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SELF-DIFFUSION COEFFICIENT PREDICTION IN LIQUIDS

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ABSTRACT

A semi-empirical equation for self-diffusion coefficient determination has been obtained using square well potential theory modified by a temperature correction function, $f = \exp(p + qT)$, where p and q are empirical constants. The proposed equation compares well in overall accuracy with the experimental data and other selected prediction methods over the complete range of investigation (13 compounds, 82 data point sets).

INTRODUCTION AND PERTINENT EARLIER WORK

Focusing around the ratio $D\eta/T$, where D is the self-diffusion coefficient, η is the coefficient of viscosity and T is temperature, K; an array of relations have been established between the self-diffusion coefficient, the viscosity and the density ρ of liquid (see references 5, 9, 14, 19, 20, 24—30, 33, 38—46, 50—52, 59, 60, 63, 68, 69, 77, 79, 80 and 84).

The oldest among these relations are those derived with the help of elementary hydrodynamic theory. Following the early work of Stokes [79], Fick [30], Nernst [63], Bassett [5], Einstein [24] and Sutherland [80], it is possible to obtain a connection between the diffusion coefficient of a solute, D_s, and the shear viscosity of a solvent, η_s, as

$$\frac{D_s\eta_s}{kT} = \frac{1}{6\pi a} \cdot \frac{1 + 3\eta_s/\beta a}{1 + 2\eta_s/\beta a} \tag{1}$$

where k is the Boltzmann constant, a is the radius of the diffusing molecules and β is the coefficient of sliding friction which depends on the size of the diffusing molecules, that is the magnitude of radius a. Since β has physical meaning only between the values of $\beta = 0$ and $\beta = \infty$, eqn. (1) yields the following two limiting cases:

(a) Fluid does not slip over the surface of the diffusing spherical molecule; hence $\beta = \infty$, and eqn. (1) reduces to

$$\frac{D_s\eta_s}{kT} = \frac{1}{6\pi a} \tag{2}$$

Relation (2) is the so called Stokes—Einstein equation. Since $\beta = \infty$, eqn. (2) should describe diffusion of large spherical molecules in solvents of much smaller molecules.

(b) Fluid slips completely over the surface of the diffusing spherical molecule. In this case, $\beta = 0$, and eqn. (1) yields

$$\frac{D_s \eta_s}{kT} = \frac{1}{4\pi a} \tag{3}$$

Because of the imposed complete slippage condition ($\beta = 0$), it is expected that eqn. (3) will correlate better for diffusing molecules which are slightly larger than or about equal to the solvent molecules. As a matter of fact, if solute and solvent molecules are of equal size we may assume that eqn. (3) is directly applicable for calculation of liquid self-diffusion coefficients *.

Li and Chang [50] set $2a = (V/N)^{1/3}$ in eqn. (3) and obtained the following relation to describe self-diffusion

$$\frac{D\eta}{kT} = \frac{1}{2\pi}\left(\frac{N}{V}\right)^{1/3} \tag{4}$$

where V is the molar volume of liquid and N is the Avogadro number. Li and Chang [50] suggested that eqn. (4) is valid for liquids whose structure is the simple cubic packing of spherical molecules, with all molecules just touching

On the other hand, the same functional form [eqns. (3) and (4)] follows from the principles of the absolute rate theory [35]. As a matter of fact, in its simplest form, the Eyring self-diffusion equation [35] is

$$\frac{D\eta}{kT} = \frac{\lambda_1}{\lambda_2 \lambda_3} \tag{5}$$

where λ_1 is the distance between two adjacent layers of the fluid molecules, while λ_2 and λ_3 are the distances between two neighbouring molecules in a layer perpendicular to and in the direction of motion If we set $\lambda_1 = \lambda_2 = \lambda_3$, then it can be proved that

$$\frac{\lambda_1}{\lambda_2 \lambda_3} = \left(\frac{N}{V}\right)^{1/3} \tag{6}$$

Putting eqn. (6) in eqn. (5), we have

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

Equation (7) gives values for the self-diffusion coefficient D which are too high by a factor 3π and 2π respectively when compared with eqns. (2)—(4). There has been a flurry of modifications proposed to remedy this situation; for instance, Li and Chang [50]. However, at this point it will suffice to note that while discussing the significant structure theory of liquids, Eyring and March [28] introduced the configurational factor ξ in eqn. (7), so that

$$\frac{D\eta}{kT} = \frac{1}{\xi}\left(\frac{N}{V}\right)^{1/3} \tag{8}$$

The introduced ξ-factor did bring the calculated self-diffusion coefficient

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* For critical discus regarding the validity of these equations, refer to references 19, 20, 25—27, 29, 33, 35, 39, 40, 42—46, 68 and 69.

values into better agreement with experimental data.

McLaughlin [59,60] reevaluated eqns. (3) and (4) for a series of liquids, and found that in these equations instead of the factor 2π one should use an empirical value of 2.035π (mean variation ±10%). Hence, eqns. (3) or (4) may be rewritten as

$$\frac{D\eta}{kT} = \frac{1}{2.035\pi}\left(\frac{N}{V}\right)^{1/3} \tag{9}$$

However, Dullien [20] having considered more systems and using slightly different values for D, η and a, found for the factor 2π an empirical value 1.9π as compared with the McLaughlin's value of 2.035π [eqn. (9)]. Lielmezs and Chan [52] obtained a value of 1.92π for the same factor: and so, using a much larger sample of experimental self-diffusion data over a range of temperature, affirmed Dullien's [20] finding.

Dullien [20] however considered this empirical value of $\leqslant 2\pi$ for liquids to be fortuitous and independent of the fact that the Stokes—Einstein formula [eqn. (3)] for $\beta = 0$ also contains 2π for the numerical coefficient *. Yet it appears to us that further work in checking the changes in the values of this averaged factor may be in order especially if interpreted in terms of liquid structure and measurable physical parameters **. Following Lamm's [42—46] theoretical work *** Dullien [19,20] proposed the following self-diffusion relation

$$\frac{D\eta V}{NkT} = 0.124 \times 10^{-16} V_c^{2/3} \tag{10}$$

where V_c is the critical molar volume.

Equation (10) through the group $D\eta V/NkT$ is temperature independent (assumption listed by Dullien [19]). However, subsequently, Dullien and coworkers [25,26] modified eqn. (10) to include temperature dependency as

$$\left(\frac{D\eta V}{NkT}\right)_{\min} = -1.42 + 0.152 V_c^{2/3} \tag{11}$$

subject to the condition

$$\left(\frac{D\eta V}{NkT}\right)_{\text{actual}} = \left(\frac{D\eta V}{NkT}\right)_{\min} \cdot \left(\frac{d}{d_{\min}}\right)^2 \tag{12}$$

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* It has been shown (Stokes [79], Ahn et al [4]; Ahn [3]) that considering the hydrodynamic fluid flow conditions, the radius of the diffusing molecule [eqns. (1)—(3)] is insensitive to the liquid structural packing arrangements, and that comparison with the experimental diffusion coefficient values favors the slip limit of $\beta = 0$ This of course indirectly supports the use of predictive relations such as eqn (9), and the notion that at least for the simple fluids, one indeed could use an empirical factor such as 1.92π (Lielmezs and Chan [52]) or for that matter, factor 2.035π, eqn. (9).

** Note the introduction of the configurational factor, ξ, by Eyring and March [28] in eqn. (8).

*** It is interesting to recall that friction coefficients found in Lamm's [42—46] theory are the reciprocal of the mobility in Nernst's work [63].

where d is the apparent molecular diameter, defined by Dullien [19] and Ertl and Dullien [25] as

$$d = 2.24\left(\frac{D\eta V}{RT}\right)^{1/2} \tag{13}$$

and d_{min} is the effective minimum molecular diameter of the fluid over a given temperature range [25]. The ration d/d_{min} is expressed in terms of the reduced temperature, $T_r = T/T_c$ (T_c is the critical temperature) as

$$\frac{d}{d_{min}} = 2.55 \times 10^{-3} T_r^{-4} + 0.35 T_r + 0.179 \tag{14}$$

Equations (11), (12) and (14) should prove especially useful for temperatures of $T_r < 0.46$ [25].

EQUATIONS DERIVED FROM HARD SPHERE AND SQUARE WELL MODELS

The simplest dense fluid is the hard sphere fluid. The hard sphere fluid is characterized only by repulsive forces, and so this fluid has only fluid—solid transition (i.e. melting point). The transport properties of this fluid depend only on the radial distribution function at the point of contact of the hard spheres. In this case, the assumption of pairwise additivity is exact, and the motion of hard spheres is described accurately by binary collisions, even at high densities. With respect to this background, and assuming that the spatial pair distribution function depends only on the temperature and density and that the velocity distribution function of a single particle is locally Maxwellian, Longuet-Higgins and Pople [54] developed an expression for the shear viscosity η_{hs}, given as

$$\eta_{hs} = \frac{4a}{3}\left(\frac{mkT}{\pi}\right)^{1/2}\left(\frac{P}{kT} - \frac{N}{V}\right) \tag{15}$$

where the subscript hs represents the hard sphere model, a is the radius of the diffusing hard sphere molecule, m is the mass of the sphere, and P is the pressure.

Assuming further that the auto-correlation function for the velocity of the particle decays exponentially, they derived also the coefficient of self-diffusion for hard spheres, given as

$$D_{hs} = \frac{a}{2}\left(\frac{\pi kT}{m}\right)^{1/2}\left(\frac{PV}{RT} - 1\right) \tag{16}$$

Combining eqn. (15) and (16), we have

$$\frac{D_{hs}\eta_{hs}}{kT} = \frac{2a^2}{5}\left(\frac{N}{V}\right) \tag{17}$$

If we let c be the fraction of the total volume occupied by the hard spheres, and if we assign the value $c = 5/9$, then eqn. (17) becomes

$$\frac{D_{hs}\eta_{hs}}{kT} = \frac{1}{6\pi a} \tag{18}$$

Equation (18) is of the same form as eqn. (2), the Stokes—Einstein relation with no slip condition over the surface of the diffusing molecule.

On the other hand, eqn. (17) may be rewritten as

$$\frac{D_{hs}\eta_{hs}V}{NkT} = \tfrac{2}{5}a^2 \tag{19}$$

Equations (19) and (10) are functionally similar since they both possess the same group $D\eta V/NkT$, equated to a constant which is characteristic of the given fluid. If we introduce the molecular hard sphere co-volume *, b_0, given as

$$b_0 = (\tfrac{16}{3})\ \pi N a^3 \tag{20}$$

$$b_0 = (\tfrac{16}{3}\ )\ \pi N a^3 = 2V_{NB}^{liq} = (2)(0.376)V_c \tag{21}$$

where V_{NB}^{liq} and V_c are the molar volumes of liquid at the normal boiling and at the critical points, respectively, then by using relations (20) and (21), we can transform eqn. (19) into

$$\frac{D_{hs}\eta_{hs}V}{NkT} = 0.070832 \times 10^{-16}V_c^{2/3} \tag{22}$$

Equation (22) was essentially derived by following hard sphere fluid arguments. It is, however, of interest to recall that Dullien [19] empirically first derived **

$$\frac{D\eta V}{RT} = 0.107 \times 10^{-16}V_c^{2/3} \tag{23}$$

and then refitted eqn. (23) to eqn. (10).

In order to calculate the values of η_{hs} and D_{hs} [eqns. (15). and (16)], we let pressure P be defined by the Percus—Yevick equation of state for hard sphere fluids [49,70] as

$$P_{hs} = \rho kT\frac{1+y+y^2}{(1-y)^3} \tag{24}$$

where $y = (\tfrac{1}{6}\pi)\rho\sigma^3$; ρ is the number density of the fluid and σ the collisional diameter given as $\sigma = 2a$ [for instance, see eqns. (15), (16) and (19)].

Comparative calculation of self-diffusion coefficients for liquid CH_4 at 95.2, 100.0, 106.1 and 110.5 K by means of eqns. (9), (10), (16) ***, (21) and (22) showed the following average percentage error with respect to the experimental values (Table 2: eqn. (9): 3.2%; eqn. (10): 5.6%; eqn. (16): 10.2%; eqn. (21): 42.2%, eqn. (22): 39.1%. The calculated self-diffusion

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* Note that the second virial coefficient is defined also as $B_2 = (16/3)\pi a^3$. Hence it is possible to prove that eqn. (17) is equivalent to the first approximation of the diffusion coefficient obtained by the Chapman and Enskog theory [54].

** For further information regarding eqns. (10) and (23) see the work by Vadovic and Colver [84] and the work of Tyn [83].

*** To obtain self-diffusion coefficient D_{hs} values [eqn. (16)], we calculated first η_{hs} (eqn. 15) values which were then substituted into eqn. 16. All these calculations were done on the basis of the pressure, P_{hs}, of the hard sphere fluid [eqn. (24)]

coefficient values for all of these equations showed very poor temperature dependency. It should be noted that eqns. (9), (10) and (16) showed the accuracy expected for the relatively symmetrical CH_4 molecule. On the other hand, eqns. (21) and (22) which were derived through the assumptions of the hard sphere model, could still be subjected to the empirical parameter-curve fitting adjustment techniques, and thus made more accurate [compare with eqn. (10), see also Dullien [19]; Ertl and Dullien [25]]. Additionally, eqn. (22) could be modified by means of empirically derived, temperature dependent correction functions. Whether this should be done with reference to the critical state properties [compare with eqns. (11), (12) and (14)] remains a question of further work [*].

As noted, the relations derived rigorously from the theory of hard sphere fluids [eqns. (15), (16) and (19)] do not reproduce satisfactorily the temperature dependence of the self-diffusion coefficient showing questionable agreement between theory and experiment (see for instance work by McCall et al [57], Douglas and Anderson [17], Kessler et al. [41]). As these equations represent assemblies of hard spheres with no attractive force interactions between constituent particles, they are in effect crude replicas of the real fluid, and so it is not surprising to find that these expressions provide rather a poor description of molecular transport in liquids. Longuet-Higgins and Valleau [55] recognized this, and replaced the hard sphere potential theory of Longuet-Higgins and Pople [54] by the more realistic square well potential model which in a rough way accounted for the attractive forces, which effect the transport properties at moderate densities of fluids. As such, the Longuet-Higgins and Valleau [55] extension of the hard sphere theory of Longuet-Higgins and Pople [54] is characterized by four types of binary collisions instead of binary collisions at the contact of the hard spheres. Even at that, the smooth sphere with the square well potential, in effect being a monatomic simple fluid, omits the effect of the rotational degree of freedom in the description of the diffusional process.

The zeroth order expressions for shear viscosity and self-diffusivity derived by Longuet-Higgins and Valleu [55] are given as

$$\eta^0_{\mathrm{SW}} = \tfrac{64}{15}(\pi m k)^{1/2}\left\{\alpha a^{*4} + \beta b^{*4}\,\Xi\left(\frac{\epsilon}{kT}\right)\right\} \tag{25}$$

$$D^0_{\mathrm{SW}} = \frac{3\rho}{32}\left(\frac{kT}{\pi m}\right)^{1/2}\left\{\alpha a^{*2} + \beta b^{*2}\,\Xi\left(\frac{\epsilon}{kT}\right)^{-1}\right\} \tag{26}$$

where superscript "0" = zeroth order: subscript SW = square well potential; m is the molecular mass; ρ is the number density of the fluid, a^* is the repulsive radius of the smooth sphere; b^* is the attractive radius of the smooth

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[*] While not discussed in this work, the Enskog theory of hard spheres (Chapman and Cowling [9], Longuet-Higgins and Pople [54], Dahler [14]) and the corrected form of Enskog's theory (Dymond [21—23], Van Loef [85]) via the method of molecular dynamics, yield expressions relating the exact self-diffusion coefficients for dense hard sphere fluids to the molar volume and hence temperature Van Loef [85] has shown that for several simple liquids the calculated values agree with the experimental self-diffusion coefficient values over a considerable temperature range.

sphere; ϵ is the depth of the attractive potential well; α, β are the particular values of the equilibrium pair number density in configurational space, ρ_2^0. The function Ξ is

$$\Xi\left(\frac{\epsilon}{kT}\right) = 1 - \left(\frac{\epsilon}{2kT}\right) \exp\left(\frac{-\epsilon}{kT}\right) + \left(\frac{\epsilon}{2kT}\right) \exp\left(\frac{-\epsilon}{2kT}\right) K_1\left(\frac{\epsilon}{2kT}\right) \tag{27}$$

where $K_1(\epsilon/2kT)$ is the modified Bessel function of the second kind.

To evaluate the required transport properties, one needs the molecular parameters of the square-well theory, a^*, b^* and ϵ, and the corresponding values of α and β of pair number density function. Indeed, eqns. (25), (26) and (27) represent the starting point of the many studies of application of the square well model to transport processes [8,15,16,56,64,72,73].

Proposed relations

The zeroth order approximation of square well potential [eqns. (25)—(27)] by Longuet-Higgins and Valleau [55] was extended to a higher order approximation by Davis et al. [16] who introduced a modified Maxwell—Boltzmann integro-differential equation valid for dense square well fluids interacting with the pair potential $V(r_{ij})$ as

$$\begin{aligned} V(r_{ij}) &= 0\,; & r_{ij} &> \sigma_2 \\ V(r_{ij}) &= -\epsilon\,; & \sigma_1 &< r_{ij} \leqslant \sigma_2 \\ V(r_{ij}) &= +\infty\,; & r_{ij} &\leqslant \sigma_1 \end{aligned} \tag{28}$$

where r_{ij} is the distance of separation of particles i and j, σ_1 is the hard sphere (or repulsive) diameter, σ_2 is the diameter measuring the range of the square well attraction, or the attractive diameter.

This Davis et al. [16] derived modification of the Maxwell—Boltzmann integro-differential equations was examined by Davis and Luks [15] who by means of an approximate pair correlation function obtained an expression for shear viscosity as

$$\eta_{\mathrm{SW}} = \frac{5}{16\sigma_1^2}\left(\frac{mkT}{\pi}\right)^{1/2}\left\{\frac{[1 + \frac{2}{5}b\rho(g(\sigma_1) + R^3 g(\sigma_2)\psi)]^2}{g(\sigma_1) + R^2 g(\sigma_2)[\Xi + \frac{1}{6}(\epsilon/kT)^2]}\right.$$
$$\left. + \frac{48}{25\pi}(b\rho)^2(g(\sigma_1) + R^4 g(\sigma_2)\,\Xi)\right\} \tag{29}$$

where $R = \sigma_2/\sigma_1$, $b = 2\pi\sigma_1^3/3$; ρ is the number density $g(\sigma_1)$ is the equilibrium radial distribution function for $r_{12} = \sigma_1 + 0$ (evaluated just inside the well). $g(\sigma_2)$ is the equilibrium radial distribution function for $r_{12} = \sigma_2 + 0$ (evaluated just outside the well).

The function ψ, however, is defined as

$$\psi = 1 - \exp\frac{\epsilon}{kT} + \frac{\epsilon}{kT}\left(1 + \frac{4}{\sqrt{\pi}}\exp\frac{\epsilon}{kT}\int_{(\epsilon/kT)^{1/2}}^{\infty} e^{-x^2}\,dx\right) \tag{30}$$

while function [Ξ] is given now [compare with eqn. (27)] as

$$\Xi = \exp \frac{\epsilon}{kT} - \frac{\epsilon}{2kT} - 2 \int_0^{\infty} x^2 \left(x^2 + \frac{\epsilon}{kT}\right)^{1/2} e^{-x^2}\, dx \tag{31}$$

To obtain the expression for the self-diffusion coefficient, Davis and Luks [15] used the results of Longuet-Higgins and Valleau [55] and rewrote eqn. (26) as

$$D_{\mathrm{SW}} = \frac{3}{8\rho\sigma_1^2} \left(\frac{kT}{\pi m}\right)^{1/2} [g(\sigma_1) + R^2 g(\sigma_2)\, \Xi]^{-1} \tag{32}$$

Luks et al. [56] have given the value of the ψ and Ξ functions [eqns. (30) and (31)] in terms of the arguments (ϵ/kT) and $(\epsilon/kT)^{1/2}$. Using the given argument values [56], we expressed the functions ψ and Ξ as polynomials in their own arguments, and by means of least squares curve fitting techniques, obtained

$$\begin{aligned} \psi = {} & -4.07238 \times 10^{-1} \pm 5.42382 \times 10^{-3} \left[\left(\frac{\epsilon}{kT}\right)^{1/2}\right] \\ & -3.25477 \times 10^{-2} \pm 2.14225 \times 10^{-4} \left[\left(\frac{\epsilon}{kT}\right)^{1/2}\right]^{10} \end{aligned} \tag{33}$$

$$\begin{aligned} \Xi = {} & 7.53430 \times 10^{-10} \pm 8.12495 \times 10^{-4} \left(\frac{\epsilon}{kT}\right)^{2} \\ & + 9.86055 \times 10^{-2} \pm 4.11847 \times 10^{-4} \left(\frac{\epsilon}{kT}\right)^{4} \\ & + 2.51934 \times 10^{-3} \pm 4.91302 \times 10^{-5} \left(\frac{\epsilon}{kT}\right)^{6} \end{aligned} \tag{34}$$

The variance for the given function is 1.75×10^{-5} for eqn. (33) and 2.95×10^{-4} for eqn. (34). To estimate the values of $g(\sigma_1)$ and $g(\sigma_2)$ we used the now classical perturbation method as developed by Davis et al. [16] and their co-workers [15,56,64]. Following this work, we assumed that the pair potential energy can be separated into two contributions

$$V(r) = V^{(0)} = V^{(1)} \tag{35}$$

where $V^{(0)}$ is the unperturbed potential energy and $V^{(1)}$ is the perturbation potential energy and r is r_{ij} with indices ij dropped. Equation (35) is subject to the following restraints

$$V^{(0)} = \begin{cases} 0 & r > \sigma_1 \\ \infty & r \leqslant \sigma_1 \end{cases} \tag{36}$$

$$V^{(1)} = \begin{cases} 0 & r > \sigma_2 \\ -\epsilon & \sigma_1 < r \leqslant \sigma_2 \\ 0 & r \leqslant \sigma_1 \end{cases} \tag{37}$$

and $V^{(1)}$ is limited through the condition that $V^{(1)} < kT$. Luks et al. [56] then approximate the perturbed pair correlation function $g(r)$ as

$$g(r) \simeq g^{(0)}\, e^{-\beta V(r)} \tag{38}$$

where $g^0(r)$ is the pair correlation function for particles interacting in accordance with the unperturbed (hard sphere) potential $V^{(0)}$ and β is the Boltzmann factor. In view of this, Luks et al [56] approximated the constant value of $g(\sigma_1)$ as

$$g(\sigma_1) = g^0(\sigma_1)\, e^{\epsilon/kT} \tag{39}$$

The value of $g^0(\sigma_1)$ has been given by Lebovitz [49] as

$$g^0(\sigma_1) = \frac{1 + \frac{1}{2}y}{(1-y)^2} \tag{40}$$

where $y = \pi/6\rho\sigma_1^3$ [compare with eqn. (24)].

The values of $g^0(\sigma_1)$ have been obtained by Throop and Bearman [82] who numerically evaluated Wertheim's [86] exact solution of the Percus—Yewick equation [49,70]. The agreement is excellent with a maximum difference less than 0.005%. On the other hand, the values of $g(\sigma_2)$ are more difficult to evaluate. Brown and Davis [8] assumed that $g(\sigma_2)$ is unity. However, for compounds such as n-heptane, where $R = \sigma_2/\sigma_1 = 1.314 < 1.70$, and $\rho\sigma_1^3 > 0.7$ (Hirchfelder et al. [39]), it is seen (Table 1, Throop and Bearman [82]) that the value of $g(\sigma_2)$ is far from unity. To resolve this difficulty, we express the values of $g(\sigma_2)$ in terms of the viscosity, η_{SW}, from eqn. (29). To do this, first note that Luks et al. [56] proposed the intermolecular contribution of the viscous transport process to be

$$\eta_V = A\left\{\frac{48}{25\pi}(b\rho)^2[g(\sigma_1) + R^4 g(\sigma)\,\Xi]\right\} \tag{41}$$

where

$$A = \frac{5}{16\sigma_1^2}\left(\frac{mkT}{\pi}\right)^{1/2}$$

Defining

$$B = \frac{48}{25\pi}(b\rho)^b \tag{42}$$

and putting relation (42) in eqn. (41), we have

$$\eta_V = A\,\{B[g(\sigma_1) + R^4 g(\sigma_2)\,\Xi]\} \tag{43}$$

The pair correlation function, $g(\sigma_2)$ now can be obtained as a first approximation from eqn. (43) by means of a parameter α^*, defined as

$$\alpha^* = R^2 g(\sigma_2)\,\Xi = \left(\frac{\eta_V}{A\cdot B} - g(\sigma_1)\right)/R^2 \tag{44}$$

TABLE 1

Square-well potential parameters

Compounds	σ (Å)	R	ϵ/k (K)	References
Neon	2 382	1.870	19 5	39
Argon	3 067	1.700	93.3	76
Krypton	3.278	1 680	136 5	76
Xenon	3.593	1.640	198 5	75
Carbon monoxide [a]	3 290	2.270	91.0	39
Ammonia	2 902	1 268	692 0	39
Water	2.606	1.199	1260 0	39
Methane	3 355	1.600	142 5	76
Ethane	3.535	1 652	244.0	39
n-Pentane	4.668	1 360	612.3	76
n-Heptane	6.397	1.314	629.0	39
Neopentane	5 422	1.450	382.6	76
Benzene	4.830	1.380	620.4	76

[a] From viscosity data

Putting α^* (eqn. 44) in eqn. (29), we have

$$\eta_{SW} = \frac{5}{16\sigma_1^2}\left(\frac{mkT}{\pi}\right)^{1/2}\left\{\frac{(1 + \frac{2}{5}b\rho[g(\sigma_1) + (R\alpha^*\psi/\Xi)])^2}{g(\sigma_1) + \alpha^* + (\alpha^*/\Xi)[\frac{1}{6}(\epsilon/kT)^2]} + \frac{48}{25\pi}(b\rho)^2[g(\sigma_1) + R^4 g(\sigma_2)\,\Xi]\right\} \tag{45}$$

If we identify parameter C as

$$C = \frac{(1 + \frac{2}{5}b\rho[g(\sigma_1) + (R\alpha^*\psi/\Xi)])^2}{g(\sigma_1) + \alpha^* + (\alpha^*/\Xi)[\frac{1}{6}(\epsilon/kT)^2]} \tag{46}$$

then we can rewrite eqn. (45) in terms of parameters as

$$\eta_{SW} = A\{C + B[g(\sigma_1) + R^4 g(\sigma_2)\,\Xi]\} \tag{47}$$

The entity $R^2 g(\sigma_2)\,\Xi$ can be refined through eqn. (47) as a new parameter γ

$$R^2 g(\sigma_2)\,\Xi = \left\{\frac{[(\eta_{SW}/A) - C]}{B} - g(\sigma_1)\right\}/R^2 = \gamma \tag{48}$$

Equation (48) contains the square well shear viscosity, η_{SW}, as determined by eqn. (47). Putting eqn. (48) in the expression for the square-well self-diffusion coefficient [eqn. (32)] we obtain

$$D_{SW} = \frac{3}{8\rho\sigma_1^2}\left(\frac{kT}{\pi m}\right)^{1/2}(g(\sigma_1) - \gamma)^{-1} \tag{49}$$

Through this substitution we have expressed the square well self-diffusion coefficient [eqn. (49)] as a function of shear viscosity, η_{SW}, and eliminated the self-diffusion coefficient's direct dependency on $g(\sigma_2)$. To perform the numerical calculations it was assumed that $g(\sigma_1) = g^0(\sigma_1)$, that is, taken just outside the well, and that we can apply eqn. (40). Then, using the derived ψ

and Ξ polynominal functions [eqns. (33) and (34)], self-diffusion coefficient, D_{SW}, values [eqn. (49)] were calculated for 13 systems (Table 1) and 82 temperatures (Table 2) with an average error of 16.1% (experimental self-diffusion coefficient, viscosity and density values are found in Table 2). Using the condition that $g(\sigma_1) = g^0(\sigma_1)$, we have deliberately neglected the temperature effect as specified by eqn. (39). To compensate for this simplification, we empirically modified eqn. (49) by a temperature function f, given as

$$f = \exp(p + qT) \tag{50}$$

and obtained the temperature corrected self-diffusion coefficient, D_{SWT}, as

$$D_{SWT} = D_{SW} \exp(p + qT) \tag{51}$$

where D_{SW} is calculated from eqn. (49) and p and q are constants. The values of constants p and q were determined from the available experimental data (13 liquids, 82 data points, Table 2) using non-linear least squares curve fitting methods as

$$p = -1.00541 \times 10^{-1} \pm 1.61369 \times 10^{-2}$$

$$q = 1.32774 \times 10^{-3} \pm 7.15517 \times 10^{-5} \tag{52}$$

Equation (51) correlates the available data of the 13 liquids (Table 2) with an average error of 5.3%. This is a considerable improvement over the calculated results of eqn. (49) which did show an average error of 16.1% This improvement is due to the empirical temperature correction function, $f = \exp(p + qT)$. As a matter of fact, at $T = 75.7$ K, $f \simeq 1.0$; and hence, below $T = 75.7$ K function $f = \exp(p + qT)$ decreases the calculated self-diffusion coefficient, D_{SW}, value (eqn 49), and above $T = 75.7$ K, increases the calculated D_{SW} value, thus bringing it into the experimental self-diffusion coefficient value range which for all liquids (Table 2) is about ±5%. The general trend of temperature dependency for our calculations [eqn. (49)] is the same as that of other investigators, that is, the calculated square well self-diffusion coefficient values are smaller than the experimental ones [15,62,72] The average error of 5.3% obtained [eqn. (51)] for all liquids (Table 9) compares excellently with the average error of 8.3% resulting from the use of eqn. (10) and with the average error of about 7% when using eqns. (11), (12) and (14) for the same data point set (Table 2). Equation (9), however, did yield an average error of 9.4%; again for the same data set. It is of interest to note that the use of eqns. (10)—(12) and (14) yields average errors which closely agree with those obtained by Pratt and Wakeham [66]. They reported self-diffusion coefficients for water and monohydric alcohols, and found that their calculations led to deviations from the experimental data of up to ±10%. Subject to the availability of the square well potential parameters, σ, ϵ and R; the results of these comparisons show that the proposed predictive method [eqn. (51)] is indeed of a general nature.

TABLE 2

Used data and calculated results

Compound	Temperature (K)	Experimental density (g/ml^{-1})	References	Experimental viscosity (millipoise)	References	Experimental self-diffusion coefficient ($\times 10^5$ cm^2 sec^{-1})	References	Calculated self-diffusion[b] coefficient ($\times 10^5$ cm^2 sec^{-1})
Neon	26.15	1.218	1	1.375	2	1.18[a]	6	1.40
	27.10	1.196	1	1.242	2	1.37[a]	6	1.56
	28.10	1.201	1	1.150	2	1.58[a]	6	1.72
	31.40	1.133	1	0.860	2	2.38[a]	6	2.35
	34.50	1.054	1	0.670	2	3.24[a]	6	3.05
	38.90	0.9645	1	0.500	2	4.61	6	4.19
Argon	84.0	1.407	12	2.83	12	1.83[a]	62	1.87
	86.0	1.396	12	2.64	12	2.02[a]	62	2.02
	88.0	1.384	12	2.47	12	2.21[a]	62	2.17
	90.0	1.374	12	2.32	12	2.41[a]	62	2.32
	100.0	1.309	12	1.7	12	3.55[a]	62	3.24
	110.0	1.238	12	1.40	12	4.84[a]	62	4.09
Krypton	116.09	2.152	7	4.399	7	1.57	62	1.62
	117.03	2.445	7	4.250	7	1.62	62	1.68
	117.91	2.439	7	4.204	7	1.66	62	1.70
	117.93	2.438	7	4.174	7	1.66	62	1.71
	118.86	2.131	7	4.081	7	1.71	62	1.76
	119.92	2.123	7	4.017	7	1.76	62	1.79
	120.43	2.419	7	3.960	7	1.78	62	1.82
	121.57	2.410	7	3.866	7	1.84	62	1.87
	122.55	2.403	7	3.765	7	1.88	62	1.92
	123.01	2.399	7	3.726	7	1.91	62	1.94
Xenon	163.31	2.952	7	5.225	7	1.78[a]	62	1.80
	164.00	2.947	7	5.154	7	1.81[a]	62	1.83
	164.73	2.942	7	5.086	7	1.84[a]	62	1.85
	165.23	2.939	7	5.036	7	1.86[a]	62	1.87
	166.14	2.933	7	4.950	7	1.90[a]	62	1.91
	166.60	2.930	7	4.915	7	1.92[a]	62	1.93
	167.54	2.924	7	4.838	7	1.96[a]	62	1.96
	168.04	2.920	7	4.795	7	1.98[a]	62	2.02

Carbon monoxide	68.97	0.8432	48	2.81	47	2.25	47	2.30
	70.42	0.8379	48	2.62	47	2.35	47	2.46
	74.07	0.8241	48	2.22	47	2.62	47	2.87
	77.52	0.8104	48	1.93	47	2.90	47	3.28
Ammonia	199.15	0.7313	48	5.24	13	2.37	57	2.23
	207.15	0.7219	48	4.40	13	2.90	57	2.67
	215.65	0.7116	48	3.73	13	3.57	57	3.18
	223.15	0.7024	48	3.26	13	4.14	57	3.68
	231.15	0.6924	48	2.84	13	5.00	57	4.26
	238.15	0.6836	48	2.57	13	5.37	57	4.76
	240.15	0.6811	48	2.49	13	5.71	57	4.93
Water	278.15	0.999964	74	15.214	74	1.290	81, 61, 53	1.30
	283.15	0.999700	74	13.083	74	1.507	81	1.52
	288.15	0.999101	74	11.389	74	1.708	81, 61	1.76
	293.15	0.998206	74	10.020	74	1.913	81	2.01
	298.15	0.997047	74	8.898	74	2.236	81, 53, 61	2.27
	303.15	0.995650	74	7.966	74	2.456	81	2.54
	308.15	0.994031	74	7.185	74	2.790	81, 61	2.83
	318.15	0.990216	74	5.953	74	3.526	53, 78	3.44
	338.15	0.980552	74	4.334	74	5.30	78	4.81
	358.15	0.968613	74	3.341	74	7.26	78	6.39
Methane	90.7	0.4501	75	2.05	75	2.60	19	2.55
	95.2	0.4442	75	1.76	75	3.05	19	3.01
	100.0	0.4378	75	1.54	75	3.70	19	3.50
	106.1	0.4294	75	1.33	75	4.45	19	4.15
	110.5	0.4231	75	1.21	75	5.45	19	4.64
Ethane	113.15	0.631	71	5.72	75	1.16	32	1.23
	123.15	0.620	71	4.41	75	1.55	32	1.67
	133.15	0.6086	71	3.58	75	2.03	32	2.14
	143.15	0.5972	71	3.00	75	2.61	32	2.65
	153.15	0.5856	71	2.56	75	3.28	32	3.23
	163.15	0.5737	71	2.21	75	4.07	32	3.86
	173.15	0.5613	71	1.94	75	5.00	32	4.54
n-Pentane	298.15	0.6212	75	2.24	75	5.45	18	4.71

TABLE 2 (*continued*)

Compound	Temperature (K)	Experimental density (g/ml^{-1})	References	Experimental viscosity (millipoise)	References	Experimental self-diffusion coefficient ($\times 10^5$ cm^2 sec^{-1})	References	Calculated self-diffusion [b] coefficient ($\times 10^5$ cm^2 sec^{-1})
n-Heptane	273.15	0.7007	75	5.246	75	2.08	31	2.09
	298.15	0.6795	75	3.955	75	3.01	31	2.97
	305.65	0.6729	75	3.67	75	3.22	31	3.27
	329.65	0.6518	75	2.94	75	4.21	31	4.38
	353.35	0.6306	75	2.41	75	5.76	31	5.73
	368.95	0.6164	75	2.14	75	6.56	31	6.76
Neopentane	298.15	0.5802	75	2.31	65	4.86	58	5.39
Benzene	288.15	0.8843	75	6.983	75	1.865	67, 11	2.10
	298.15	0.8738	75	6.010	75	2.209	11, 36	2.47
	308.15	0.8631	75	5.236	75	2.605	11	2.88
	318.15	0.8523	75	4.615	75	3.010	11	3.31
	328.15	0.8414	75	4.11	75	3.56	67	3.77
	338.15	0.8303	75	3.68	75	4.07	67	4.28
	373.15	0.7929	48	2.61	47	6.2	37	6.39
	423.15	0.7310	48	1.71	47	10.3	37	10.6
	473.15	0.6605	48	1.21	47	16.0	37	16.3
	523.15	0.558	48	0.82	47	24.0	37	24.9

[a] Values corrected to saturated pressure.

[b] Calculated from equation (51)

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