_E}{(D_1)_2/(D_{12})_E}$	
V/V_0	(*a*)	(*b*)
1.5	0.986	3.10
1.6	1.034	2.83
1.7	1.060	2.62
1.8	1.068	2.46
2.0	1.101	2.26
2.5	1.134	2.10
3.0	1.150	2.02

[a] $\sigma_1 = \sigma_2$, $m_1 = 0.5m_2$. [b] $\sigma_1 = 0.5\sigma_2$, $m_1 = m_2$

Attempts to obtain $(D_{12})_{SHS}/(D_{12})_E$ for calculation of interdiffusion coefficients in the equimolar mixture were unsuccessful. It was proposed that for mixtures with a small departure from ideality this correction factor could be taken as the mean of the factors for the intradiffusion coefficients. A comparison of $(D_{12})_{SHS}/(D_{12})_E$ with values predicted by the Czworniak, Andersen, and Pecora equation[62] showed reasonable agreement at $V/V_0 = 1.6$, but successively poorer agreement at $V/V_0 = 1.7$ and 1.5. This reinforces the need for accurate computer studies on different mixtures.

Measured inter-diffusion and intra-diffusion coefficients for 11 binary liquid mixtures were analysed and values calculated for $(A_1)_2$ and $(A_2)_1$. For mixtures where there was no strong specific interaction, there was a good correlation between A_R, the ratio of A_{12} to the mean of $(A_1)_2$ and $(A_2)_1$, and the thermodynamic factor $(\partial \ln a_1/\partial \ln x_1)_{T,P}$, though these were not identical (see corrigenda, *ref.* 77). The ratio of $(D_2/D_1)_c$ from the simulations agreed with the measured ratio of the intra-diffusion coefficients within the combined uncertainties of calculation and experiment, except for mixtures containing an associated component.

6 Viscosity Coefficients

A. Monatomic Fluids at Supercritical Temperatures.—Analysis of dense gas viscosity coefficient data on the basis of the smooth hard-sphere model can be carried out in an analogous manner to the analysis of diffusion coefficient data described in Section 3. A quantity η^* is defined by

$$\eta^* = (\eta/\eta_E)(\eta_E/n_0)(V/V_0)^{\frac{2}{3}} \tag{31}$$

where η_E is the Enskog dense gas value, (η/η_E) is the computed correction[11] to Enskog theory, and (η_E/η_0) is given by equation 9.

Values of η^* can be obtained from experimental data by substitution of the hard-sphere expressions to give

$$\eta^* = 6.035 \times 10^8\, \eta V^{\frac{2}{3}}/(MRT)^{\frac{1}{2}} \tag{32}$$

The range of applicability of this model is tested by superimposing curves of η^* *versus* log (V/V_0) from theory, equation 31, and η^* *versus* log V from experiment, equation 32. Using extensive measurements at above critical densities for neon,[78] argon,[78–81] krypton,[80,82] and xenon,[80] it was shown[27] that the density depend-

Table 6 *Comparison of calculated smooth hard-sphere viscosity coefficients with experiment*

Argon at 308 K				*Krypton at* 323 K			
	Viscosity/mPa s				*Viscosity*/mPa s		
P/bar	*Calc.*	*Expt.*		*P*/bar	*Calc.*	*Expt.*	
6 060	31.05	31.37	(*ref.* 84)	6 540	57.92	57.40	(*ref.* 83)
5 835	29.94	30.08		6 020	53.08	53.10	
5 540	28.50	28.68		5 560	49.06	49.35	
5 290	27.35	27.50		5 000	44.28	44.95	
5 055	26.20	26.38		4 560	40.70	41.70	
4 800	24.97	25.13		4 030	36.52	37.30	
4 590	24.01	24.15		3 540	32.72	33.32	
4 100	21.72	21.83		2 930	28.11	28.75	
3 540	19.14	19.20		2 480	24.74	25.20	
3 020	16.84	16.73		2 005	21.16	21.50	
2 500	14.51	14.34		1 755	19.27	19.37	
2 355	13.87	13.66					
1 990	12.20	11.88					
1 755	11.08	10.86		2 079	21.71	22.10	(*ref.* 82)
1 403	9.39	9.22		1 347	16.07	16.33	
1 060	7.73	7.62		881.7	12.12	12.41	
994.0	7.38	7.30		603.0	9.44	9.79	
883.5	6.82	6.76		415.8	7.36	7.63	
726.5	5.99	5.99		308.3	6.03	6.19	
625.5	5.44	5.45		244.7	5.21	5.26	
496.0	4.69	4.74		193.0	4.59	4.47	
389.5	4.13	4.13					
302.0	3.67	3.62					

[78] N. J. Trappeniers, A. Botzen, H. R. Van Den Berg, and J. Van Oosten, *Physica*, 1964, **30**, 985.
[79] A. Michels, A. Botzen, and W. Schuurman, *Physica*, 1954, **20**, 1141.
[80] E. G. Reynes and G. Thodos, *Physica*, 1964, **30**, 1529.
[81] J. A. Gracki, G. P. Flynn, and J. Ross, *J. Chem. Phys.*, 1969, **51**, 3856.
[82] N. J. Trappeniers, A. Botzen, J. Van Oosten, and H. R. Van Den Berg, *Physica*, 1965, **31**, 945.

ence of the data at above critical temperatures was very satisfactorily represented by the hard-sphere theory at densities from above twice the critical density down to about 1.2-times the critical density. Since then accurate experimental measurements have been made for krypton at 323 K[83] and for argon at 308 K[84,85] at pressures up to 6 000 atm, where the density approaches the point of solidification. These provide a much more critical test of the theory. The density dependence of these measurements, together with the earlier data, is compared with that given by the hard-sphere theory in Figure 10. Although the computed corrections to Enskog theory are less well known than the corresponding corrections to the diffusion coefficient, nevertheless it can be concluded that the smooth hard-sphere theory gives a very satisfactory fit to the viscosity coefficient data at densities down to 1.2-times the critical density. This corresponds, in the case of krypton data at 323 K, to a pressure range from 6 500 atm down to 250 atm in which the viscosity coefficient changes by a factor of eleven. For argon at 308 K, the data are closely fitted by the theory from a pressure of 6 000 atm down to 300 atm, with a factor of nine variation in the viscosity. A comparison with the calculated values is given in Table 6 and the

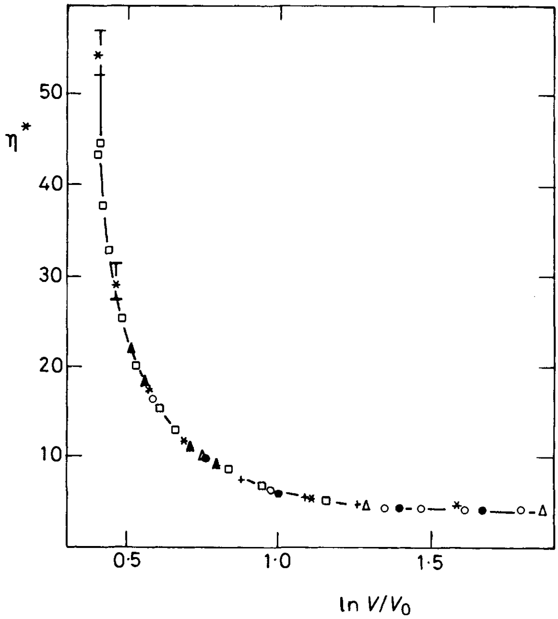

Figure 10 *Variation of* η^* *(equation* 32) *with logarithm of reduced volume. Values given by the hard-sphere theory are denoted by* * *with error bars. Experimental data for argon* ○, ref. 79; ●, ref. 84; □, ref. 85; +, ref. 93: *for krypton* ▲, ref. 83; △, ref. 82. *Solid line is given by equation* 34

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[83] J. Vermesse, M. Provansal, and J. Brielles, *Physica*, 1978, **92A**, 282.

[84] J. Vermesse and D. Vidal, *C.R. Hebd. Seances Acad. Sci. Ser. B.*, 1973, **277**, 191.

[85] N. J. Trappeniers, P. S. Van Der Gulick, and H. Van Den Hoof, *Chem. Phys. Lett.*, 1980, **70**, 438.

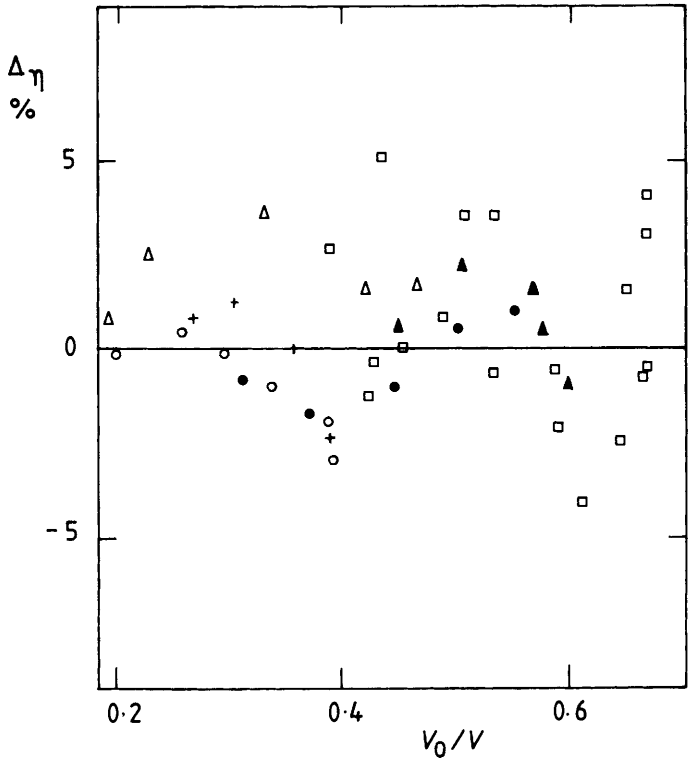

Figure 11 *Percentage deviation of experimental viscosity data from values calculated on the basis of hard-sphere theory for argon at* 308 K *and krypton at* 323 K. *Key as for Figure* 10

deviations shown in Figure 11, as a function of reduced density, demonstrate that the fit is generally better than the uncertainties in the measured viscosity coefficients. Values obtained for the core sizes are summarized in Table 7.

Table 7 *Molecular core sizes* (nm) *for the rare gases*

T/K	173	223	298	323	348
Argon	0.334	0.328	0.320	0.318	0.316
Krypton				0.344	

The core sizes have an estimated uncertainty of less than 0.5%. The values for argon are higher than those given earlier[27] which had a greater uncertainty because the viscosity data did not at that time extend to the high densities necessary to define the diameter closely. These core sizes for argon can be expressed in the form

$$\sigma = \sigma_0[1 - B(T - T_0)/T_0] \qquad (33)$$

where σ_0 is the hard-sphere diameter at reference temperature T_0. For a reference temperature of 300 K, the value of B for argon is 0.080. These core sizes can be compared with diameters obtained by application of the hard-sphere theory to gas solubilities,[86] which correspond to temperatures approximately equal to the well-depth of the pair potential.

In view of the uncertainties in the computed corrections to Enskog theory, the results given by the rare-gas data at densities greater than 1.2-times the critical density can be considered as the exact hard-sphere results.

The solid line in Figure 10 can be expressed by the equation

$$1/\eta^* = \sum_{i=0} a_i(V_0/V)^i \qquad (34)$$

with the values for the coefficients a_i given in Table 8.

From this, the corrections to Enskog theory are given by the equation.

$$(\eta_E/\eta) = \sum_{j=0} a_j(V_0/V)^i \qquad (35)$$

with coefficients a_j listed in Table 8.

An alternative approach,[87] based on liquid viscosity coefficient data, compared data for methane[88] with values calculated using the Enskog expression with core diameters determined from the expression (equation 18) for randomly close-packed hard-spheres at the freezing point

$$\sigma/\mathrm{nm} = 0.116\,11\ (V/\mathrm{cm}^3\ \mathrm{mol}^{-1})^{\frac{1}{3}} \qquad (18)$$

where V is the molar volume at the freezing pressure obtained from the density data of Cheng, Daniels, and Crawford.[89] This gave the correction to Enskog theory η/η_E as a polynomial in V/V_0 with coefficients listed in Table 8. (The coefficients have been rounded off here to the appropriate number of significant figures.)

Table 8 *Coefficients of the equations for* η^* *and* (η/η_E)

	a_0	a_1	a_2	a_3	a_4	a_5	a_6
$1/\eta^*$	0.044 55	2.1789	−5.9822	−6.421	40.258	−51.208	21.39
(η_E/η) (this work)	0.975	1.86	−17.56	94.9	−269.13	363.2	−189.51
(η/η_E) (*ref.* 87)	5.023	−46.748	205.41	−432.18	430.62	−155.98	

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[86] E. Wilhelm and R. Battino, *J. Chem. Phys.*, 1971, **55**, 4012.

[87] A. J. Easteal and L. A. Woolf, *Physica*, 1984, **124B**, 173.

[88] D. E. Diller, *Physica*, 1980, **104A**, 417.

[89] V. M. Cheng, W. B. Daniels, and R. K. Crawford, *Phys. Rev.*, 1975, **B11**, 3972.

The results obtained from liquid methane data are compared with the correction factors calculated from rare-gas data and with the computed corrections to Enskog theory in Figure 12. The hard-sphere values[90] are a combined result of extrapolations of computations for a square-well system and interpolations of the earlier results[11] for a 108 hard-sphere system. The uncertainty is estimated to be between 5% and 7%.

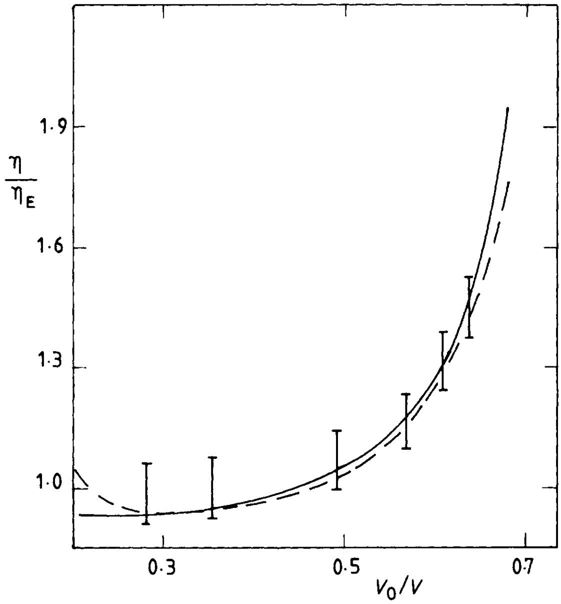

Figure 12 *Density dependence of* η/η_E. *Vertical lines with error bars, hard-sphere theory,* ref. 90; – – – *from liquid methane data,* ref. 87; —— *from rare-gas data, this work*

This close agreement supports the conclusion of previous studies[91,92] that methane behaves as a smooth hard-sphere fluid with regard to transport properties, and provides a reliable estimate of the corrections to Enskog theory. Furthermore, it illustrates that the hard-sphere theory can be satisfactorily applied to fluids at temperatures below the critical temperature where non-uniformities in the attractive potential energy surface for real fluids have been shown in computer simulation studies to have only a small effect on the molecular trajectories.

B. Monatomics at Subcritical Temperatures.—Easteal and Woolf[87] have recently applied the corrected Enskog theory to the viscosities of the liquified rare gases.

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[90] J. P. J. Michels and N. J. Trappeniers, *Physica*, 1980, **104A**, 243.

[91] J. H. Dymond, *Chem. Phys.*, 1976, **17**, 101.

[92] J. J. Van Loef, *Physica*, 1978, **95B**, 34.

The corrections to Enskog theory were based on the use of methane as a model smooth hard-sphere fluid, as described in the above section, and core diameters calculated from liquid densities along the freezing curve according to equation 18. The calculated results are compared with experimental data for argon,[93,94] krypton[95] and xenon[96] in Figure 13, which is based on Figure 3 of their paper.

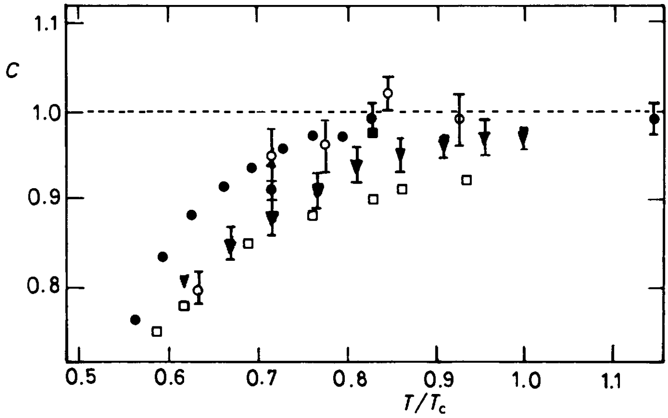

Figure 13 *Ratio of experimental viscosity coefficients to values calculated on the basis of the hard-sphere theory with core sizes given by equation* 18. *Argon* ●, ref. 94; ○, ref. 93; *krypton* ▼, ref. 95; *xenon* □, ref. 96

It is found that for argon at temperatures from about 0.7-times the critical temperature T_c to 1.2 T_c the agreement is better than 3%, which is within the combined uncertainties of the corrections to Enskog theory and the experimental uncertainties. For krypton and xenon, the deviation is about 10% at 0.8 T_c but within the estimated probable uncertainty of the experimental data.

It is apparent that at lower reduced temperatures there is a systematic and increasing discrepancy between experimental data and values calculated by this application of the smooth hard-sphere theory. This is explained[87] by a breakdown of equation 18 for these liquids as the temperature approaches the triple point. Values calculated for the core diameters of argon to give agreement at these low reduced temperatures were given by the equation

$$\begin{aligned} \sigma &= \sigma_p \text{ for } T_R > 1.5 \\ \sigma &= \sigma_p R_\sigma \text{ for } 1.0 \leqslant T_R \leqslant 1.5 \end{aligned} \tag{36}$$

where T_R is the temperature reduced by the triple point temperature and σ_p,

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[93] A. De Bock, W. Grevendonk, and W. Herremann, *Physica*, 1967, **37**, 227.

[94] W. N. Haynes, *Physica*, 1973, **67**, 440.

[95] A. Michels and C. Prins, *Physica*, 1962, **28**, 101.

[96] S. A. Ulybin and V. I. Makarushkin, *High. Temp. (USSR)*, 1977, **15**, 430.

obtained from density data, was given by the following expression (here rounded off to give significant figures):

$$\sigma_p/(\mathrm{nm}) = 0.409\,36 - 1.0492 \times 10^{-3}\,(T/\mathrm{K}) + 5.491 \times 10^{-6}\,(T/\mathrm{K})^2 - 1.117 \times 10^{-8}\,(T/\mathrm{K})^3 \quad (37)$$

The ratio R_σ was found to vary with temperature according to the equation

$$R_\sigma = 0.4102 + 1.2941T_\mathrm{R} - 0.9611T_\mathrm{R}^2 + 0.2402T_\mathrm{R}^3 \quad (38)$$

The σ values so derived agree to within 1% with the values previously obtained by Dymond[97] from fitting liquid argon viscosity coefficients.

Application of the same modifications to the core diameters, equations (36) and (38), lead to a significant improvement to the viscosity data fit for krypton and xenon with the σ values from densities along the freezing curve given by the expressions

$$\begin{aligned}&\text{Krypton: } \sigma/(\mathrm{nm}) = 0.417\,40 - 4.389 \times 10^{-4}\,(T/K) + 7.944 \times 10^{-7}\,(T/\mathrm{K})^2\\ &\text{Xenon: } \sigma/(\mathrm{nm}) = 0.449\,60 - 2.988 \times 10^{-4}\,(T/\mathrm{K}) + 3.468 \times 10^{-7}\,(T/\mathrm{K})^2\end{aligned} \quad (39)$$

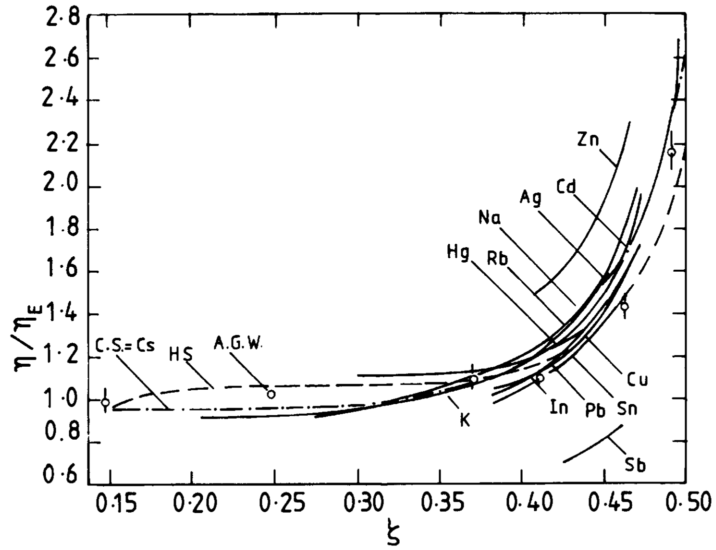

Figure 14 *The ratio of the viscosity coefficient* η *for the smooth hard-sphere fluid and for various metals to the Enskog theory approximation* η_E, *plotted as a function of packing fraction,* ξ. *The circles are hard-sphere molecular dynamics results* (ref. 11) *and curve* HS *is a smoothed representation of these results. The other curves are obtained from analysis of experimental data for liquid metals (for data references, see* ref. 98)
(Reproduced by permission from *Chem. Phys.*, 1975, **8**, 21)

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[97] J. H. Dymond, *Physica*, 1975, **79A**, 65.

C. Liquid Metals.—The smooth hard-sphere theory has been applied to the viscosity coefficients of liquid metals,[98] using core diameters determined as in Section 3B. The authors obtained smooth values for the correction factor (η/η_E) by using the observation of Alder, Gass, and Wainwright[11] that the product of the self-diffusion coefficient and the viscosity coefficient for a smooth hard-sphere system varies slowly with packing fraction. These ratios of exact to Enskog viscosity coefficient are compared with values obtained from experiment for several metals in Figure 14.

Although these curves do not coincide exactly, there is generally close agreement with the theoretical curve, with the exception of antimony and zinc which are significantly different. The authors suggest that the caesium curve should be taken as the universal (η/η_E) curve for metals. This leads to a greatly improved fit to the liquid metal viscosity data at low temperatures and, for 15 of the 23 metals studied, the agreement over the complete temperature range was within the typical scatter of the measurements. Whether the theory is applicable or not depends on the position of the metal in the Periodic Table, as shown in Table 9.

Table 9 *Applicability of the hard-sphere theory for viscosity*

IA	IIA	VIII			IB	IIB	IIIB	IVB	VB
Li									
0.060									
Na	Mg						Al		
0.095	0.065						0.050		
K	Ca	Fe	Co	Ni	Cu	Zn	Ga		
0.133	0.099	0.076	0.074	0.072	0.096	0.074	0.062		
Rb					Ag	Cd	In	Sn	Sb
0.148					0.126	0.097	0.081	0.071	0.062
Cs					Au	Hg		Pb	Bi
0.169					0.137	0.110		0.084	0.074

The dashed line represents the dividing line between the elements for which the theory is accurate, those below and to the left, and those for which it is not. The number given is the radius (nm) of the ion when all valence *s* and *p* electrons have been removed. The metals for which agreement is poor were either transition metals for which accurate data were difficult to obtain because of the high melting-point, or else elements having less metallic character, appearing at the top of the Groups and to the right of the rows. It appears that for metals having two or more valence electrons in *s* and *p* orbitals, there is a critical value of 0.073 nm for the ionic radius such that, for all metals with a radius greater than this, the viscosity is accurately described by the hard-sphere theory.

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[98] P. Protapapas, H. C. Andersen, and N. A. D. Parlee, *Chem. Phys.*, 1975, **8**, 17.

D. Polyatomic Fluids.—For a system of fairly spherical polyatomic molecules at densities greater than twice the critical density, Chandler[42] showed that the viscosity coefficient is equivalent to the rough hard-sphere viscosity coefficient η_{RHS}. When account is taken of the effect of changes in the angular momentum as well as changes in the linear momentum of a particle upon collision, then it is found that the rough hard-sphere coefficient is directly related to the smooth hard-sphere coefficient:

$$\eta \approx \eta_{RHS} \approx C\eta_{SHS} \tag{40}$$

where C is assumed to be constant. It obeys the inequality

$$C \geqslant 1$$

and equals one when coupling between angular and translational motions is absent.

Most tests of the rough hard-sphere model for viscosity have been made using the full equation

$$\eta = C(\eta/\eta_E)\eta_E \tag{41}$$

where (η/η_E) is the Alder,'Gass, and Wainwright[11] computed correction to Enskog theory. Values of the core size were obtained either from fitting the high density diffusion coefficient data for the fluids or from plots of $\ln(1/\eta)$ *versus* $\ln \rho$, from which the slope was determined and σ derived using the smooth hard-sphere expressions for fluidity given by Dymond.[44] Values for the core diameters agreed closely with values obtained from self-diffusion coefficient data. Typical values for the translational–rotational coupling factor are given in Table 10.

Table 10 *Translational-rotational coupling factor C for viscosity*

Compound	*T range*/K	*σ range*/nm	*C*	*Ref.*
Chlorotrifluoromethane	303—348	0.460—0.458	0.77 ± 0.02	48
Carbon tetrachloride	283—328	0.527—0.522	1.74	42
Tetramethylsilane	298—373	0.560—0.555	1.39	99
Benzene	303—433	0.514—0.506	1.32	99
Perfluorocyclobutane	323—423	0.558—0.554	1.23	50
Cyclohexane	313—383	0.555—0.551	1.61—1.31	52
Methylcyclohexane	223—298	0.578—0.574	3.90—2.48	53
Pyridine	303—423	0.499—0.492	1.49—1.22	54

The coupling factor is practically temperature independent for those molecules which can be considered pseudospherical but shows a marked temperature dependence where there is a significant departure from spherical shape or where the molecules can hydrogen-bond.

The rough hard-sphere model of transport properties has been treated in a

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[99] H. J. Parkhurst, Jr. and J. Jonas, *J. Chem. Phys.*, 1975, **63**, 2705.

different way by Dahler with the derivation[100,101] and solution[102,103] of an appropriate kinetic equation. The transport coefficients depend on the internal mass distribution, characterized by the moment of inertia which in reduced form is given by

$$k = \frac{4I}{m\sigma^2} \tag{42}$$

The dimensionless moment of inertia can have values from zero when the mass is at the centre, to two-thirds when the mass is evenly distributed over the surface of the sphere. The coefficient of viscosity can be written[104] in terms of k and the reduced volume V/V_0. It is found that $(\eta_{\mathrm{RHS}})_{\mathrm{D}}/\eta_{\mathrm{SHS}}$ has a maximum value of 1.64 and, more important, is constant to within 2% for a given value of k over the range of V/V_0 from 1.5 to 2.5. This supports the result obtained by Chandler[42] that the rough hard-sphere coefficient is proportional to the smooth hard-sphere coefficient, though in Chandler's theory there is no way of evaluating the proportionality constant. The disadvantage of the Dahler theory is that it overemphasizes the role of inelastic collisions.

Generally, the values derived for the translational–rotational coupling factor derived from viscosity are greater than unity as postulated by Chandler.[42] However, for chlorotrifluoromethane Harris[48] obtained the figure of 0.77 for C which he showed to be not unreasonable since application of the slip and stick boundary conditions of the Stokes–Einstein equation leads to the inequality

$$\tfrac{2}{3} \leqslant AC \leqslant 1$$

where A is the coupling factor from self-diffusion.

More recently, Easteal and Woolf[36] have used their calculated corrections to the approximate Enskog theory, based on methane data, to determine the density and temperature dependence of the translational–rotational coupling factor for relatively simple polyatomic fluids. They find that the coupling factor may have a strong density dependence, as illustrated in Figure 15 for carbon tetrachloride.

For other liquids such as benzene, the coupling has a strong temperature dependence in addition, as shown in Figure 16.

The core sizes for these molecular fluids were calculated from the molar volumes at the freezing pressure, equation 18, which as in the case of monatomic fluids (Section 6B) may not be appropriate at these low reduced temperatures. Further work is required to establish conclusively whether the translational–rotational coupling factors do have such a strong density and temperature dependence. If this is indeed the case, it contradicts the basic postulate of Chandler and the rough hard-

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[100] W. Condiff, W. Lu, and J. S. Dahler, *J. Chem. Phys.*, 1965, **42**, 3445.

[101] B. J. McCoy, S. I. Sandler, and J. S. Dahler, *J. Chem. Phys.*, 1966, **45**, 3485.

[102] M. Theodosopulu and J. S. Dahler, *J. Chem. Phys.*, 1974, **60**, 3567.

[103] M. Theodosopulu and J. S. Dahler, *J. Chem. Phys.*, 1974, **60**, 4048.

[104] S. F. Y. Li, Ph.D. Thesis, University of London, 1984.

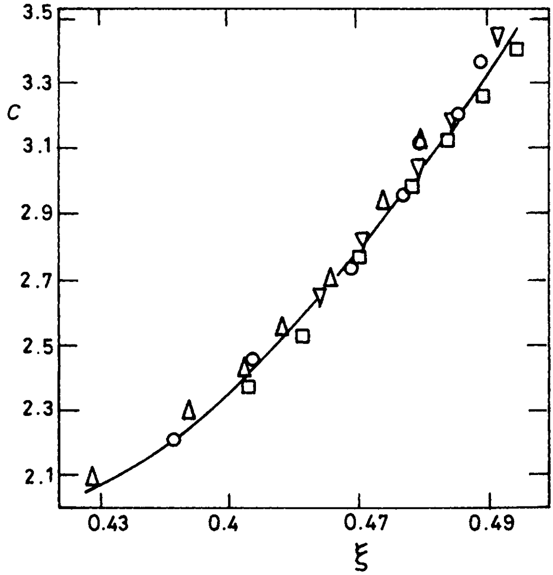

Figure 15 *Density dependence of the translational–rotational coupling factor for viscosity for carbon tetrachloride.* ∇, 283.2 K; □, 298.2 K; ○, 313.2 K; △, 328.2 K (Reproduced by permission from *Physica*, 1984, **124B**, 187)

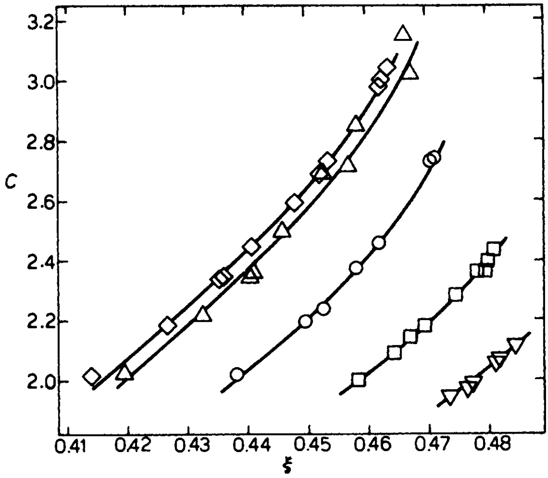

Figure 16 *Density dependence of the translational–rotational coupling factor for viscosity for benzene.* ∇, 288.2 K; □, 298.2 K; ○, 313.2 K; △, 328.2 K; ◇, 333.2 K (Reproduced by permission from *Physica*, 1984, **124B**, 188)

sphere theory is not appropriate. However, for the purpose of data correlation, the model can still be retained and the dependence of the coupling factors on temperature and density allowed to remain.

E. Binary Mixtures.—Shear viscosities for mixtures of argon + methane, calculated by Kandiyoti and McLaughlin[105] on the basis of the smooth hard-sphere theory using Thorne's extension[55] to the Enskog theory, were found to be in poor agreement with experiment. However, Jhunjhunwala, Boon, Frisch, and Lebowitz[106] found good agreement using this theory with measured viscosities for argon + krypton mixtures. As pointed out by McDonald,[107] this agreement was somewhat fortuitous in view of the fact that the core diameters were derived from viscosity coefficients for the pure liquids using the approximate Enskog theory. When the computed corrections for correlated motion[11] were taken into account, the core sizes were found to be close to values obtained from the position of the first peak in the structure factor. For the calculation of mixture viscosities, the correction factors to the Thorne–Enskog expression were taken as equal to the factors for the single component system at the same packing fraction. The calculated viscosities were then in closer agreement with experiment, but this too was fortuitous because the Percus–Yevick approximation was used for the radial distribution function at contact.

This approximation can be readily removed using correct expressions for $g_{12}(\sigma)$,[60] but a rigorous test of the applicability of the smooth hard-sphere theory for mixture viscosities awaits the accurate computation of the correction factors.

7 Thermal Conductivity Coefficients

A. Monatomic Gases at Supercritical Temperatures.—It is convenient to test the applicability of the smooth hard-sphere theory for interpretation of thermal conductivity data by considering the function λ^* defined by:

$$\lambda^* = (\lambda/\lambda_E)(\lambda_E/\lambda_0)(V/V_0)^{\frac{2}{3}} \tag{43}$$

where (λ/λ_E) gives the computed correction to Enskog theory,[11] (λ_E/λ_0) is the ratio of Enskog dense hard-sphere thermal conductivity coefficient to the dilute hard-sphere value, equation 10, and λ^* is core size independent.

Substitution of the hard-sphere expressions leads to the following relationship for a monatomic fluid which behaves as an assembly of hard spheres:

$$\lambda^* = 1.610 \times 10^8 \, \lambda V^{\frac{2}{3}}(M/R^3T)^{\frac{1}{2}} \tag{44}$$

This theory can be tested, using the extensive experimental measurements at high

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[105] R. Kandiyoti and E. McLaughlin, *Mol. Phys.*, 1969, **17**, 643.

[106] N. Jhunjhunwala, J. P. Boon, H. L. Frisch, and J. L. Lebowitz, *Physica*, 1969, **41**, 536.

[107] I. R. McDonald, *Physica*, 1973, **65**, 630.

pressures and at temperatures above the critical temperature for argon[108,109] and krypton,[109] for which values for the core sizes have been obtained by application of the hard-sphere theory to viscosity coefficient data, Table 7. There are thus no adjustable parameters, and λ^* from experiment, equation 44, can be compared directly with λ^* from theory, equation 43, by plotting *versus* $\ln(V/V_0)$. The results are illustrated in Figure 17, which shows very close agreement over the density range from about 0.8- to 2.5-times the critical density. At higher densities, the experimental results are lower than the hard-sphere predictions. This may possibly be due to errors in the computed corrections to Enskog theory. Although recent calculations for a 108-particle system[110] agree closely with the earlier results,[11] the number dependence of the results has not yet been established. Resolution of this discrepancy therefore awaits the results of further computer studies.

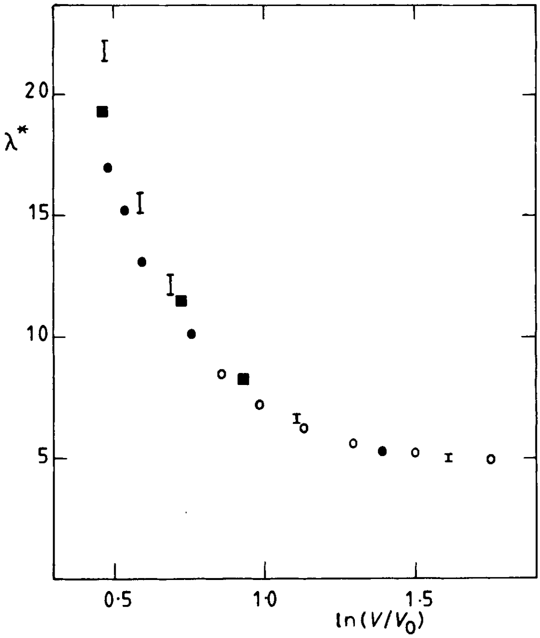

Figure 17 *Variation of* λ^* (*equation* 43) *with logarithm of reduced volume. Verticle lines with error bars are smooth hard-sphere values. Experimental data for argon at* 298 K; ○, ref. 108; ●, ref. 109; *for krypton at* 298 K; ■, *ref.* 109

A comparison of calculated thermal conductivities with experimental values at densities below 0.8-times the critical density shows the predicted values to be lower

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[108] A. Michels, J. V. Sengers, and L. J. M. Van de Klundert, *Physica*, 1963, **29**, 149.

[109] R. Tufeu, D. Vidal, M. Lallemand, and B. Le Neindre, *High Temp.-High Press.*, 1979, **11**, 587.

[110] J. P. J. Michels and N. J. Trappeniers, *Physica*, 1981, **107A**, 299.

and this difference increases as the density is decreased. This is attributable to neglect of intermolecular attractions which become significant at lower densities. These differences can be empirically related[97] to the reduced temperature and reduced volume.

There is an additional factor with regard to the thermal conductivity and that is the anamolous behaviour in the critical region. The smooth hard-sphere theory, modified to account for the effects of intermolecular attractions[97] is unable to reproduce this behaviour. This is not unexpected, but it is interesting that deviations begin to appear at temperatures as high as 1.7 T_c. This effect has been confirmed in a recent accurate experimental study.[111]

B. Polyatomic Fluids.—The thermal conductivity coefficient for a rough hard-sphere fluid has been treated by Theodosopulu and Dahler.[102,103] Li[104] has evaluated their expressions and shown that although the translational and rotational contributions vary quite significantly with change in the moment of inertia, the reduced total thermal conductivity, λ^*, given by analogy with equation 43 as

$$\lambda^* = \frac{(\lambda_{\mathrm{RHS}})_{\mathrm{D}}}{\Lambda_0}\left(\frac{V}{V_0}\right)^{2/3} \tag{45}$$

where $$\Lambda_0 = \frac{75}{64} \cdot \frac{1}{\sigma^2}\left(\frac{k^3 T}{\pi m}\right)^{1/2} \tag{46}$$

varies by less than 10% with change in the moment of inertia over the whole density range.

To test Dahler's theory for the thermal conductivity it is first necessary to establish values of volume V_0 and coupling factor C from analysis of viscosity coefficient data in terms of Chandler's rough hard-sphere model. Since the theories of Chandler and Dahler are mutually consistent for viscosity of rough hard-sphere systems, a value for the dimensionless moment of inertia, k, can be derived from C and the thermal conductivity calculated and compared with experiment. Li[104] applied this method to n-hexane at 298 K, for which he found $C = 1.45$, $V = 78 \times 10^{-6}$ m^3 mol^{-1}, $k = 0.44$, and n-octane at 298 K for which $C = 1.7$, $V = 105 \times 10^{-6}$ m^3 mol^{-1}, $k = 0.66$. The calculated thermal conductivity coefficients agreed with measured values for n-hexane to within 5% over the density range for which the smooth hard-sphere model is stable (corresponding to pressures up to 150 MPa). For n-octane, the differences were somewhat greater but still less than 10%, which is remarkably good in view of the simplicity of the model.

8 Correlation and Prediction of Transport Coefficients

From a chemical engineering viewpoint, it is essential to be able to make accurate

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[111] C. A. N. de Castro and H. M. Roder, *J. Res. Nat. Bur. Stand.*, 1981, **86**, 293.

predictions of thermophysical properties. The most satisfactory representation of experimental data is one which is based on theory. As discussed above, the physically realistic hard-sphere models lead to a satisfactory fit of experimental transport coefficient measurements for dense fluids and their mixtures where the molecules are reasonably spherical in shape. The problem lies in the transition to a metastable state that occurs for hard-sphere systems at high densities. For many real fluids this density corresponds to a pressure far below the experimental freezing pressure at a given temperature. However, the methods used to demonstrate the applicability of the hard-sphere theories for the transport properties can be successfully extended to give correlation/prediction schemes of high accuracy at all densities.

A. Self-Diffusion Coefficients.—On the basis of the rough hard-sphere theory, the reduced self-diffusion coefficient D^*_{RHS} is given by

$$D^*_{\mathrm{RHS}} \approx A D^*_{\mathrm{SHS}} \tag{47}$$

$$\text{where } D^*_{\mathrm{SHS}} = 5.030 \times 10^8 \, (M/RT)^{\frac{1}{2}} D/V^{\frac{1}{3}} \tag{15}$$

If the coupling factor is density independent and temperature independent, D^*_{RHS} is just a function of molar volume for a given fluid at a constant temperature. Plots of D^*_{SHS} (or log D^*_{SHS}) *versus* log V for different isotherms will therefore be superimposable laterally, and the amount by which the curve at a given temperature has to be moved to superimpose it on a curve at a reference temperature T_{R} leads to a value for $V_0(T)/V_0(T_{\mathrm{R}})$.[31] Typical results, for tetramethylsilane, are shown in Figure 18. The curves for different temperatures are superimposable on the single curve given by data at the reference temperature of 373.2 K, not only over the density range for which the hard-sphere theory is valid (up to 150 MPa at 298.2 K), but over the whole density range (for pressures up to 400 MPa). Values derived for $V_0(T)/(V_0(T_{\mathrm{R}})$ were as follows:

T/K	298.2	323.2	348.2	373.2
$V_0(T)/V_0(T_{\mathrm{R}})$	1.043	1.033	1.014	1.000

Once the reference curve has been established for a given fluid, self-diffusion coefficients at other temperatures and densities can be accurately predicted.

B. Viscosity Coefficients.—A method analogous to that described above for self-diffusion coefficients can be used for the successful correlation and prediction of viscosity coefficients over the whole density range. A quantity η' was defined[112] as $10^4 \eta V^{\frac{2}{3}}/(MT)^{\frac{1}{2}}$ in the cgs system of units, or more generally, as

$$\eta' = 9.118 \times 10^7 \eta V^{\frac{2}{3}}/(MRT)^{\frac{1}{2}} \tag{48}$$

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[112] J. H. Dymond and T. A. Brawn, *Proc. 7th Symp. Thermophys. Prop., Am. Soc. Mech. Engrs.*, New York, 1977, 660.

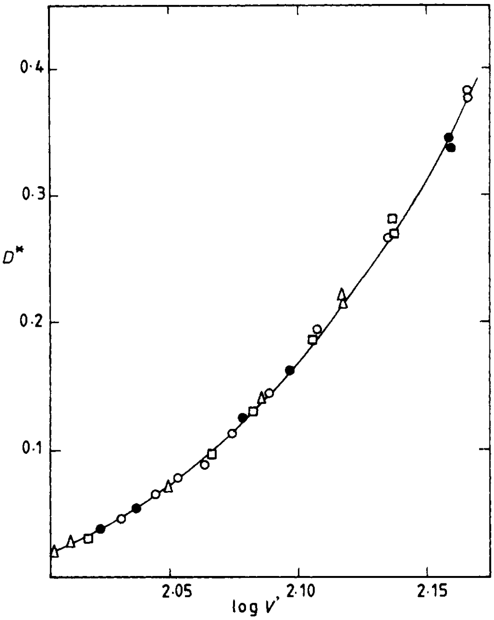

Figure 18 *Correlation of experimental self-diffusion coefficient data for tetramethylsilane at different temperatures and pressures, based on the* 373.2 K *isotherm.* D^*_{SHS} *is defined in equation* 15 *and* $V' = V \cdot V_0(T_R)/V_0(T)$. △, 298.2 K; □, 323.2 K; ●, 348.2 K; ○, 373.2 K (Reproduced by permission from Proceedings of a Symposium on Transport Properties of Fluids, National Engineering Laboratories, East Kilbride, H.M.S.O., 1979)

For the density region where the rough hard-sphere theory is applicable, η' will be proportional to $(\eta_{SHS}/\eta_0)(V/V_0)^{\frac{2}{3}}$ and so will depend only on (V/V_0) for a given fluid at a given temperature, providing that the translational–rotational coupling factor for viscosity is density- and temperature-independent. Plots of η' (or of log η') *versus* log V using data for a given compound at different temperatures should be superimposable on the curve obtained for any reference temperature. The amount of adjustment gives a value for $V_0(T)/V_0(T_R)$. Results obtained[112] for carbon tetrachloride and for tetramethylsilane showed that the curves were superimposable not only over the density range for which the rough hard-sphere theory was applicable, but over the whole density range. This method also gives an excellent correlation[112] of the viscosity data for large aspherical molecules such as bicyclic hydrocarbons, and has been successfully applied to the correlation of viscosity data for liquid normal alkanes, aromatic hydrocarbons, and for their binary mixtures.[113–116] A typical plot is shown in Figure 19, for n-hexane.

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[113] J. H. Dymond, K. J. Young, and J. D. Isdale, *Int. J. Thermophys.*, 1980, **1**, 345.
[114] J. H. Dymond, J. Robertson, and J. D. Isdale, *Int. J. Thermophys.*, 1981, **2**, 133.
[115] J. H. Dymond, J. Robertson, and J. D. Isdale, *Int. J. Thermophys.*, 1981, **2**, 223.
[116] J. H. Dymond, N. F. Glen, and J. D. Isdale, *Int. J. Thermophys.*, in press.

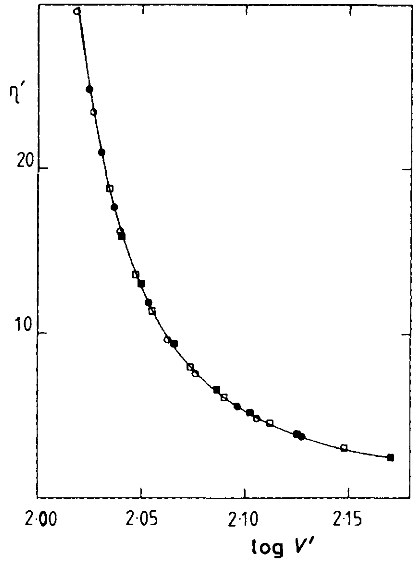

Figure 19 *Correlation of experimental viscosity coefficient data for n-hexane at different temperatures and pressures based on the* 373.2 K *data.* η' *is defined by equation* 48, $V' = V{\cdot}V_0(T_R)/(V_0(T)$. ○, 298.2 K; ●, 323.2 K; □, 348.2 K; ■, 373.2 K
(Reproduced by permission from *Int. J. Thermophys.*, 1980, **1**, 364)

C. Thermal Conductivity Coefficients.—On the basis of the rough hard-sphere theory of Dahler,[102,103] the thermal conductivity coefficient of a fluid can be represented by the general equation:

$$\frac{(\lambda_{\mathrm{RHS}})_{\mathrm{D}}}{\Lambda_0} = c_1\left(\frac{1}{g(\sigma)}\right) + c_2\left(\frac{b}{V}\right) + c_3\left[\frac{1}{g(\sigma)}\left(\frac{b}{V}\right)^2\right] \tag{49}$$

where Λ_0 is given by equation 46 and c_1, c_2, and c_3 are algebraic functions of the dimensionless moment of inertia, k. As shown by Li[104] the dependence of the thermal conductivity on k is weak. For this model system, k is temperature independent and for a real fluid the temperature dependence is likely to be small.

Substitution for Λ_0 and V_0 in equation 45 allows λ^* to be calculated from experimental measurements:

$$\lambda^* = 1.936 \times 10^7 \lambda V^{\frac{2}{3}} (M/RT)^{\frac{1}{2}} \tag{50}$$

By analogy with D^* for diffusion and η' for viscosity, λ^* is expected to be a function only of (V/V_0). Plots of λ^* *versus* log V at different temperatures for a given fluid should therefore be superimposable on the curve for a reference temperature. The relative shift along the log V axis provides a value for the ratio of the V_0 values at the different temperatures. Li[104] has tested this approach using very accurate measurements on n-hexane, n-octane, benzene, and cyclohexane, using the lowest isotherm as reference in each case. A very satisfactory correlation was obtained, with values for $V_0(T)/V_0(T_R)$ in close agreement with values obtained by Dymond[113–115] for the same liquids by interpretation of viscosity coefficients on the basis of the rough hard-sphere theory.

Since λ^* is so weakly dependent on k, there is the possibility of a universal correlation for λ^*. This was investigated by Li[104] using accurate results for eleven hydrocarbons over a wide range of thermodynamic states. The results are shown in Figure 20, with the 307 K isotherm for n-hexane as the reference curve. The V_0 value at this temperature was taken as 72.64×10^{-6} m^3 mol^{-1}.

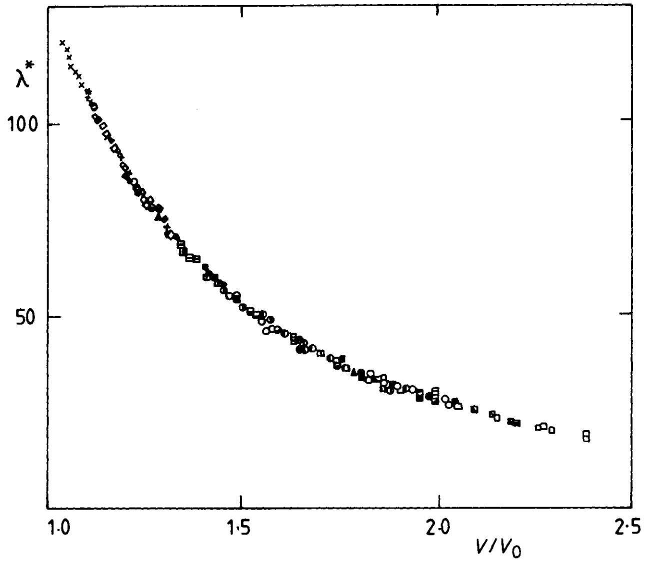

Figure 20 *Reduced thermal conductivity* versus *reduced volume for eleven hydrocarbons* (Reproduced by permission from *ref.* 104)

The universality of this reduced plot for hydrocarbons is striking, especially in view of the wide range of temperature and pressures at which the measurements were made. Though the deviation of some individual points from the best curve is slightly greater than the uncertainty estimated on the basis of the measured thermal conductivity and density, it is apparent that this near universality will provide a very good estimate of the thermal conductivity for members of the n-alkane series at different temperatures and pressures. A similar result is to be expected for other homologous series.

9 Conclusions

Significant progress towards a successful molecular interpretation of transport properties in dense fluids and their mixtures has resulted from consideration of hard-sphere theories. The hard-sphere model, with a temperature dependent core size, gives a simple yet physically reasonably realistic description of molecular trajectories in the dense fluid state. The transport coefficients of monatomic species can be satisfactorily reproduced by the smooth hard-sphere theory. For pseudospherical polyatomic species, the derived translational–rotational coupling factors appear to be in general accord with expectations for the molecules concerned. However, a fuller discussion of these factors and their dependence on density and temperature must await more accurate computer calculations of the corrections to the approximate hard-sphere transport coefficients. Furthermore, for a rigorous examination of the limits of applicability of the hard-sphere theories for transport properties it is essential to have very accurate experimental data over a wide range of temperature and pressure for spherical, pseudospherical, and indeed non-spherical molecular fluids and their mixtures.

Although the hard-sphere model is only an approximation, at the present time it provides the most satisfactory basis for the interpretation, correlation, and prediction of transport properties of dense fluids and their binary mixtures.