On predicting self-diffusion coefficients from viscosity in gases and liquids

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Abstract

The relations between self-diffusion and viscosity for compressed liquids and gases have been reviewed, and a new equation for correlating viscosities over wide ranges of temperature and pressure is proposed. This formula is inspired by the Lennard-Jones Chain model of Yu and Gao for self-diffusion, and represents the viscosities of 15 compounds (1046 data points) with an average absolute deviation of 6.95%. Moreover, as the presented equation and the Yu-Gao model require the same fitting parameters, the ability to calculate self-diffusion coefficients from the viscosity parameter is studied. Some of the classic reviewed relations, such as the Stokes-Einstein formula, are also contrasted with the available experimental data of both transport properties.

Contents

1. Introduction

Viscosity is probably the most widely known and studied transport property, and there exists a great amount of experimental data in the literature leading to the establishment of theoretical or empirical models for this (Monnery et al., 1995; Reid et al., 1987). On the other hand, self-diffusion has not received so much attention, partly due to the difficulties in measuring: isotope tracer techniques or more recently, nuclear magnetic resonance are complex methods that can not compete with viscosimeters (Tyrrell and Harris, 1984). Both properties imply a movement of molecules, and so a relation between them could exist, the hydrodynamic equation of Stokes-Einstein being the most popular.

Despite common opinion, methods for predicting viscosities in dense gases and compressed liquids do not abundant. For dense gases, the equations of Reichenberg, Lucas and Chung are useful (Monnery et al., 1995; Reid et al., 1987), but in liquids, only the saturated liquids have been widely studied (Hsu et al., 2002; Monnery et al., 1995; Reid et al., 1987). For all fluid states, only the methods of Ely and Hanley (1981), Monnery et al. (1998) and the viscosity equations of state (Guo et al., 2001) can be employed, but none are problem free. The method of Ely-Hanley is based on the extended corresponding states, but is not good to predict the properties of non-hydrocarbon substances (Hwang and Whiting, 1987) and all the posterior modifications make the method correlative, not predictive (Huber et al., 2003; Hwang and Whiting, 1987; Monnery et al., 1991). Monnery and coworkers developed a modified square well intermolecular potential model, but this is a function of a molecular diameter calculated by group contributions, and viscosity is highly sensitive to this diameter (Galliero et al., 2005). Finally, the viscosity equations of state are empirical cubic equations

of state based on the morphological analogy between *P-V-T* graphs and *P-η-T* diagrams, and were only used for alkanes.

Regarding self-diffusion coefficients, there is no predictive way of obtaining these, except for dilute gases. The classic charts based on the corresponding states principle (CSP) were elaborated with scarce experimental data (Bird et al., 1982; Bueno et al., 1990; Ramanan and Hamrin, 1972; Takahashi, 1974; Tee et al., 1966b) and the Lennard-Jones (LJ) models are very sensitive to molecular diameters, and so can only can be used in a correlative way (Bachl et al., 1992; Liu et al., 1998; Ruckenstein and Liu, 1997; Yu and Gao, 1999). These last models are all based on molecular dynamics simulations, and transform expressions for hard-sphere (HS) fluids into formulas for LJ fluids by means of effective HS molecular diameters and additional terms of attractive forces.

In the present work, the models relating viscosity and self-diffusion are reviewed, and a new LJ correlative equation for viscosity is proposed. This equation would be "complementary" to the Yu-Gao equations for self-diffusion (Yu and Gao, 1999, 2001), which describe molecules as chains of tangent LJ spheres. The adjustable parameters for the viscosities of real fluids (two for non-hydrogen-bonding substances and four for hydrogen-bonding compounds) are expected to be the same as those for self-diffusion. The prediction of the Yu-Gao equations with these parameters for 16 substances are compared with the results of the other models.

2. Relations between viscosity and diffusion coefficients in liquids

2.1. *Hydrodynamic theories*

These are all based on the Nernst-Einstein equation (Bird et al., 1982; Simons and Ponter, 1975), which states that the diffusivity of an isolated particle or solute molecule A through a solvent B is

$$D_{AB} = kT\frac{v_A}{\mathrm{F}_A} = \frac{kT}{\xi_{AB}}$$ (1)

where k is the Boltzmann constant, T the absolute temperature, v_A the particle velocity and F_A the force that is acting on it. The ratio between velocity and force is termed the "movility" of the particle, and is equal to the inverse value of the friction coefficient, ξ_{AB}. Starting from the hydrodynamic basis, Basset has obtained a relation between the force and the velocity of one rigid sphere moving as "creeping flow" through a continuous fluid:

$$\mathrm{F}_A = 3\pi\eta_B v_A \sigma_A \left(\frac{2\eta_B + 0{,}5\sigma_A J_{AB}}{3\eta_B + 0{,}5\sigma_A J_{AB}} \right)$$ (2)

the J_{AB} parameter is the sliding friction coefficient, σ_A the molecular diameter of the solute and η_B the viscosity of the solvent. When the fluid does not slip on the sphere surface, this coefficient has an infinite value, and the previous equation becomes the Stokes formula:

$$\mathrm{F}_A = 3\pi\eta_B v_A \sigma_A$$ (3)

Substituting this expression of the force in the Nernst-Einstein equation, the well-known Stokes-Einstein equation is obtained:

$$D_{AB} = \frac{kT}{3\pi\eta_B \sigma_A}$$ (4)

If the fluid slips on the sphere surface, $J_{AB} = 0$ and the other limiting case of Basset expression is obtained: the so-called Sutherland equation

$$F_A = 2\pi \eta_B v_A \sigma_A \tag{5}$$

$$D_{AB} = \frac{kT}{2\pi \eta_B \sigma_A} \tag{6}$$

The most important modification of the Sutherland formula is due to Li and Chang (1955), who supposed that fluid molecules were organized in a cubic cell, so in a pure substance, $A=B$, and the molecular diameter can be calculated from molar volume (V) and Avogadro's number (N_{av}),

$$D = \frac{kT}{2\pi \eta} \left(\frac{N_{av}}{V} \right)^{1/3} \tag{7}$$

Eq. (7) predicts the self-diffusivities in polar, non-polar, hydrogen-bonding compounds and liquid metals at atmospheric pressure with average deviations of 12%.

Although the Stokes-Einstein equation supposes that the spherical particle moves through a continuous solvent, it has been applied to self-diffusion (molecules of the same size), and to non-spherical particles obtaining molecular diameters smaller than the real ones. On the other hand, the Sutherland equation provides much more meaningful diameters, and even molecular dynamics simulation data verifies it (Alder et al., 1970). Nevertheless, the products $D\eta/T$ and $D\eta V^{1/3}/T$ are not constant along the liquid saturation line, increasing when the temperature

rises (Ertl et al., 1974; Gaven et al., 1962a; Rathbun and Babb, 1961). At elevated pressures it seems that only in a few compounds is $kT/D\eta\pi\sigma$ invariable, although not exactly equal to 2. These substances are tetramethylsilane (Parkhurst and Jonas, 1975b), carbon tetrachloride (McCool and Woolf, 1972b), perfluorocyclobutane (Finney et al., 1977), cyclohexane (Jonas et al., 1980), methylcyclohexane (Jonas et al., 1979) and hexadecane (Vardag et al., 1991). The last two have values of $kT/D\eta\pi\sigma$ equal to 1.45 and 4.2, respectively. In benzene, McCool et al. (1972) consider that it is not constant, but Parkhust and Jonas (1975b) observe the opposite. The same contradiction between the data of different researchers appears in water and its isotopic derivatives: Krynicki et al. (1978) and Kiselnik et al. (1973) consider that Sutherland expression is roughly applicable, but the majority claim that is not valid (Harris and Woolf, 1980; Wilbur et al., 1976; Woolf, 1975, 1976). In substances like pyridine (Fury et al., 1979), hexane (Harris, 1982), carbon dioxide (Groβ et al., 1998), alcohols (Jonas and Akai, 1977; Meckl and Zeidler, 1988), 2-ethylhexylbenzoate (Walker et al., 1988), 1,2-dichloroethane (Malhotra et al., 1990) and even the methane (Easteal and Woolf, 1984a), the group $D\eta/T$ is temperature and/or pressure dependent.

The influence of temperature and pressure on the group $D\eta V^{1/3}/T$ has been overly studied, but in liquid and supercritical carbon dioxide (Etesse et al., 1992) this group is not constant.

2.2. *Empirical modifications of Stokes-Einstein or Sutherland*

The most well-known modification of Eqs. (4) and (6) are due to Hayduk and Cheng (1971). These authors studied the binary diffusion at infinite dilution of a solute in a wide variety of solvents, and proposed

$$D\eta^{C_1} = C_2 \tag{8}$$

where C_1 and C_2 were only functions of solute properties if there were not strong solute-solvent interactions. Davis et al. (1980) proposed

$$D\eta^{C_1} = \frac{C_2 T}{298.2} \tag{9}$$

$$C_1 = 1.166 - \frac{2.592 \times 10^{-10}}{\sigma} \tag{10}$$

$$Ln\left(10^{10} C_2\right) = -11.67 C_1 + 6.013 \tag{11}$$

with the molecular diameter determined as in Eq. (7) from low-temperature saturated liquid densities.

2.3. Intermolecular potential models: the hard-sphere

An HS liquid is a system in which only repulsive forces are present. Longuet-Higgins and Pople (1956) developed theoretical expressions for the tree transport coefficients in this fluid. These expressions for self-diffusion and viscosity were

$$D^{HS} = \frac{\sigma}{4}\sqrt{\frac{\pi kT}{m}}\frac{1}{(Z-1)} \tag{12}$$

$$\eta^{HS} = \frac{2}{5}\rho\sigma\sqrt{\frac{mkT}{\pi}}(Z-1) \tag{13}$$

where m is the mass of the sphere, ρ the numerical density and Z the compressibility factor. Vadovic and Colver (1972) combined both equations, obtaining

$$\frac{(\eta D)^{HS}}{\rho kT} = \frac{1}{10}\sigma^2 \tag{14}$$

They assumed that the HS diameter was proportional to the liquid volume at melting point, V_f, and empirically adjusted the proportionality constant with experimental data of polar, non-polar, hydrogen-bonding compounds and liquid metals at atmospheric pressure

$$\frac{\eta D}{\rho kT} = 0.2707 \times 10^{-16} V_f^{2/3} \tag{15}$$

with an average error of 6%.

2.4. Intermolecular potential models: the rough-HS

The equations obtained by Enskog for the three transport properties in HS fluids (Hirschfelder et al., 1964) were corrected by the molecular dynamics simulations of Alder et al. (1970). These corecctions were adjusted empirically by Dymond (1974), who obtained in the high density range, $1.5 \leq V/V_0 \leq 2.0$,

$$D^{HS} = 1.271(1 - 1.384 V_0/V)D^0 \tag{16}$$

$$\eta^{HS} = \frac{\eta^0}{0.2195(V/V_0 - 1.384)} \tag{17}$$

where V_0 is the close-packed molar volume, equal to

$$V_0 = \left(\frac{3\sqrt{2}}{\pi}\right)\left[\frac{4\pi N_{av}}{3}\left(\frac{\sigma}{2}\right)^3\right] = \frac{N_{av}\sigma^3}{\sqrt{2}} \tag{18}$$

and the superscript 0 indicates that the property is evaluated at low-pressure limit (Hirschfelder et al., 1964),

$$D^0 = \frac{3}{8\rho\sigma^2}\sqrt{\frac{kT}{\pi m}} \tag{19}$$

$$\eta^0 = \frac{5}{16\sigma^2}\sqrt{\frac{mkT}{\pi}} \tag{20}$$

The only adjustable parameter was the molecular diameter, which could be temperature and pressure dependent. Dymond obtained σ from the viscosity at the same temperature and pressure that the self-diffusion data, and predicted the values of compressed liquid CCl_4 with an average deviation of 7%. Krynicki et al. (1978) and Woolf (1975) did the same for water and Van Loef (1977a, b) applied Eqs. (16) and (17) to hydrogen and other satutated liquids.

Nevertheless, the procedure of Dymond has an important limitation: it supposed that the coupling factors for diffusion and viscosity, A_D and A_η, are equal to unity. These factors were introduced by Chandler (1975) who states that

$$D^{real} \approx D^{RHS} = A_D D^{SHS} \tag{21}$$

$$\eta^{real} \approx \eta^{RHS} = A_\eta \eta^{SHS} \qquad (22)$$

The transpor property of a real system is supposed to be the same as that of a rough-hard-sphere (RHS) fluid, which is described as the product of a coupling factor to the property of a smooth-hard-sphere (SHS) liquid. The SHS property would be calculated with the HS expressions using effective diameters (temperature and/or pressure dependent). In general, A_D <1.00 and A_η>1.00, and they are temperature dependent (Finney et al.,1977; Fury et al., 1979; Jonas et al., 1979, 1980), but in some cases A_D can be a function of density as well (Easteal and Woolf, 1984c, 1987; Malhotra et al., 1990; Walker et al., 1988). Nevertheless, this density dependence is probably due to the fact that the authors do not fit the molecular diameters from self-diffusivities, but from the liquid molar volume at melting point as suggested by Easteal and Woolf (1984a, b) so the whole weight of the fitting falls on A_D. According to Chandler the coupling factors had to be constant, so the temperature and/or density dependence is due to the influence on D and η of all the effects neglected in the HS model, e.g. attractive forces, deviations from spherical symmetry and anisotropic interactions. There is no known method to estimate these, and the authors who have tried to correlate the tree transport properties at the same time with equal diameters (there also exists a coupling factor for thermal conductivity), have had to use these coupling factors as adjustable parameters (Assael et al., 1992; Bleazard and Teja, 1996).

2.5. Houghton's model

Houghton (1964) treats viscosity and self-diffusion as stochastic processes, in which the liquid molecules are confined in cubic cells of side length λ. With the Navier-Stokes and Langevin equations, he obtained

$$\xi = 24\frac{\eta}{\rho\lambda^2} \tag{23}$$

and as X-rays measures indicated that the side length was $\lambda = 2(V/N_{av})^{1/3}$,

$$D = \frac{kT\rho}{6\eta}\left(\frac{V}{N_{av}}\right)^{2/3} \tag{24}$$

The average deviation is 9% in liquids at atmospheric pressure, but Eq. (24) indicates that product $D\eta V^{1/3}/T$ is constant, like the Li-Chang modification of the Sutherland equation.

2.6. Dullien's model

From Lamm's theory for binary diffusion, Dullien (1963) has derived an expression for calculating the mean distance of momentum transfer between colliding molecules, d, measured in the normal direction of the transport plane in function of intradiffusion coefficients. For one component system, it is simplified to

$$\text{d} = \sqrt{\frac{2\eta D}{\rho kT}} \tag{25}$$

Later, Dullien (1972) found a relation between this distance and the molecular diameter. He did not use hydrodynamic or kinetic theories; only supossing that in a liquid near melting point the molecules were very compacted, without translating, and that they could only

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oscillate between their neighbours: the momentum transfer was produced when one vibrating molecule collided with these neighbours. This assumption, and the Newton's law gave

$$\sigma = 2.24 \sqrt{\frac{\eta D}{\rho k T}} \tag{26}$$

Starting from the dumbbell model, Allal et al. (2001) obtained, for liquid viscosity, that $\eta = \rho \xi L^2$, which introduction in Eq. (1) gives a similar relation (Boned et al., 2004). L was a characteristic molecular distance.

Dullien applied Eq. (26) to saturated liquids, from melting point to boiling point, and obtained near-constant values of molecular diameters, excepting methanol and ethanol (these are both hydrogen-bonding liquids, and these bonds break when temperature increases). At temperatures higher than boiling, the molecular diameter increases with the temperature. The diameter could be empirically related with the critical volume, V_c, with an average deviation of 4% as

$$\frac{\eta D}{\rho k T} = 0.1240 \times 10^{-16} V_c^{2/3} \tag{27}$$

This equation is similar to Eq. (15) if the relation $V_f = 0.31 V_c$ is taken. Nevertheless, Ertl and Dullien (1973) revised this for many compounds, and observed that the diameter was not constant between melting point and boiling point: there was a minimum in the curve σ vs. T_r, so they proposed

$$\sigma = \left[\frac{2.55 \times 10^{-3}}{T_r^4} + 0.35 T_r + 0.79 \right] \sigma^{\min} \tag{28}$$

$$\sigma^{\min} = 2.24 \times 10^{-10} \sqrt{1520 V_c^{2/3} - 1.42} \tag{29}$$

Concerning the temperature and pressure influence on the group $\eta D / \rho k T$, this has only been studied for water (Krynicki et al., 1978; Woolf, 1975) and 1,2-dichloroethane (Malhotra et al., 1990), and dependence of both variables has been found.

2.7. Packed-bed model

Sęk (1996) combined the Basset equation with the Blake-Kozeny-Carman formula to obtain an expression for the force in the Nernst-Einstein expression. He supposed that the bed volume was equal to the molar volume of the liquid, that the number of packed particles coincided with the Avogadro number, and that the porosiy could be identified with the free-volume fraction between molecules, obtaining

$$\frac{\eta D}{kT} = \frac{1}{f^{Sek}} \left(\frac{\pi}{6} \right)^{2/3} \frac{\left[1 - \frac{V^{free}}{V} \right]^{4/3}}{\left[\frac{V^{free}}{V} \right]} \left(\frac{N_{av}}{V} \right)^{1/3} \tag{30}$$

The factor f^{Sek} included two other factors: that of tortuosity and the proportionality constant in the Blake-Kozeny-Carman formula. Contrary to packed-beds, this factor was not constant, but was a function of both temperature and pressure. Porosity was calculated as

$$\frac{V^{free}}{V} = 1 - \frac{\pi N_{av}}{6V}\sigma^3 \tag{31}$$

and the diameter with Eq. (26). After analyzing a lot of experimental saturated liquids (polar, non-polar and hydrogen-bonding), Sęk proposed

$$\frac{1}{f^{Sek}}\left(\frac{\pi}{6}\right)^{2/3} = 0.05405\left[\frac{V^{free}}{V}\right]^{-2,062} - 0.07060 \tag{32}$$

which is not valid near the critical point. The self-diffusion has to be obtained by trial and error in Eq. (30).

Despite good predictions, if the global equation is examined, a considerable error is observed: this is that $F(D\eta V^{1/3}/T)=0$, so $D\eta V^{1/3}/T$ must be constant. The concordance between calculated and experimental data is due to the sensitivity of Sęk's formula to the initial test values, and to the tolerance imposed in order to accept the final result.

2.8. Empirical correlations

Harris (1982) and Harris et al. (1993) correlated, at the same time, viscosity and self-diffusion with eight fitting parameters. The reference temperature was arbitrarily chosen as 273.16 K, and the excluded volume was defined as in Eq. (18).

$$\frac{\rho D}{(\rho D)^0}\left(\frac{V}{V_0}\right)^{2/3} = \vartheta_1 + \frac{\vartheta_2 V^{ref}}{\left(1 + \dfrac{\vartheta_3}{V^{ref}}\right)} \tag{33}$$

$$\frac{\eta^0}{\eta}\left(\frac{V_0}{V}\right)^{2/3} = \vartheta_4 + \frac{\vartheta_5 V^{ref}}{\left(1 + \dfrac{\vartheta_6}{V^{ref}}\right)} \tag{34}$$

$$V^{ref} = V\left[1 - \vartheta_7(T - T^{ref}) - \vartheta_8(T - T^{ref})^2\right] \tag{35}$$

The good correlations obtained for hexane, octane, toluene and trichloromethane, together with the fact that only $\vartheta_3 \approx \vartheta_6$ could indicate that it is not possible to obtain any simple relation between self-diffusion and viscosity.

3. Relations in all fluid states

3.1. The Enskog approach and the kinetic theory of dilute gases

Enskog developed equations for the three transport properties in HS fluids assuming that only binary molecular collisions were important and that there was no correlation between succesive collisions (Reid et al., 1987; Stephan and Lucas, 1979),

$$D^{HS} \approx D^E = \frac{D^0}{g(\sigma)} \tag{36}$$

$$\eta^{HS} \approx \eta^E = \eta^0\left[\frac{1}{g(\sigma)} + 0.8\frac{b}{V} + 0.761\left(\frac{b}{V}\right)^2 g(\sigma)\right] \tag{37}$$

$$\kappa^{HS} \approx \kappa^E = \kappa^0\left[\frac{1}{g(\sigma)} + 1.2\frac{b}{V} + 0.755\left(\frac{b}{V}\right)^2 g(\sigma)\right] \tag{38}$$

where b= $(2/3)\pi N_{av}\sigma^3$ is the second virial coefficient of the HS fluid and $g(\sigma)$ the radial distribution, which can be obtained by an equation of state as

$$Z=PV/RT=1+bg(\sigma)/V \tag{39}$$

being the expression of Carnahan and Startling (1969) the most widely used for calculating this radial distribution

$$g(\sigma) = \frac{\left(1-\dfrac{\pi}{12}\rho*\right)}{\left(1-\dfrac{\pi}{6}\rho*\right)^3} \tag{40}$$

where $\rho* =\rho\sigma^3 =2^{1/2}V_0/V$ is the molecular reduced density. As real fluids are not hard-spheres, Enskog employed the thermal pressure, $T(\partial P/\partial T)_V$ instead of P and the second virial coefficients of the real substances, B(T) in Eq. (39). So, $g(\sigma)$ and b were then defined as (Hanley et al., 1972)

$$\frac{bg(\sigma)}{V} = \frac{V}{R}\left(\frac{\partial P}{\partial T}\right)_v -1 \tag{41}$$

$$b = B + T\frac{dB}{dT} \tag{42}$$

Nevertheless, even in gases at low pressures Eqs. (19) and (20) fail because of the inadequacy of the hard-sphere potential. If the LJ intermolecular potential is selected, the results at atmospheric pressure are very good (Hirschfelder et al., 1964): Eqs. (19) and (20) only have to be divided by $\Omega^{(1,1)}$ and $\Omega^{(2,2)}$, respectively, which are the collision integrals for diffussion

and viscosity, and are exclusively functions of reduced molecular temperature $T^*=kT/\varepsilon^{LJ}$, where ε^{LJ} is the Lennard-Jones characteristic energy. A lot of values of σ^{LJ} and ε^{LJ} are tabulated (Hirschfelder et al., 1964) and empirical formulas are available to calculate these two parameters (Chen and Othmer, 1962; Stiel and Thodos, 1962; Tee et al., 1966a; Tham and Gubbins, 1969).

$$\Omega^{(1,1)} = \frac{1.06036}{(T^*)^{0.15610}} + \frac{0.19300}{\exp(0.47635T^*)} + \frac{1.03587}{\exp(1.52996T^*)} + \frac{1.76474}{\exp(3.89411T^*)} \qquad (43)$$

$$\Omega^{(2,2)} = \frac{1.16145}{(T^*)^{0.14874}} + \frac{0.52487}{\exp(0.77320T^*)} + \frac{2.161778}{\exp(2.43787T^*)} -$$
$$- 6.435 \times 10^{-4}(T^*)^{0.14874}\sin\left\{18.0323(T^*)^{-0.76830} - 7.27371\right\} \qquad (44)$$

These numerical adjustments were made by Neufeld et al. (1972) and are valid in the range of $0.3 < T^* < 100$. The resultant expressions for the transport properties are known as Chapman-Enskog formulas. Self-diffusion can now be obtained from viscosity without the knowledge of σ^{LJ} as (Weissman and Mason, 1962)

$$PD^{LJ} = \frac{6kT\eta^{LJ}}{5m}\frac{\Omega^{(2,2)}}{\Omega^{(1,1)}} \qquad (45)$$

where the ratio between collision integrals is not too temperature dependent, so the influence of the value of ε^{LJ} is low.

The popular generalized chart of Slattery and Bird is based on the Enskog theory together with the Chapman-Enskog formulas (Bird et al., 1982; Mathur and Thodos, 1965; Stiel and Thodos, 1965). bg (σ)/V was obtained from Eq. (41) and $g(\sigma)$ was calculated from Eq. (37) replacing η^E and η^0 with η^{real} and η^{LJ}, respectively. The generalized chart was compared with scarce data, but years later, when more experimental data were available, Takahashi (1974) tried to reapply the ideas of Slattery and Bird, and observed that the Enskog theory was unable to give good results.

Another example of Enskog's failure could be the method of Chung et al. to calculate viscosities and thermal conductivities (Reid et al., 1987). The formulas are similar to Eqs. (37) and (38), but the numerical constants are temperature dependent and g (σ) is replaced with empirically determined functions, that differ from viscosity to thermal conductivity.

3.2. The expression of Hippler et al.

This is an empirical interpolation between Chapman-Enskog and Stokes-Einstein (Hippler et al., 1984; Otto et al., 1984). In principle, it was only developed for binary diffusion:

$$\frac{kT}{\eta D} = \left(\frac{kT}{\eta D}\right)^{Stokes}\left[1 - \exp\left(-\frac{\dfrac{\rho kT}{\eta^{LJ}(\rho D)^{LJ}}}{\left(\dfrac{kT}{\eta D}\right)^{Stokes}}\right)\right] \tag{46}$$

3.3. CSP extension of Eq. (8)

Riazi and Witson (1993) expressed the ratio $\rho D/(\rho D)^{LJ}$ as a potential function of η/η^{LJ},

$$\frac{(\rho D)}{(\rho D)^{LJ}} = 1.07\left(\frac{\eta}{\eta^{LJ}}\right)^{-0.27-0.38\omega-(0.05-0.1\omega)P_r} \tag{47}$$

where ω is the Pitzer's acentric factor and P_r the reduced pressure ($=P/P_c$). The systems employed to develop this were methane, carbon dioxide and binary mixtures of hidrocarbons, but the authors claimed that the formula could be applied to other systems.

3.4. Equations of Funazukuri and coworkers

These two equations are based on relations between the Schmidt number at any condition (Sc) and the same adimensional number at atmospheric pressure (Sc^0)

$$Sc = \frac{\eta}{m\rho D} \tag{48}$$

Funazukuri et al. (1992) combined the Chapman-Enskog equations with the expressions of Dymond, and supposed that

$$\frac{Sc}{Sc^0} = \frac{Sc}{Sc^0}(\text{diluted gas}) + \frac{Sc}{Sc^0}(\text{dense gas}) \tag{49}$$

so for self-diffusion of CO_2 and CH_4

$$\frac{Sc}{Sc^0} - 1 \propto \frac{\left(\dfrac{V}{1.384V_0}\right)}{\left(\dfrac{V}{1.384V_0} - 1\right)^2} \frac{\Omega^{(2,2)}}{\Omega^{(1,1)}} \tag{50}$$

the proportionality constant was 2.18, but the right-side term had to be empirically elevated to the 1.12 power.

In 2000, they adjust self-diffusivities and binary diffusion coefficients at infinite dilution to the following formula (Funazukuri et al., 2003, 2004; Higashi et al., 1998, 2001; Kong et al., 2006):

$$Ln\left(\frac{Sc - Sc^0}{Sc^0}\right) = -4.92519817 + 54.5529385\left(\frac{V_0}{V}\right) - 245.231443\left(\frac{V_0}{V}\right)^2 +$$

$$+ 607.893924\left(\frac{V_0}{V}\right)^3 - 708.884016\left(\frac{V_0}{V}\right)^4 + 329.611433\left(\frac{V_0}{V}\right)^5 \tag{51}$$

In Eq. (51), the Schmidt number at atmospheric pressure was calculated as in a HS gas (the collision integrals were not considered).

The first problem of these formulas is that V_0 is temperature dependent, so predictive purposes are not considered. By way of example, for carbon dioxide

$$1.384V_0 = 4.452 \times 10^{-5} - 1.152 \times 10^{-7}T +$$

$$+ 2.749 \times 10^{-10} T^2 - 3.073 \times 10^{-13} T^3 + 1.29 \times 10^{-16} T^4 \tag{52}$$

3.5. Woerlee model

Woerlee (2001) started from the kinetic theory of gases and from the Eyring theory for liquids, supposing that the mean free path for self-diffusion is not the same for viscosity.

$$D = \frac{1}{3\pi\rho(\sigma^{eff})^2} \sqrt{\frac{3kT}{m}} \exp\left(-\frac{\Delta G_D}{RT}\right) \tag{53}$$

$$\eta = \frac{m\rho}{3}\left[\frac{1}{\pi\rho\,(\sigma^{eff})^2} + (\sigma^{eff})\right]\sqrt{\frac{3kT}{m}} \exp\left(\frac{\Delta G_\eta}{RT}\right) \tag{54}$$

and if the activation energy for self-diffusion is equal to the viscosity activation energy, then

$$D = \frac{3kT\left(1+\dfrac{3b}{2V}\right)}{9\pi^2\eta(\sigma^{eff})^4} \frac{V}{N_{av}} \tag{55}$$

The effective diameter is calculated as an exponential interpolation between de hard-sphere diameter (high densities) and the gaseous particle diameter, which Woerlee assumed to be $\sigma\sqrt{1+T_c/T}$,

$$\sigma^{eff} = \sigma + \left[\frac{1}{2} + \frac{1}{2}\tanh\left(\frac{V}{b} - \frac{V_c}{b}\right)\right]\left(\sqrt{1+\frac{T_c}{T}} - 1\right)\sigma \tag{56}$$

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b is the same as in Enskog's formulas, and the molecular diameter can be taken as the LJ diameter. The model attempts to be general, applicable to all types of substances, but the average deviation is 24%, and it can be probed (although Woerlee does not specify this) that Eqs. (55) and (56) do not reproduce the low density limit defined by Chapman-Enskog equations.

4. Theory for LJ Chain fluids

4.1. Self-diffusion and viscosity in the LJ fluids

Alder et al. (1970) were the first to calculate numerical corrections to Eqs. (36-38) using computer simulations, the same as Dymond used to develop Eqs. (16) and (17). The corrections were given as three density-dependent factors, F_D, F_η and F_κ which multiply the avobe-mentioned Eqs. (36-38). Their effects can be seen in Fig. 1. As long as the Enskog formulas represent viscosity and thermal conductivity with good accuracy to high reduced densities (the numerical factors do not deviate much from the unity), the failure in self-diffusion begins at low densities.

The resulting equations can be combined with the translational-rotational coupling parameters of Chandler (1975) and effective diameters to obtain

$$D^{RHS} = A_D D^{SHS} = \frac{3A_D}{8(\sigma^{eff})^2 \rho} \sqrt{\frac{kT}{\pi m}} \frac{F_D(\rho^*)}{g(\sigma^{eff})} \tag{57}$$

$$\eta^{RHS} = A_{\eta}\eta^{SHS} = \frac{5A_{\eta}}{16(\sigma^{eff})^2}\sqrt{\frac{mkT}{\pi}}\left[\frac{1}{g(\sigma^{eff})}+1.6755\rho*+3.3381\rho*^2\ g(\sigma^{eff})\right]F_{\eta}(\rho*)$$

(58)

$$\rho* = \rho(\sigma^{eff})^3 \tag{59}$$

If the temperature dependence of molecular diameter and rotational-coupling parameters is known, Eqs. (57) and (58) can be employed to correlate self-diffusivities and viscosities of real substances. Furthermore, Eq. (59) can describe computer simulation data of dense and dilute LJ fluids if the following dependences are assumed (Bachl et al., 1992):

$$A_D = \exp\left(-\frac{\varepsilon^{LJ}}{2kT}\right) \tag{60}$$

$$\sigma^{eff} = \sigma^{LJ}\left(\frac{2}{1+\sqrt{(1+2kT/\varepsilon^{LJ})}}\right)^{1/6} \tag{61}$$

$$F_D(\rho*) = g(\sigma^{eff})\left(1-\frac{\rho*}{1.09}\right)\left[1+0.4\rho*^2-0.83\rho*^4\right] \tag{62}$$

Eq. (62) is not based on the work of Alder et al. (1970) but on the molecular simulation of Easteal et al. (1983), which differs in some ways from the first one. The high-density results of Woodcock and Angell (1981) were also taken into account, which stipulate that at $\rho*=1.09$ the self-diffusion coefficient is zero. As simple real fluids are in good aproximation to LJ fluids, Bachl et al. (1992) applied Eqs. (57) and (60-62) to correlate them, using σ^{LJ} and

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ε^{LJ} as fitting parameters. Surprisingly, the results were good for long-chain alkanes and polar compounds; not only monoatomic and apolar substances were well correlated.

4.2. The Ruckenstein-Liu model for LJ fluids

Ruckenstein and Liu (1997) proceeded as Bachl et al., using a RHS equation for correlating self-diffusivities of real substances. Nevertheless, they used the data of Alder et al. instead of the data points of Easteal et al., and did not introduce the effect of attractive forces in the coupling parameter, but started from Eq. (1), assuming that the friction coefficient is the sum of an HS friction coefficient and an attractive friction coefficient.

$$D = \frac{kT}{\xi^{HS} + \xi^{att}} = \left[\frac{1}{D^{HS}} + \frac{1}{D^{att}} \right]^{-1} \tag{63}$$

$$D^{HS} = \frac{kT}{\xi^{HS}} = D^0 \frac{F_D(\rho*)}{g(\sigma)} \tag{64}$$

$$D^{att} = \frac{kT}{\xi^{att}} = D^0 \frac{(T*)^4}{0.4} \tag{65}$$

To make Eq. (63) valid for LJ fluids, they replace the molecular diameter with the effective diameter. There are two fitting parameters: A_D and σ^{LJ}, because ε^{LJ} is calculated with the empirical formula of Chung et al. (Reid et al., 1987). The coupling parameter is now constant, because it does not include the attractive forces, and only captures the influence of molecular geometry. For noble gases and methane $A_D = 1.00$,

$$D = \frac{A_D kT}{\frac{8}{3}\rho(\sigma^{eff})^2(\pi mkT)^{1/2}\left[\dfrac{g(\sigma^{eff})}{F_D(\rho^*)} + \dfrac{0.4}{(T^*)^{1.5}}\right]} \tag{66}$$

$$\sigma^{eff} = 1.1532\sigma^{LJ}\left[1+\left(\frac{T^*}{0.527}\right)^{1/2}\right]^{-1/6} \tag{67}$$

$$F_D(\rho^*) = 1 + 0.94605\rho^{*1.5} + 1.4022\rho^{*3} - 5.6898\rho^{*5} + 2.6626\rho^{*7} \tag{68}$$

Eq. (68), as Eq. (62) is zero near the value of $\rho^*=1.09$.

4.3. The Yu-Gao model for LJ Chain fluids

The Lennard-Jones Chain (LJC) fluid model of Yu and Gao (1999) is an improvement of Eq. (66). Yu and Gao used the molecular dynamics simulations of Smith et al. (1995) to treat the molecules as chains of tangent hard spheres, with two other fitting parameters: N (the number of spheres) and σ_N^{LJ} (the diameter of each sphere). The total diameter is now $\sigma^{LJ}=N^{1/3}\sigma_N^{LJ}$, and $\sigma^{eff}=N^{1/3}\sigma_N^{eff}$,

$$D^* = \frac{D}{\sigma^{LJ}}\left(\frac{m}{\varepsilon^{LJ}}\right)^{1/2} = \frac{\sqrt{T^*}}{\frac{8}{3}\left(\dfrac{\sigma^{eff}}{\sigma^{LJ}}\right)^2 \rho^*\left[\dfrac{g(\sigma^{eff})}{F_D(N,\rho^*)} + \dfrac{0.4}{(T_N^*)^{1.5}}\right]} \tag{69}$$

$$\sigma_N^{eff} = 1.1532\sigma_N^{LJ}\left[1+\left(\frac{T_N*}{0.527}\right)^{1/2}\right]^{-1/6}$$ (70)

$$Ln\left[\frac{F_D(N,\rho*)}{F_D(\rho*)}\right] = -0.06356(N-1)-\left[0.05212\left(\frac{N-1}{N}\right)+1.9709\left(\frac{N-1}{N}\right)^2\right]\rho*$$

(71)

$$T_N* = kT/\varepsilon_N^{LJ}$$ (72)

$$\frac{\varepsilon_N^{LJ}}{k} = \frac{\varepsilon^{LJ}/k}{N}$$ (73)

$F_D(N,\rho*)$ is the correction of Smith et al. to the Enskog theory for HS Chain fluids, and the radial distribution employed is given by Eq. (40). As in the Yu-Gao formula the coupling factor disappears, it could be interesting to develop a model for viscosity based on LJ Chain fluids and on Eq. (58) to operate like Dymond, obtaining N and σ_N^{LJ} from η.

Yu and Gao (2001) also extended their model to associated fluids with four fitting parameters

$$D = D^{nhb}\exp\left[-\frac{5303.8N^{1/2}(1-X^\alpha)}{RT}\right]$$ (74)

D^{nhb} is the self-diffusion coefficient obtained from Eq. (69) and X^α the mole fraction of molecules not bonded at association site α. This mole fraction is taken from the Statistical Association Fluid Theory of Huang and Rasdoz (1990),

$$X^{\alpha} = \frac{1}{1 + \sum_{\beta} \rho X^{\beta} I^{\alpha\beta}}$$

(75)

$$I^{\alpha\beta} = g(\sigma_N^{eff}) \left[\exp\left(\frac{E_N^{hb}}{RT}\right) - 1 \right] (\sigma_N^{eff})^3 \theta_N^{hb}$$

(76)

$I^{\alpha\beta}$ is the association strength between the sites α and β, and is a function of an specific energy E^{hb} and a bond volume $(\sigma_N^{eff})^3 \theta_N^{hb}$. For alcohols and hydrogen fluoride, the association strength is given by

$$X^{\alpha} = \frac{-1 + (1 + 4\rho I)^{1/2}}{2\rho I}$$

(77)

and for water

$$X^{\alpha} = \frac{-1 + (1 + 8\rho I)^{1/2}}{4\rho I}$$

(78)

4.4. Proposed model for viscosity of HS Chain fluids and LJC fluids

On the basis of Eq. (63), the treatment of the friction coefficient is assumed to be applicable to viscosity. In this way, viscosity will be a sum of an attractive term and a repulsive term

$$\eta = \eta^{att} + \eta^{HS}$$

(79)

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$$\eta^{HS} = \eta^0 \left[\frac{1}{g(\sigma)} + 1.6755\rho* + 3.3381\rho*^2 \, g(\sigma) \right] F_\eta(\rho*) \tag{80}$$

and for LJ fluids

$$\eta = \frac{5}{16(\sigma^{eff})^2} \sqrt{\frac{mkT}{\pi}} \left[\frac{\eta^{att}}{\eta^0} + \frac{\eta^{HS}}{\eta^0} \right] \tag{81}$$

When the fluid is a sphere, and $\rho* \to 0$, Eqs. (66) and (69) become the Chapman-Enskog expression

$$D = D^0 \frac{\left[1 + \left(\frac{T*}{0.527} \right)^{1/2} \right]^{2/6}}{1.1532^2 \left[1 + \frac{0.4}{(T*)^{1.5}} \right]} = D^0 \frac{\left[1 + \left(\frac{T*}{0.527} \right)^{1/2} \right]^{2/6}}{1.1532^2 \left[1 + \frac{D^0}{D^{att}} \right]} = \frac{D^0}{\Omega^{(1,1)}} \tag{82}$$

Analogously, taking the effective diameter for viscosity and the low-density limit, the attractive part of Eq. (81) could be written as

$$\frac{\eta_{att}}{\eta^0} = \frac{1.1532^2}{\Omega^{(2,2)}} \left[1 + \left(\frac{T_N*}{0.527} \right)^{1/2} \right]^{-2/6} - 1 \tag{83}$$

For the HS part of Eq. (81), the molecular dynamics simulation data of Sigurgeirsson and Heyes (2003) have been taken for $F_\eta(\rho*)$ and the data of Smith et al. (1995) have been used to obtain $F_\eta(N,\rho*)$. The first two authors carried out computer simulations for F_D, F_η and F_κ

in the range 0.19<ρ*<1.06, which had been never done before. Until then, all data were restricted to ρ*<0.943. Nevertheless, the point at 1.06 is too high and is no compatible with experimental data. So, the extrapolation of Assael et al. (1992) has been chosen for 1.04<ρ*<1.09. Assael and coworkers adjusted F_η to a polynomial expression, and extended the avobe curve ρ*>0.943 with the help of experimental viscosities of n-alkanes. Moreover, the curve of Assael et al. coincides very well with the data of Sigurgeirsson and Heyes in the range 0.943<ρ*<1.04 as can be seen in Fig. 2. So, for HS fluids composed by spheres (not chains of spheres), we have fitted the data to

$$F_\eta(\rho*) = \exp\left\{\frac{1}{35.06 + 9.37\rho* + 173.55\rho*^2 - 849.665\rho*^3 + 974.876\rho*^4 - 342.33\rho*^5}\right\}$$

(84)

The polynomial expression of Assael can not be directly taken because it is not valid for low reduced densities (ρ*<0.1). The AAD of Eq. (84) for both data series of Sigurgeirsson-Heyes and Assael et al. in the range 0.0<ρ*<1.09 is 2.2%.

When chains are considered, the following expression together with Eq. (80) and σ =$N^{1/3}\sigma_N$ correlates the data of Smith et al. (1995) with an AAD of 4.8%, as can be seen in Fig. 3.

$$F_\eta(N,\rho*) = \left[1 + 0.489(N-1) + 0.014(N-1)^2\right]\rho*^{\left[\frac{N-1}{1.7287N - 1.151(N-1)}\right]} F_\eta(\rho*)$$

(85)

So, combining Eqs. (81), (83) and (85), the "complementary" of the Yu-Gao equation for viscosity in LJC fluids is

$$\eta^* = \frac{\eta(\sigma^{LJ})^2}{(m\varepsilon^{LJ})^{1/2}} = \frac{5}{16}\sqrt{\frac{T^*}{\pi}}\left\{\frac{1.1532^2}{\Omega^{(2,2)}}\left[1+\left(\frac{T_N^*}{0.527}\right)^{1/2}\right]^{-2/6}-1\right\}+$$

$$\frac{5}{16}\sqrt{\frac{T^*}{\pi}}\left\{\frac{1}{g(\sigma^{eff})}+1.676\rho^*+3.338\rho^{*2}\ g(\sigma^{eff})\right\}F_\eta(N,\rho^*)$$

(86)

Eq. (86) can be compared with simulation data of LJ viscosities when N=1.00. For example Meier et al. (2004a, b) and Galliero et al. (2005) performed these simulations in the ranges 0.0<ρ^*<1.275 and 0.6<T^*<6.0. The global AAD is 8.11%, although at high densities the errors are higher.

Finally, the extension of this model for hydrogen-bonding substances could be

$$\eta = \eta^{nhb}\exp\left[\frac{5303.8N^{1/2}\left(1-X^\alpha\right)}{RT}\right]$$

(87)

5. Results and discussion

The selected experimental data can be seen in Table 1. Table 2 shows the properties of these substances: all were obtained from the Korea thermophysical properties Data Bank (KDB, at website http://infosys.korea.ac.kr/kdb/), except for tetramethylsilane, which was

obtained from the databank of the software HYSYS. The molar volumes at melting point are from Lee and Thodos (1988) and from the handbook of Perry and Green (2001), except for 1,2-dichloroethane. For this compound, 278.15 K is the minimum temperature at which densities are available (Malhotra et al., 1990), the melting point being 237.6 K.

As the Eqs. (7), (9) and (27) can not be applied to dilute gases, we have combined these with the interpolation of Hippler et al. So, the term $(kT/\eta D)^{Stokes}$ of Eq. (46), which for self-diffusion should be equal to $2\pi\sigma^{LJ}$ (the Sutherland approach) is modified to give

$$\left(\frac{kT}{\eta D}\right)^{Stokes} = 2\pi\left(\frac{V}{N_{av}}\right)^{1/3} \quad \text{for Hippler et al. + Li-Chang} \tag{88}$$

$$\left(\frac{kT}{\eta D}\right)^{Stokes} = \frac{298.2}{C_2}k\eta^{C_1-1} \quad \text{for Hippler et al. + Davis et al.} \tag{89}$$

$$\left(\frac{kT}{\eta D}\right)^{Stokes} = \frac{1}{0{,}124.10^{-16}\rho V_c^{2/3}} \quad \text{for Hippler et al.+ Dullien} \tag{90}$$

The parameters σ^{LJ} and ε^{LJ} were calculated with the formulas of Chung et al. (Reid et al., 1987). The expressions of Funazukuri and coworkers were not employed because the sensitivity of both expressions to the molecular diameter: very small changes in the value of this parameter cause high increases in errors, like in self-diffusion or viscosity separately (Galliero et al., 2005; Ruckenstein and Liu, 1997). Results are shown in Table 3. The best equation is Eq. (88), closely followed by Eq. (90) and the original interpolation of Hippler et al. Besides, Eq. (88) reproduce the self-diffusion coefficients of water with relatively good

accuracy, as can be seen in Fig. 4. The introduction of the Davis et al. generalization of Eq. (8) makes the AAD of associated substances much worse, and its improvement is almost negligible except for *n*-hexane. The model of Woerlee systematically underestimates the low-density self-diffusivity and is only reasonably good for liquid tetramethylsilane and ethanol. The equation of Riazi and Whitson reflects a pressure dependence which is more pronounced than the real, and for some substances even predicts an increase in self-diffusion when the pressure rises. The failures of these two equations are shown in Figs. 5 and 6.

The results of using Eqs. (69) and (86) together can be seen in Tables 4 and 5. The AAD of obtaining N and σ_N^{LJ} from correlating self-diffusion coefficients of each substance and introducing them in the viscosity equation is reported in Table 3. When the number of spheres and the diameter of each sphere are obtained from viscosities and introduced in the Yu-Gao equation, the resulting AAD can be seen in Table 4. The characteristic parameters por hydrogen-bonding, E^{hb} and θ^{hb} do not vary. ε^{LJ}/k is calculated with the Chung's formula, except for water, in which ε^{LJ}/k =809.10 K. Neither the Yu-Gao model nor ours can be applied to methylcyclohexane. Predicting self-diffusivities from viscosities or vice versa is in general not to good, except for methane, xenon, methanol and ethanol. In the first two cases, this is not strange, because they are small, apolar and nearly spherical molecules, in which the sensivity fitting parameters is not great (Ruckenstein and Liu, 1997). Nevertheless, the good results for the two alkanols are unexpected. N and σ_N^{LJ} there are not true properties of molecules, but fitting parameters that vary from property to property.

Finally, there exist some incongruencies between the derived HST formulas and the self-diffusion coefficients in the middle-density range. Nevertheless, since available experimental data in this range are scarce, we have used LJ simulations (Galliero et al., 2005; Meier et al.,

2004a, b) which provide reduced self-diffusivities, D^*, and viscosities, η^*, over wide ranges of ρ^* and T^*. Eq. (46) can be written as

$$\frac{T^*}{\eta^* D^*} = 2\pi\sigma^* \left[1 - \exp\left(-\frac{64\rho^*}{15\sigma^*}\Omega^{(1,1)}\Omega^{(2,2)} \right) \right] \qquad (91)$$

where $\sigma^* = 1.00$ if the classical Stokes-Einstein approach is employed, $\sigma^* = (\rho^*)^{-1/3}$ if Li-Chang and $\sigma^* = 5.0176/(2\pi\rho^*)$ if Dullien.

In Figs. 7-9 some results are printing. Saturated vapours and liquids are represented in Fig. 10. As some diffusion coefficients are placed in the thermodynamic metaestable liquid-vapour biphasic zone, these have been rejected when saturated liquid and vapour densities were calculated with the formula of Okrasinski et al. (2001). In general, the predictions of Eq. (81) for ρ^*D^* worsen at elevated reduced temperatures, and only the combination of Hippler et al. with Li-Chang gives reasonable agreement (compare Fig. 8 with Figs. 7 and 9). The maximum deviation in the range $0.1 < \rho^* < 0.8$ concerns to original interpolation of Hippler et al., but it is notable that the Dullien equation overestimates the computer simulations near the freezing density at high values of T^*.

6. Conclusions

The performances of several equations connecting viscosity and self-diffusion coefficients have been studied, and a new correlative expression for viscosity has been developed. This expression employs two fitting parameters, that have the same meaning as those of the Yu-Gao model. Nevertheless, it was not possible to use the same values of these for the two transport properties.

In addition, the empirical equation of Hippler et al. has proved to be reasonably good for predicting diffusivities of all type of substances and LJ fluids, but it overestimates the group ρD at not very high densities, so some correction should be made in order to improve its results.

Symbols

A_D	coupling parameter for diffusion
A_η	coupling parameter for viscosity
b	second virial coefficient of the HS fluid, m^3/mol
B	second virial coefficient of a real fluid, m^3/mol
C_1, C_2	fitting constants
d	Dullien's length, m
D	diffusion, m^2/s
E_N^{hb}	specific energy of the hydrogen bonds, J /mol
f^{sek}	Sęk factor
F_A	force that acts on a particle A, N
F_D, F_K, F_η	corrections to Enskog theory
$g(\sigma)$	radial distribution function
ΔG_D	activation energy for diffusion, J /mol
ΔG_η	activation energy for viscosity J/mol
HS	hard-sphere
$I^{\alpha\beta}$	association strength between the sites α and β, m^3/mol
J_{AB}	sliding friction coefficient, kg/(m s)
k	Boltzmann constant= 1.380658×10^{-23} J/(K mol)
LJ	Lennard-Jones
m	molecular mass, kg/mol
M	molar mass, kg/mol
N	number of spheres that forms a molecule
N_{av}	Avogadro number

P	pressure, Pa
R	universal gas constant= 8.314 J/(K mol)
RHS	rough-hard-sphere
Sc	Schmidt number
SHS	smooth-hard-sphere
T	absolute temperature, K
v_A	velocity of the particle A, m/s
V	molar volume, m^3/mol
V^{free}	free volume, m^3/mol
V_0	close-packed volume, m^3/mol
X^α	mole fraction of molecules not bonded at association site α
Z	compressibility factor

Greek symbols

ε	molecular energy, J/mol
η	viscosity, kg/(m s)
θ_N^{hb}	proportionality factor of hydrogen-bond volume
ϑ	empirical fitting constants
κ	thermal conductivity, J/(s m^3 mol)
λ	length of a cell side, m
ξ	friction coefficient, kg/s
ρ	number density, particles/m^3
σ	molecular diameter, m

ω	acentric factor
$\Omega^{(n,n)}$	collision integral. When $n=1$ this refers to diffusion, and when $n=2$ this refers to viscosity.

Superscripts

*	molecular reduced parameter
0	low density
att	attractive forces
HS	Hard-Sphere
E	Enskog
eff	effective
min	minimum
nhb	non-hydrogen-bonding
real	refers to a real property
ref	reference
Stokes	refers to the Stokes-Einstein equation

Subscripts

f	freezing
c	critical conditions
r	reduced with respect to the critical point
N	relative to the number of spheres that form a molecule

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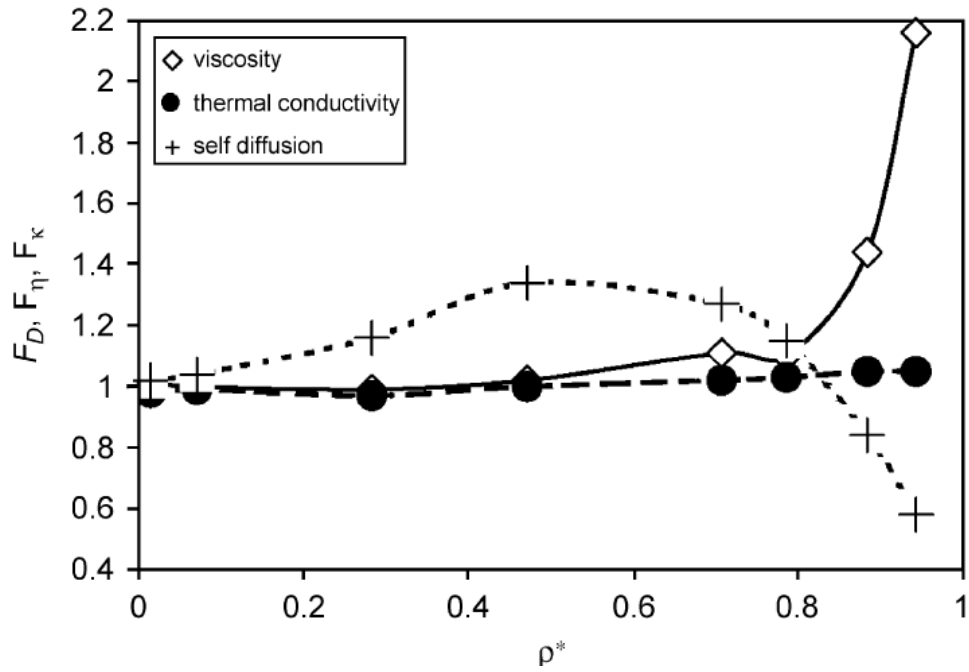
LIST OF THE CAPTIONS

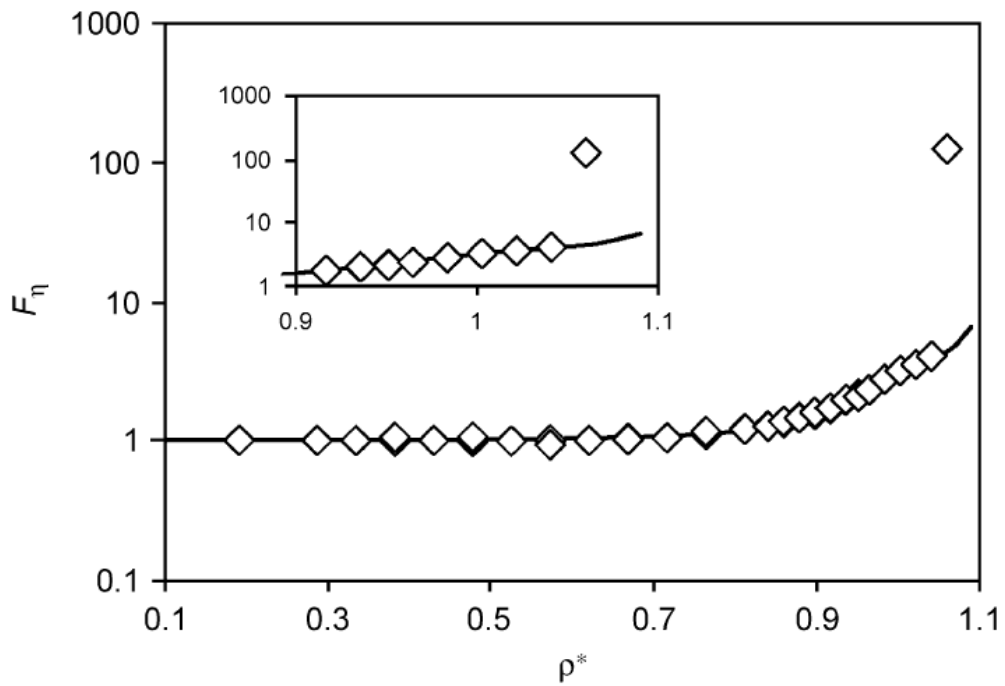Fig.1. Density-dependent corrections to Enskog equations.

Fig. 2. Density-dependent correction to Enskog viscosity according to Sigurgeirsson and Heyes, (symbols) Assael et al (solid line).
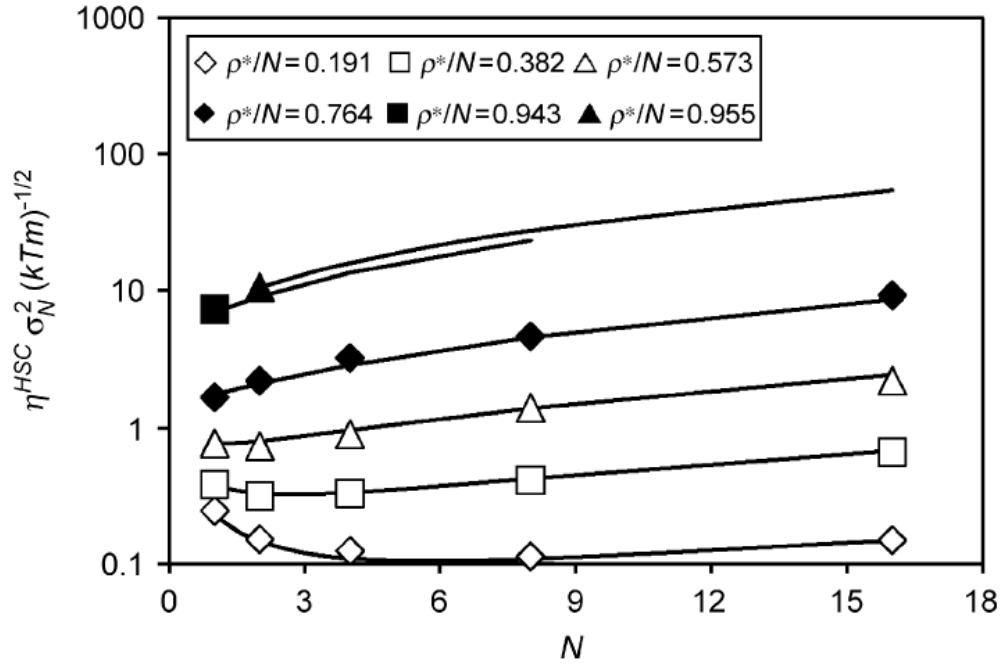
Fig. 3. Reduced viscosity of the hard-sphere chain fluids according Smith et al. Solids lines are calculated with (80) and (85).
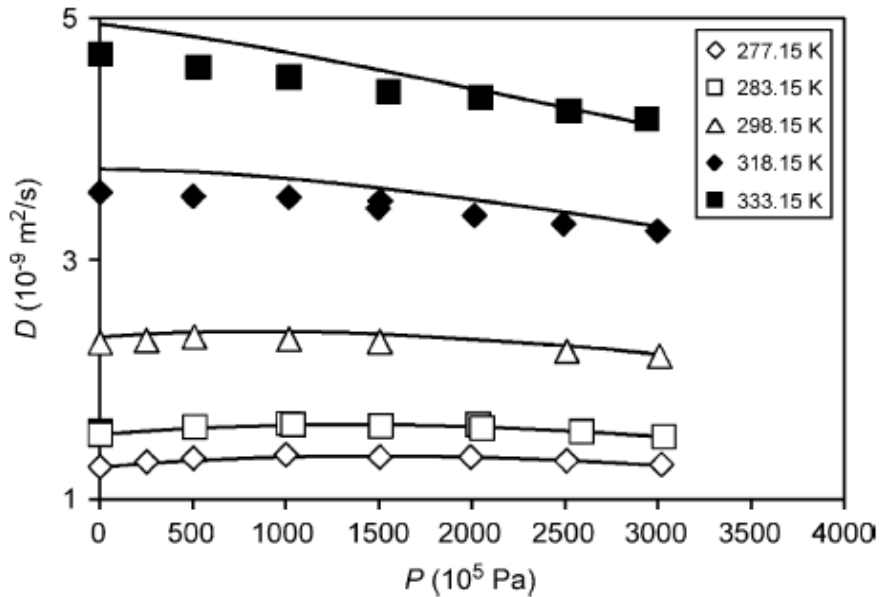

Fig. 4. Self-diffusion coefficients as a function of temperature and pressure for subcritical water. Solid lines refer to the results of Eq. (88); symbols refer to the experimental values.

Fig. 5. Self-diffusion coefficients as a function of temperature and pressure for perfluorocyclobutane. Solid lines refer to the results of the Woerlee model; symbols refer to the experimental values. The last temperature is above the critical.
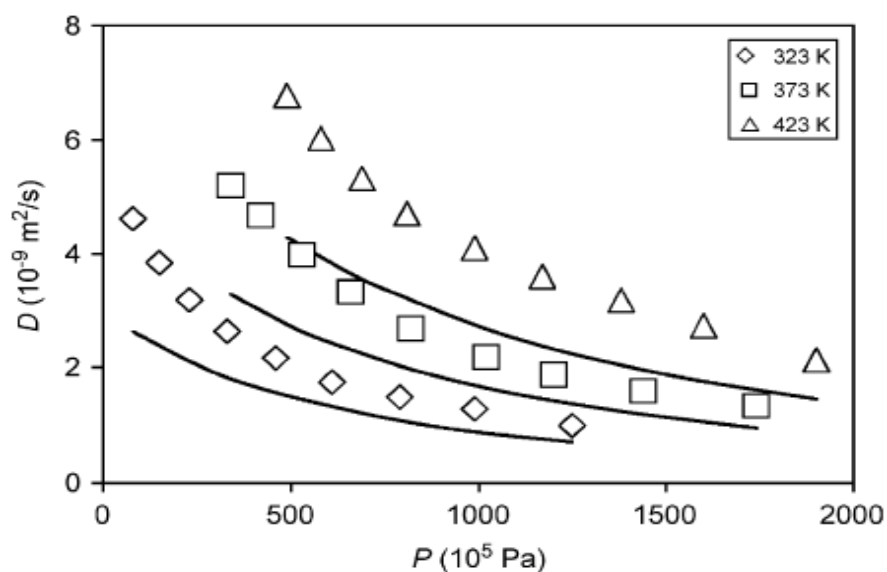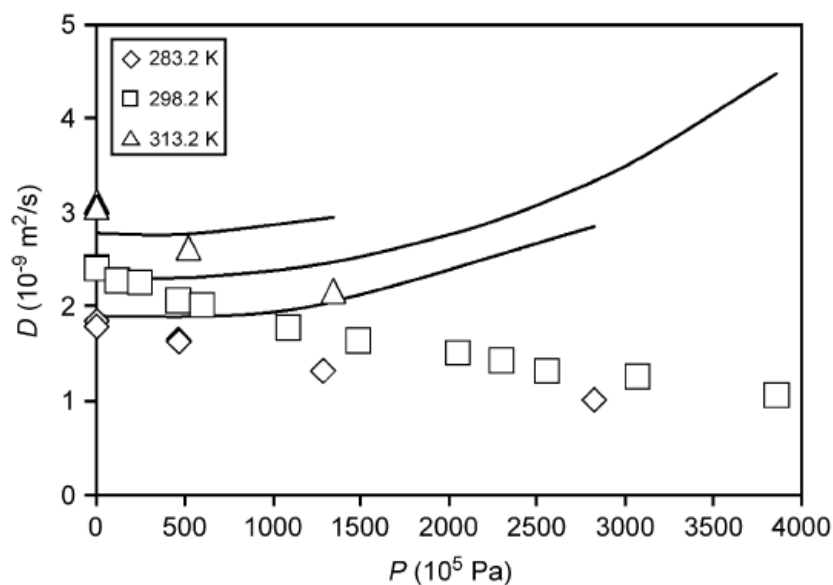

Fig. 6. Self-diffusion coefficients as a function of temperature and pressure for liquid methanol. Solid lines refer to the results of the Riazi-Whitson equation; symbols refer to the experimental values.
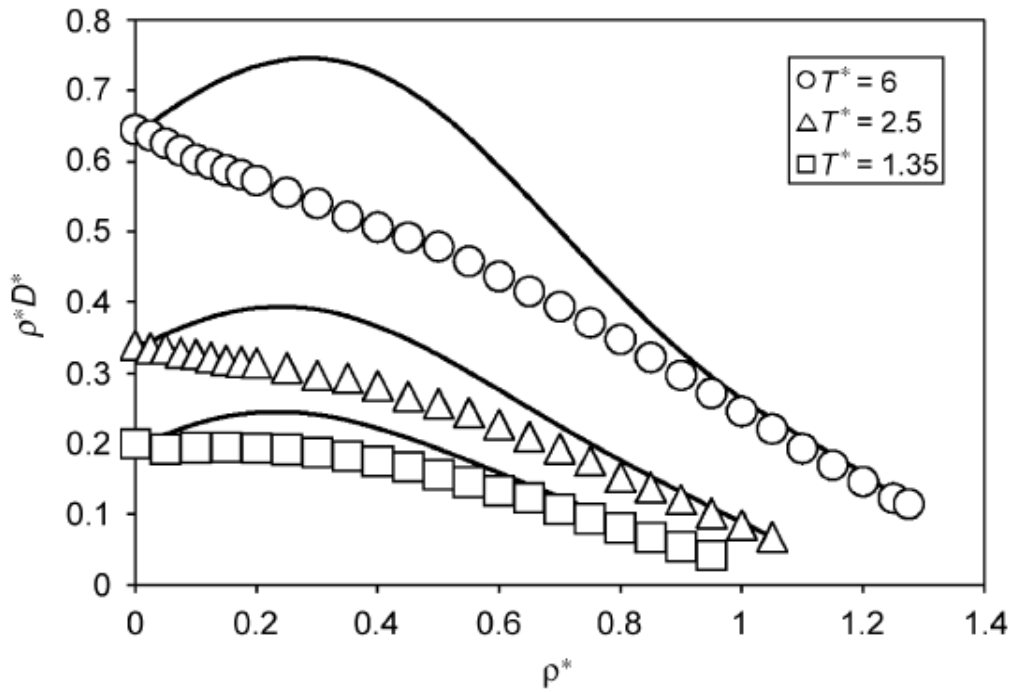
Fig. 7. ρ^*D^* from the molecular simulation of Meier et al. Solid lines are calculated with the original equation of Hippler et al.
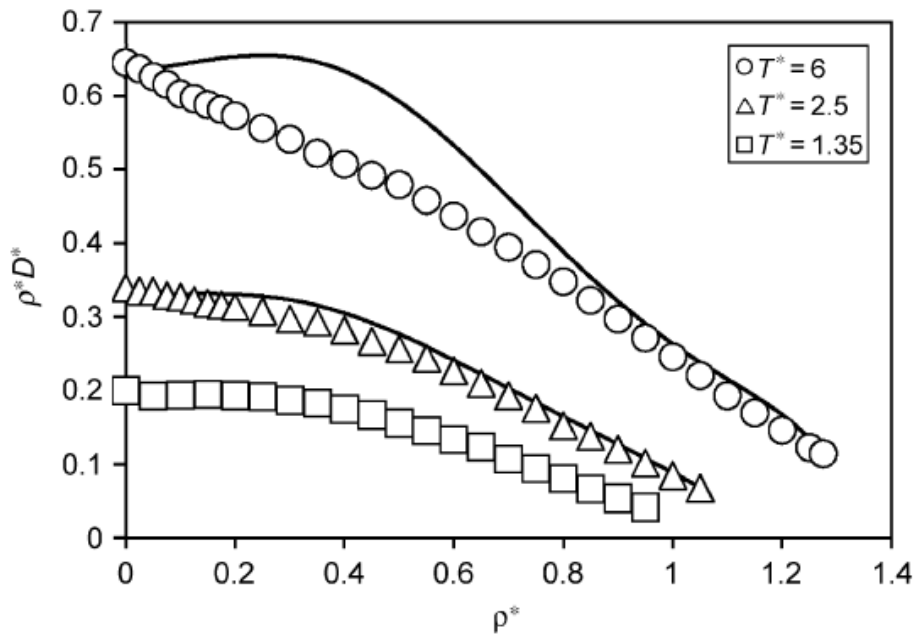
Fig. 8. ρ^*D^* from the molecular simulation of Meier et al. Solid lines are calculated with the combination of Hippler et al. and Li-Chang.

Fig. 9. ρ^*D^* from the molecular simulation of Meier et al. Solid lines are calculated with Hippler et al. +Dullien.
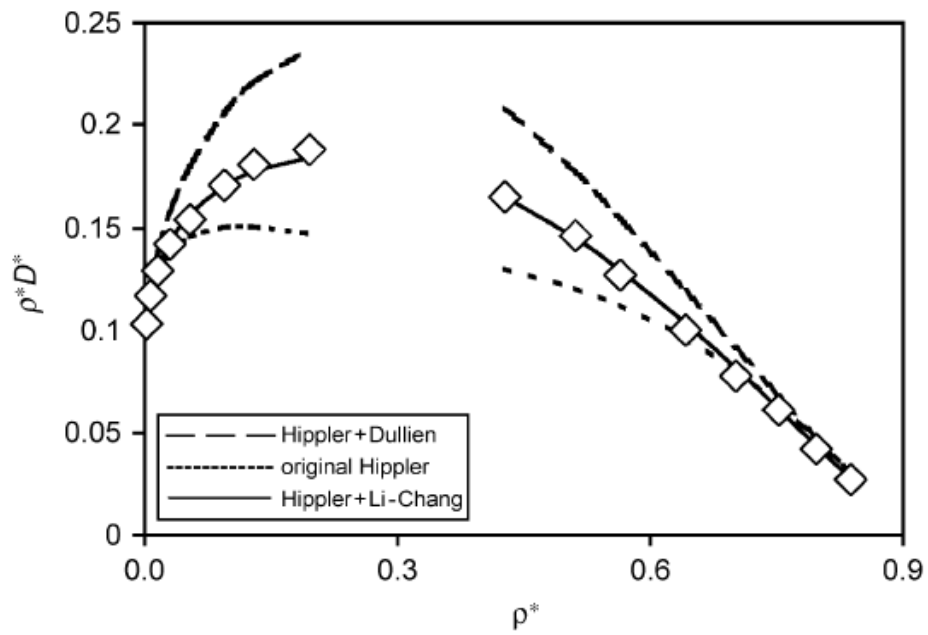
Fig. 10. ρ^*D^* from the molecular simulation of Meier et al. (symbols) along the saturation curve, and calculated with Hippler+Dullien, original Hippler, Hippler+Li-Chang.

LIST OF THE TABLES

Table 1
Selected compounds.

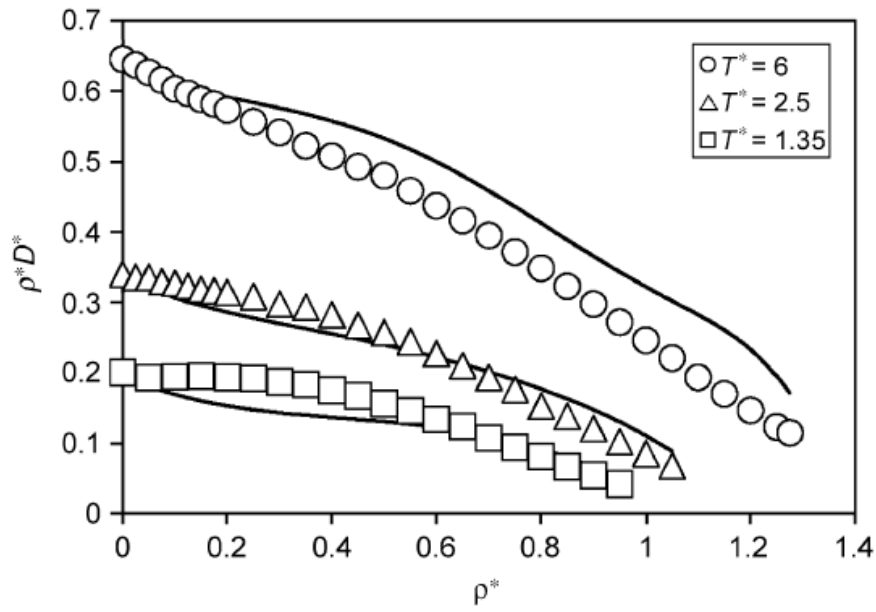| Substance	NDP	Fluid state	Sources of self-diffusion
Methane[a]	403	All fluid states	Greiner-Schmid et al. (1991) ; Harris and Trappeniers (1980); Harris (1978); Winn (1950) ; Naghizadeh and Rice (1962); Mueller and Cahill (1964); Dawson et al. (1970); Oosting and Trappeniers (1971); Helbæk et al. (1996); Gaven et al. (1962b); Rugheimer and Hubbard (1963)
Propane[b]	103	Saturated and compressed liquid, dense gas	Greiner-Schmid et al. (1991); Robinson and Stewart (1968)
n-Hexane	38	Saturated and compressed liquid	Harris (1982)
Cyclohexane	19	Compressed and saturated liquid	McCool and Woolf (1972a,b)
Methylcyclohexane	24	Compressed liquid	Jonas et al. (1979)
Benzene	74	Compressed and saturated liquid	McCool et al. (1972); Collings and Mills (1970); Parkhurst and Jonas (1975a)[c]
Pyridine	55	Saturated and compressed liquid	Fury et al. (1979)
Tetramethylsilane[c]	42	Compressed liquid	Parkhurst and Jonas (1975a)
Carbon tetrachloride	27	Compressed liquid	McCool and Woolf (1972b)
Trichlorofluoromethane	13	Compressed liquid, dense gas	DeZwaan and Jonas (1975)

1,2-Dichloroethane	23	Compressed liquid	Malhotra et al. (1990)
Perfluorocyclobutane	27	Compressed liquid, dense gas	Finney et al. (1977)
Xenon[d]	57	Saturated and compressed liquid, dense gas	Peereboom et al. (1989); Ehrlich and Carr (1970)
Water[e]	75	Compressed liquid, dense gas	Harris and Woolf (1980); Lamb et al. (1981)
Methanol[f]	35	Compressed and saturated liquid	Karger et al. (1990); Hurle et al. (1985)
Ethanol[f]	55	Compressed and saturated liquid	Meckl and Zeidler (1988); Karger et al. (1990)

[a] Viscosities calculated with the equation of Allal et al. (2001). If densities were not available in the same reference that self-diffusion coefficients, they were calculated with the equation of state of Harris and Trappeniers (1980) or Fang-Wieh (1973). For saturated liquid, densities were taken from the handbook of Perry and Green (2001).

[b] Viscosities calculated with the equation of Allal et al. (2001). Densities calculated with the corresponding states principle and the Hackinston-Brob-Thompson method as cited by Reid et al. (1987). For saturated liquid, densities were taken from the handbook of Perry and Green (2001).

[c] Viscosities obtained from Parkust and Jonas (1975b).

[d] Viscosities from Stephan and Lucas (1979) and the handbook of Perry and Green (2001). Densities from Michels et al. (1954) and from the aforesaid handbook.

[e] Viscosity of liquid water from Woolf (1975).

[f] Viscosity of methanol and ethanol from Meckl-Zeidler (1988). Densities from Cibulka and Zikova (1994).

Table 2
Properties of studied substances

Substance	Formula	T_c (K)	P_c (10^5 Pa)	V_c (10^{-6} m^3/mol)	M (10^{-3}kg/mol)	ω	V_f (10^{-6} m^3/mol)
Methane	CH_4	190.56	45.99	98.60	16.0426	0.01100	35.37
n-Propane	C_3H_8	369.83	42.48	200.00	44.0962	0.15300	60.28
n-Hexane	C_6H_{14}	507.60	30.25	368.00	86.1766	0.29900	113.45
Cyclohexane	C_6H_{12}	553.80	40.80	308.00	84.1608	0.21200	106.30
Methylcyclohexane	C_7H_{14}	572.10	34.80	369.00	98.1876	0.23600	110.89
Benzene	C_6H_6	562.05	48.95	256.00	78.1134	0.21200	87.31
Pyridine	C_5H_5N	620.00	56.70	243.00	79.1012	0.24300	75.79
Tetramethylsilane	$(CH_3)_4Si$	450.41	28.14	357.00	88.2200	0.22400	114.14
Carbon tetrachloride	CCl_4	556.60	45.16	276.00	153.8230	0.19300	91.96
Trichlorofluoromethane	CCl_3F	471.20	44.10	248.00	137.3680	0.18900	78.14
1,2-Dichloroethane	$C_2H_4Cl_2$	561.00	54.00	225.00	98.9596	0.27800	77.62
Perfluorocyclobutane	C_4F_8	388.46	27.84	324.00	200.0310	0.35600	117.77
Xenon	Xe	289.73	58.40	118.00	131.2900	0.00800	42.66
Water	H_2O	647.14	220.60	56.00	18.0152	0.34400	17.99
Methanol	CH_3OH	512.50	80.84	117.00	32.0420	0.55600	33.50
Ethanol	C_2H_5OH	514.00	61.37	168.00	46.0688	0.64400	48.42

Table 3
AAD (%) for several predictive equations

Substance	NDP	Eq. (46)	Eq. (47)	Eq. (55)	Eq. (88)	Eq. (89)	Eq. (90)
Methane	403	22.87	27.78	27.05	7.35	17.73	12.19
n-Propane	103	11.58	72.03	36.29	9.70	38.36	11.49
n-Hexane	38	32.68	82.27	55.47	32.82	20.18	31.13
Cyclohexane	19	9.32	48.81	40.84	12.14	8.59	15.25
Methylcyclohexane	24	30.93	93.69	56.98	30.03	63.68	26.17
Benzene	74	17.35	63.25	35.44	17.27	22.53	18.40
Pyridine	55	29.43	80.61	53.75	29.60	24.10	27.92
Tetramethylsilane	42	21.42	82.34	15.70	19.20	44.76	20.31
Carbon tetrachloride	27	6.52	68.72	30.79	4.66	51.86	4.85
Trichlorofluoromethane	13	19.07	67.27	36.43	23.16	20.84	30.37
1,2-Dichloroethane	23	6.47	63.51	37.41	6.41	49.83	5.94
Perfluorocyclobutane	27	8.02	70.16	31.63	11.85	16.17	18.96
Xenon	57	15.57	13.67	36.29	5.20	11.90	21.28
Water	75	7.67	28.84	38.96	3.93	167.66	14.26
Methanol	35	12.85	48.49	28.90	11.01	132.81	9.59
Ethanol	55	20.57	173.91	19.88	17.81	135.60	15.59
Overall	1070	18.88	54.00	32.94	11.89	43.96	15.51

Table 4

Correlation for self-diffusion with Eq.(69) and prediction for viscosity with the proposed model

Substance	N_{Diff}	$\sigma_N^{LJ}{}_{\text{Diff}}$ (10^{-10}m)	E_N^{hb}/R (K)	θ_N^{hb}	AAD_{Diff} (%)	AAD_{visc} (%)
Methane	1.077	3.570			7.66	6.80
n-Propane	2.578	3.411			9.59	28.23
n-Hexane	2.021	4.524			2.45	46.30
Cyclohexane	1.351	5.032			6.24	17.13
Methylcyclohexane	-	-			-	
Benzene	1.585	4.411			4.57	21.18
Pyridine	1.634	4.206			10.17	39.39
Tetramethylsilane	2.533	4.297			5.43	9.51
Carbon tetrachloride	2.017	4.236			2.72	15.64
Trichlorofluoromethane	1.800	4.232			1.88	27.55
1,2-Dichloroethane	2.300	3.770			4.48	28.57
Perfluorocyclobutane	1.102	5.510			4.50	15.46
Xenon	1.000	3.890			6.80	9.25
Water	1.000	2.530	3674.52	5.798×10^{-6}	8.46	26.44
Methanol	1.500	3.120	1080.42	3.142×10^{-2}	5.09	6.96
Ethanol	2.000	3.310	1560.13	1.095×10^{-2}	1.82	5.26
Overall					6.76	16.03

Table 5

Correlation for viscosity with Eq. (86) and prediction for self-diffusion with Eq. (69)

Substance	N_{visc}	$\sigma_N^{LJ}{}_{\text{visc}}$ (10^{-10}m)	E_N^{hb}/R (K)	θ_N^{hb}	AAD_{visc} (%)	AAD_{Diff} (%)
Methane	1.047	3.617			6.04	7.90
n-Propane	3.591	3.134			9.61	41.89
n-Hexane	5.041	3.503			2.38	54.61
Cyclohexane	2.216	4.359			4.98	31.80
Methylcyclohexane	-	-				
Benzene	2.510	3.857			16.3	28.74
Pyridine	3.424	3.418			9.64	52.90
Tetramethylsilane	3.022	4.090			4.17	15.85
Carbon tetrachloride	3.515	3.600			2.57	28.52
Trichlorofluoromethane	5.516	2.985			17.08	33.21
1,2-Dichloroethane	4.020	3.218			2.22	35.74
Perfluorocyclobutane	2.706	4.216			1.89	32.60
Xenon	1.000	3.980			5.09	11.65
Water	1.000	2.645	3674.52	5.798×10^{-6}	11.14	25.73
Methanol	1.214	3.388	1080.42	3.142×10^{-2}	3.30	6.89
Ethanol	1.456	3.726	1560.13	1.095×10^{-2}	2.02	8.00
Overall					6.95	21.09