Self-diffusion in a fluid of square-well spheres

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The self-diffusion coefficients for a dense fluid of particles interacting with a square-well potential are described. The expression for self-diffusion coefficients obtained by the Chapman–Enskog method of solution is corrected by the molecular dynamics simulation data. The structural data for the square-well fluid required in the calculation are obtained from explicit analytic equations for the radial distribution function. The corrected equation represents the self-diffusion coefficients with an average absolute deviation of 4.63% for the square-well fluid. The results are compared with those of other expressions. In addition, the self-diffusion coefficients for real fluids composed of simple, near spherical molecules are correlated using the square-well potential, and acceptable agreement is obtained between the calculated and experimental diffusion data.

Introduction

Diffusion is caused by random molecular motion that leads to complete mixing.[1] It is important not only for chemical engineers and chemists but also for life scientists, environmental administrators and workers in many other fields. Diffusion is involved in the efficiency of mass transfer equipment, the dispersal of pollutants, the dyeing of wool, and the transport phenomena in living cells.[2] Several authors have investigated the self-diffusion coefficients for real dense fluids interacting according to hard-sphere (HS),[3,4] square-well (SW)[5] and Lennard-Jones (LJ)[5–7] potentials. In these studies, molecular dynamics simulation data were used to develop the self-diffusion coefficient equations.

The square-well (SW) fluid is the simplest one possessing the basic characteristics of a real fluid. It has proved to be an excellent model for a liquid in which the internal degrees of freedom of the individual atoms are not important. Longuet-Higgins and Valleau[8] were the first to use the square-well model to describe the self-diffusion coefficients of a dense fluid. Davis, Rice and Sengers (DRS)[9] developed a transport equation for the singlet distribution function, which is essentially a modification of the equation derived by Enskog for a dense hard-sphere fluid. This model was extended to a binary mixture by McLaughlin and Davis.[10] Brown and Davis[11] derived expressions for the self-diffusion coefficients for smooth, rough and loaded hard-spheres interacting according to the square-well potential. They found that replacing a smooth hard-sphere core with a rough sphere core lowered the square-well results for the self-diffusion coefficient. Scarfe et al.[12] compared the results of square-well and square-well rough sphere models with the experimental data for methane. A little improvement was found for the square-well rough sphere model. The model proposed by Davis, Rice and Sengers[9] admits only partial collisions at each initial separation, such that momentum transfer at the outer edge of the well and at the core are uncorrelated. This model is also referred to as the partial collision model.[13] The partial collision model is inappropriate at low densities since it does not yield the Boltzmann limit or a reasonable approximation to it. Furthermore, it is not appropriate at high densities since it does not predict the correct temperature dependence. Dufty et al.[13] compared the self-diffusion coefficients from three theoretical models, i.e. the partial collision model, the complete collision model and the repeat ring approximation theory, with the molecular dynamics simulation data at low and moderate densities, and found that only the last one gives acceptable predictions. However, it is not convenient to use because of its complexity and the obligatory numerical integrations involved. Much effort should be made to generalize the repeat ring kinetic theory to liquid densities.

Wilbertz et al. (WMBL)[14] developed a kinetic theory similar to the DRS theory. They used their theory to calculate the diffusion coefficient for the SW fluid and compared the results to those of computer simulations. The WMBL theory makes reasonable predictions only at intermediate densities. The DRS theory[9] is not entirely satisfactory because, in general, energy conservation is not obeyed. This problem is avoided in the SW theory of Karkheck et al.,[15] using the method of maximization of entropy. The theory of Karkheck et al.[15] exhibits energy conservation, satisfies an H theorem,[16] and leads to the correct equilibrium solutions. Yet, already the fulfillment of all conservation laws renders this theory more satisfactory.[14] Due to the complications caused by the finite time-length of collisions and the presence of many-body interactions, the present state of the kinetic theory of transport processes in dense fluids is unsatisfactory, despite many valiant attempts.[14] Hence computer simulations are carried out for model fluids. It is very important for guiding new simulations to examine how well different model fluids simulate real fluid behavior. The purpose of this work is to establish an accurate expression for the self-diffusion coefficient for the SW fluid by modifying the DRS theory with molecular simulation data,[17–19] and examine whether the SW model fits well to real fluids.

Theory

Self-diffusion coefficient from the Chapman–Enskog method

The pair potential for a square-well fluid is defined by

$$u(r) = \begin{cases} \infty & r \leqslant \sigma \\ -\varepsilon & \sigma < r < \lambda\sigma \\ 0 & r \geqslant \lambda\sigma \end{cases} \tag{1}$$

where r is the radial coordinate, σ is the diameter of the hard core, $\lambda\sigma$ is the diameter of the surrounding well, and ε is the magnitude of the attractive part of the potential. The well

width, λ, is set to 1.5 throughout this paper, because this value provides a good compromise between fitting second virial coefficient data and critical temperature and volume for real fluids.[20] Furthermore, this value was adopted in most of the molecular dynamics simulations, and with a constant value of λ the calculation of radial distribution functions is considerably simpler.

The theory involved in the derivation of the transport equation for a dense gas of hard-sphere molecules is a modification of the corresponding dilute gas equation to which the Chapman–Enskog method of solution may be applied. The same method was applied to the square-well fluid by Davis *et al.*[9,10] To evaluate the collision integral, one has to deal with hard-core collisions and three additional impulsive collision processes due to the presence of the attractive square-well part of the potential. The self-diffusion coefficient obtained by using the Chapman–Enskog method of solution is[9,10]

$$D = \frac{3}{8\rho\sigma^2}\left(\frac{kT}{\pi m}\right)^{1/2}[g(\sigma) + \lambda^2 g(\lambda\sigma)\varXi]^{-1} \quad (2)$$

where ρ is the number density of the fluid, m is the mass of the particle, T is the absolute temperature, k is the Boltzmann constant, $g(\sigma)$ and $g(\lambda\sigma)$ are the equilibrium radial distribution functions evaluated at the points $\sigma + 0$ and $\lambda\sigma + 0$, respectively, and $\varXi$ is expressed as

$$\varXi = \exp\left(\frac{\varepsilon}{kT}\right) - \frac{\varepsilon}{2kT} - 2J \quad (3)$$

$$J = \int_0^\infty y^2(y^2 + \varepsilon/kT)^{1/2}\exp(-y^2)\,\mathrm{d}y \quad (4)$$

Eqn. (2) was also obtained by Longuet–Higgins and Valleau[8] under the assumption that the velocity autocorrelation function of a particular particle was an exponentially decaying function of time. So in the case of self-diffusion, the Chapman–Enskog and Longuet-Higgins and Valleau methods give the same result.

For a given component at a given density and temperature, eqn. (2) requires knowledge of the radial distribution functions $g(\sigma)$ and $g(\lambda\sigma)$ for the square-well fluid. In this work, the expression for $g(\sigma)$ was obtained from the first-order perturbation term of the pressure equation as follows[21–23]

$$g(\sigma) = -3\left(I + \eta\frac{\partial I}{\partial\eta}\right) + \lambda^3 g^{\mathrm{HS}}(\lambda\sigma) \quad (5)$$

where

$$I = \int_1^\lambda g^{\mathrm{HS}}(x)x^2\,\mathrm{d}x \quad (6)$$

$$\eta = \pi\rho^*/6 = \pi\rho\sigma^3/6 \quad (7)$$

In these expressions, $x = r/\sigma$ is the reduced distance between two particles, and $g^{\mathrm{HS}}(x)$ is the radial distribution function of the hard-sphere fluid at a specified distance and density.

By using the analytic expression for the radial distribution function of hard spheres of Chang and Sandler,[22,23] the integral I of eqn. (6), and its first derivative, can be obtained analytically and as explicit functions of η and λ:

$$I = \int_1^\lambda g^{\mathrm{HS}}(x)x^2\,\mathrm{d}x = a_1 t_1 + a_2 t_2 + a_3 t_3 \quad (8)$$

$$\frac{\partial I}{\partial\eta} = \sum_{i=1}^3\left(a_i\frac{\partial t_i}{\partial\eta} + t_i\frac{\partial a_i}{\partial\eta}\right) \quad (9)$$

The explicit analytic expressions for a_i and t_i ($i = 1, 2$ and 3) can be found in appendix A of Tavares *et al.*[24] For $\lambda = 1.5$, the value of the radial distribution function for the hard-sphere fluid at $\lambda\sigma$ can be determined from a correlation of

Monnery *et al.*[25]

$$g^{\mathrm{HS}}(\lambda\sigma) = 0.999\,48 + 0.824\,04\eta - 3.469\,76\eta^2 \quad (10)$$

This correlation matches the Monte Carlo (MC) simulation results of Barker and Henderson[26] with an overall average absolute deviation (AAD) of 0.35% over a reduced density range of $0.2 \leqslant \rho^* \leqslant 0.9$.

The radial distribution functions for the square-well fluid at $\sigma + 0$ are plotted as a function of reduced density in Fig. 1. From Fig. 1 one can see that the radial distribution functions calculated from eqn. (5) are in good agreement with the MC results[27,28] except in the reduced density range from 0.1 to 0.4 at $T^* = 1.5$. In this region, eqn. (5) slightly underestimates the radial distribution functions for the square-well fluid.

The radial distribution function values for the square-well fluid at $\lambda\sigma + 0$ can be approximated by the following equation:

$$g(\lambda\sigma) = g^{\mathrm{HS}}(\lambda\sigma)\exp(\alpha/T^* + \beta/T^{*2}) \quad (11)$$

where $T^* = kT/\varepsilon$. The values of α and β were determined to be -0.4317 and -0.1177, respectively, by minimizing the deviations between the predicted values from eqn. (11) and the MC simulation values of Henderson *et al.*,[27] reproducing the MC values with the AAD of 2.56%. Fig. 2 shows that the calculated $g(\lambda\sigma)$ are in good agreement with the MC results at different reduced temperatures and densities.
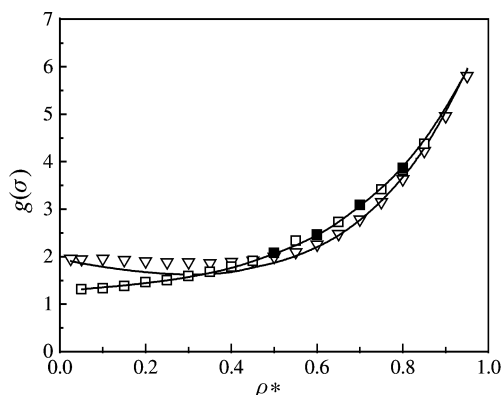

Fig. 1 Radial distribution function for the square-well fluid at $\sigma + 0$. Symbols are the MD results: ■, data of Henderson *et al.*[27] at $T^* = 4.0$; □ data of Tavares *et al.*[28] at $T^* = 4.0$; ▽, data of Tavares *et al.*[28] at $T^* = 1.5$. Solid lines are the values calculated with eqn. (5).
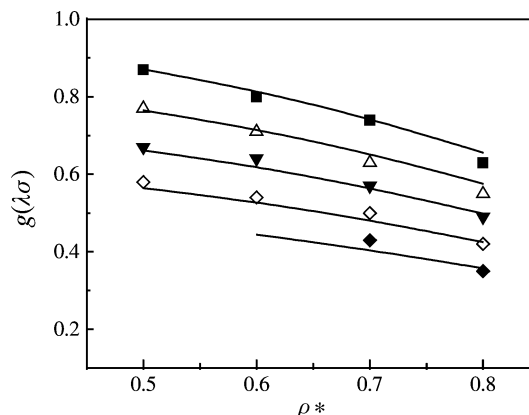

Fig. 2 Radial distribution function for the square-well fluid at $\lambda\sigma + 0$. Symbols are the MD results of Henderson *et al.*:[27] ■ $T^* = 4.0$; △, $T^* = 2.0$; ▼, $T^* = 1.333$; ◇, $T^* = 1.0$; ◆, $T^* = 0.8$. Solid lines are the results calculated with eqn. (11).

In order to simplify the calculation, the integral J can be approximated by the following algebraic equation:[25]

$$J = \frac{0.5 + 0.283\,04/T^*}{1 + 0.153\,60/T^*} \quad (12)$$

With the radial distribution function values determined from eqns. (5)–(11) and Y from eqns. (3) and (12), eqn. (2) can now be used to calculate the self-diffusion coefficient for the square-well fluid.

Correction to the self-diffusion coefficient

As pointed by Dufty et al.,[13] eqn. (2) is not appropriate to describe the self-diffusion coefficient for a square-well fluid at low and high densities. Therefore, it was corrected by using the MD simulation data[17–19] in this paper. The friction coefficient for a square-well fluid can be written as $\xi = \xi_R + \xi_S$.[9,29] Then the self-diffusion coefficient can be expressed as:

$$D = kT/(\xi_R + \xi_S) \quad (13)$$

where ξ_R represents the friction coefficient due to the hard-core repulsive potential, and ξ_S represents that due to the attractive one. The friction coefficient ξ_R can be obtained from the expression for the self-diffusion coefficient of a hard-sphere fluid.

For a hard-sphere fluid, the self-diffusion coefficient can be obtained from the well-known Enskog equation:

$$D^E = \frac{3}{8\rho\sigma^2}\left(\frac{kT}{\pi m}\right)^{1/2}\frac{1}{g^{HS}(\sigma)} \quad (14)$$

where $g^{HS}(\sigma)$ is the radial distribution function at contact for the hard-sphere fluid. It can be determined by the Carnahan–Starling[30] expression:

$$g^{HS}(\sigma) = \frac{1 - 0.5\eta}{(1 - \eta)^3} \quad (15)$$

From eqn. (14) one can obtain the hard-core contribution to the friction coefficient, i.e.

$$\xi_R^E = kT/D^E = \tfrac{8}{3}\rho\sigma^2(\pi m kT)^{1/2}g^{HS}(\sigma) \quad (16)$$

Eqn. (2) can be rewritten as

$$D = \frac{kT}{\tfrac{8}{3}\rho\sigma^2(\pi m kT)^{1/2}[g(\sigma) + \lambda^2 g(\lambda\sigma)\Xi]} \quad (17)$$

If the expression for the friction coefficient due to the hard core for the hard-sphere fluid is assumed to be similar to that for the square-well fluid, the friction coefficient due to the attractive potential for the square-well fluid can be obtained from eqns. (13), (16) and (17):

$$\xi_S = \tfrac{8}{3}\rho\sigma^2(\pi m kT)^{1/2}\lambda^2 g(\lambda\sigma)\Xi \quad (18)$$

As we know, the Enskog equation is valid only at low densities. A correction factor must therefore be introduced to obtain accurate results for the hard-sphere fluid in moderate- and high-density ranges:

$$\xi_R^{HS} = \xi_R^E f_R(\rho^*) = \tfrac{8}{3}\rho\sigma^2(\pi m kT)^{1/2}g^{HS}(\sigma)f_R(\rho^*) \quad (19)$$

The correction function $f_R(\rho^*)$ in eqn. (19) can be determined by using MD simulation results for the hard-sphere fluid. On the basis of MD simulations, Speedy[4] proposed the following equation for the hard-sphere fluid:

$$D^{HS} = D_0(1 - \rho^*/1.09)(1 + 0.4\rho^{*2} - 0.83\rho^{*4}) \quad (20)$$

where D_0 is the self-diffusion coefficient at very low densities,

$$D_0 = \frac{3}{8\rho\sigma^2}\left(\frac{kT}{\pi m}\right)^{1/2} \quad (21)$$

From eqn. (20), the friction coefficient due to the hard-core repulsive potential can be obtained as

$$\xi_R^{HS} = \frac{\tfrac{8}{3}\rho\sigma^2(\pi m kT)}{[1 - (\rho^*/1.09)](1 + 0.4\rho^{*2} - 0.83\rho^{*4})} \quad (22)$$

Comparing eqn. (19) with eqn. (22), the following expression can be obtained for the correction function $f_R(\rho^*)$:

$$f_R(\rho^*) = \frac{(1 - \eta)^3}{(1 - 0.5\eta)(1 - \rho^*/1.09)(1 + 0.4\rho^{*2} - 0.83\rho^{*4})} \quad (23)$$

Assuming that the correction function $f_R(\rho^*)$ for the hard-sphere fluid is the same as that for the square-well fluid, the friction coefficient due to the hard-core repulsive potential for the square-well fluid can be expressed as:

$$\xi_R = \tfrac{8}{3}\rho\sigma^2(\pi m kT)^{1/2}g(\sigma)f_R(\rho^*) \quad (24)$$

Because eqn. (2) does not predict the correct temperature dependence, a correction function must also be introduced for the attractive friction coefficient, i.e.

$$\xi_S = \tfrac{8}{3}\rho\sigma^2(\pi m kT)^{1/2}\lambda^2\Xi g(\lambda\sigma)f_S(\rho^*) \quad (25)$$

By using the MD results of Alley and Alder[17] and of Michels and Trappeniers,[18,19] the correction function $f_S(\rho^*)$ can be determined. It has the form:

$$f_S(\rho^*) = 70.771\rho^{*3} - 58.971\rho^{*2} + 19.903\rho^* - 1.3708 \quad (26)$$

Substituting eqns. (24) and (25) into eqn. (13), the corrected self-diffusion coefficient for the square-well fluid can be obtained:

$$D = \frac{3}{8\rho\sigma^2}\left(\frac{kT}{\pi m}\right)^{1/2}[g(\sigma)f_R(\rho^*) + \lambda^2\Xi g(\lambda\sigma)f_S(\rho^*)]^{-1} \quad (27)$$

Comparison with simulated data

With the equilibrium radial distribution functions $g(\sigma)$ and $g(\lambda\sigma)$ calculated from eqns. (5) and (11), the self-diffusion coefficient can be obtained from eqn. (27) for a square-well fluid. A comparison of the corrected self-diffusion coefficient, eqn. (27), with computer simulation results[18] at $T^* = 1.3158$, 2.0 and 5.0 is given in Fig. 3. The reduced self-diffusion coefficient for a square-well fluid used in this paper is defined as

$$D^* = D\rho\sigma^2(m/kT)^{1/2} \quad (28)$$

From Fig. 3, one can see that the corrected self-diffusion coefficient, eqn. (27), agrees remarkably well with the simulation data. In Figs. 4 and 5, the deviations of the self-diffusion coefficients obtained with eqn. (27) are plotted against reduced density and reduced temperature, respectively. Big discrep-
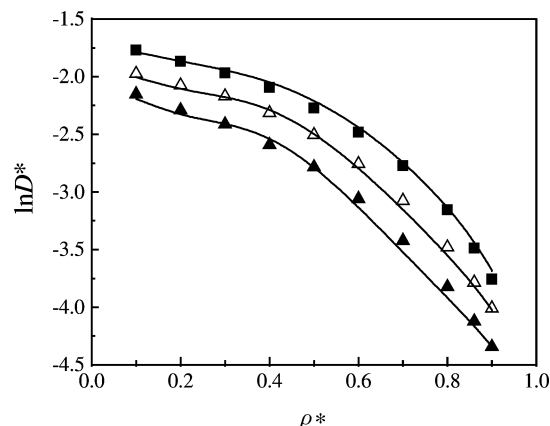

Fig. 3 Reduced self-diffusion coefficient as a function of reduced temperature and density for the square-well fluid. Symbols are the MD results of Michels and Trappeniers:[18] ■, $T^* = 5.0$; △, $T^* = 2.0$; ▲, $T^* = 1.316$. Solid lines are the results calculated with eqn. (27).
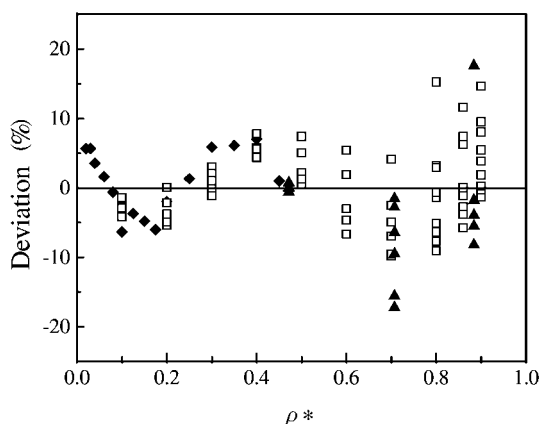
Fig. 4 Deviation of the self-diffusion coefficient obtained with eqn. (27) *vs.* reduced density for the square-well fluid. Symbols are as follows: ▲, Alley and Alder;[17] □, Michels and Trappeniers;[18] ◆, Michels and Trappeniers.[19]

ancies can be observed in the high-density and low-temperature regions, respectively. All the deviations are within 18% over the density range from $\rho^* = 0.02$ to $\rho^* = 0.9$ and the temperature range from $T^* = 0.79$ to $T^* = 8.84$.

Recently, Liu *et al.*[5] proposed an expression for the self-diffusion coefficient of a SW fluid. The proposed expression takes the form:

$$D^* = 0.211\,57 \exp\left(-\frac{0.75\rho^*}{1.2588 - \rho^*}\right)\exp\left(-\frac{0.810\,61}{T^*}\right) \quad (29)$$

Table 1 shows the average absolute deviations (AAD) from the corrected self-diffusion coefficient equation [eqn. (27)], the original equation [eqn. (2)] obtained from the Chapman–Enskog method, and eqn. (29). The average absolute deviation
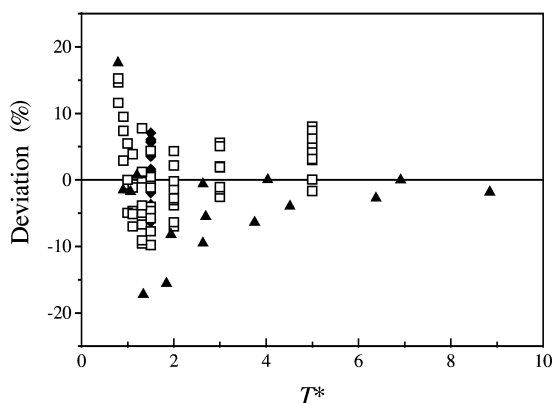
(AAD) used in this work is defined as

$$\mathrm{ADD} = \frac{1}{\mathrm{NDP}} \sum_{i=1}^{\mathrm{NDP}} |(D_i^{\mathrm{cal}} - D_i^{\mathrm{exp}})/D_i^{\mathrm{exp}}| \times 100\% \quad (30)$$

where NDP is the number of data points, D_i^{cal} is the calculated self-diffusion coefficient, and D_i^{exp} represents the MD simulation data or experimental measured data.

At lower densities, $0 < \rho^* \leqslant 0.2$, both eqns. (27) and (29) give reasonably good results, while eqn. (2) produces large discrepancies, as can be seen from Table 1. At moderate densities, $0.25 \leqslant \rho^* \leqslant 0.5$, all three models describe the simulation data[17–19] with acceptable deviations. At high densities, $0.6 \leqslant \rho^* \leqslant 0.9$, the corrected self-diffusion coefficient equation, eqn. (27), continues to yield a good approximation, while there are very large discrepancies for the other models. Fig. 6 shows the same trend for the self-diffusion coefficients calculated from the three models at $T^* = 1.5$. The original equation, eqn. (2), underestimates the self-diffusion coefficients at lower densities and overestimates them at higher densities. The expression proposed by Liu *et al.*[5] also overestimates the self-diffusion coefficients at higher densities, but it gives acceptable results at lower and moderate densities. The equation obtained in this work gives excellent agreement with the MD simulation results. From Table 1 and Fig. 6, one can see that the corrected equation is more accurate than the expression of Liu *et al.*[5]

The expression of Liu *et al.*[5] relies on a tenuous analysis of the relation between hard-sphere and square-well fluid behavior. In their expression, the effects of temperature on the self-diffusion coefficient for the SW fluid at all densities are of the
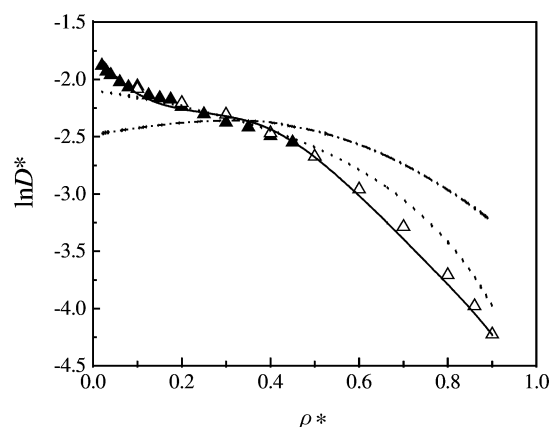

Fig. 5 Deviations of the self-diffusion coefficient obtained with eqn. (27) *vs.* reduced temperature for the square-well fluid. The meaning of the symbols is the same as in Fig. 4.

Fig. 6 Comparison of simulated self-diffusion coefficient with the results of different models for the square-well fluid at $T^* = 1.5$. Symbols are the MD simulation results: △, ref 18; ▲, ref 19. Solid line represents the results obtained with eqn. (27); dotted line represents the results of Liu *et al.*;[5] and dash-dot line denotes the results obtained with eqn. (2).

Table 1 Calculated results with the three models for the square-well fluids in different density ranges ($T^* = 0.79$–8.84)

Density range	NDP	AAD (%)		
		Eqn. (27)	Eqn. (2)	Eqn. (29)
$0 < \rho^* \leqslant 0.1$	11	3.43	30.04	9.21
$0.125 \leqslant \rho^* \leqslant 0.2$	9	3.65	15.96	2.41
$0.25 \leqslant \rho^* \leqslant 0.3$	7	2.09	5.20	2.10
$0.35 \leqslant \rho^* \leqslant 0.4$	7	5.87	8.86	3.38
$0.45 \leqslant \rho^* \leqslant 0.5$	10	1.86	15.42	5.67
$\rho^* = 0.6$	6	4.40	38.85	17.49
$\rho^* = 0.7$	7	6.42	76.84	31.27
$0.7071 \leqslant \rho^* \leqslant 0.8$	15	6.98	119.57	38.11
$0.86 \leqslant \rho^* \leqslant 0.9$	24	5.17	191.50	37.11
$0 < \rho^* \leqslant 0.9$	96	4.64	82.16	20.88

Table 2 Data sources, temperature and pressure ranges of the real substances studied in this work

No.	Substance	Formula	M/g mol^{-1}	T/K	P/MPa	Ref.
1	Argon	Ar	39.948	79.5–325.2	0.1–200.0	31, 32
2	Krypton	Kr	83.800	199.6–293.0	6.5–11.10	33, 34
3	Xenon	Xe	131.290	203.0–343.0	0.1–10.20	35
4	Carbon disulfide	CS_2	76.131	268.2–313.2	0.1–385.1	36
5	Methane	CH_4	16.043	110.0–323.2	1.5–221.6	37
6	Carbon tetrachloride	CCl_4	153.823	283.2–328.2	0.1–147.5	38
7	Fluoromethane	CH_3F	34.033	153.0–440.0	Sat–200.0	39
8	Chloromethane	CH_3Cl	50.488	186.0–440.0	Sat–200.0	40
9	Chlorotrifluoromethane	$CClF_3$	104.459	303.2–348.2	3.7–188.4	41
10	Isopentane	C_5H_{12}	72.151	298.0–328.0	0.1–200.0	42
11	Sulfur hexafluoride	SF_6	146.050	240.0–370.0	Sat–182.7	43, 44
12	Cyclopentane	C_5H_{10}	70.135	298.0–328.0	0.1–200.0	42
13	Cyclohexane	C_6H_{12}	84.162	313.0–383.0	0.1–214.0	45
14	Trimethylamine	$(CH_3)_3N$	59.111	273.0–375.0	10.0–200.0	46

same magnitude, and the density dependence of D_{SW}^* is comparable with that for the HS fluid over the entire density range. But this is not the case for the SW fluid. It is known from molecular dynamics[18,19] that if an attractive potential with a square-well shape is superimposed on the hard core, the result is a first-order density dependence of $\rho^* D_{SW}^*$ and there is a concave shape in the function $\rho^* D_{SW}^*$ at $\rho < 0.2$. The density dependence of D_{SW}^* is comparable with that for the HS fluid only in the density range of $0.2 < \rho^* < 0.5$. Therefore, the expression of Liu et al.[5] is valid only in this density range, as can be seen from Table 1 and Fig. 6. This limitation shows that the expression of Liu et al.[5] is not adequate to describe
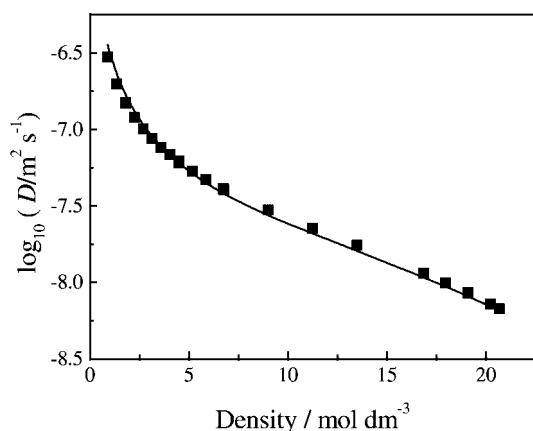
the SW fluid behavior. In our corrected eqn. (27), the effects of temperature on the radical distribution functions are considered, and the results are more reasonable over the entire density range. All these facts show that our treatment is preferable to that of Liu et al.[5]

Calculation of real systems

The parameters of the corrected self-diffusion coefficient equation [eqn. (27)] were then fitted to the data of real systems. The data sources, and the temperature and pressure ranges of the self-diffusion coefficients for the 14 substances studied in this work are listed in Table 2. In Table 2, P is the pressure and M is the molar mass. The density data of the substances are from the same references as the self-diffusion coefficients. The substances studied in this work are composed of simple and near spherical molecules, because the square-well potential model is not suitable for non-spherical or polar systems. They were chosen only when self-diffusion coefficients at different temperatures and pressures are available.

The corrected self-diffusion coefficient equation [eqn. (27)] contains two parameters: σ and ε. They can be determined from diffusion coefficient data by the least squares regression method. The obtained parameters along with the AADs in the self-diffusion coefficient are listed in Table 3. As seen from Table 3, eqn. (27) provides acceptable correlation for all the substances studied in this work, and the AADs for the 14 substances are within 10%. These results are a significant improvement over those of the HS model, and show that the attractive part of the intermolecular potential has a remarkable influence on the diffusion coefficient. The AADs in Table 3 from the SW model are bigger than those of LJ and

Fig. 7 The logarithm of the self-diffusion coefficient of xenon as a function of density at 343 K. Symbols represent the experimental data[35] and solid line denotes the values calculated with eqn. (27).

Table 3 Calculated results with the corrected self-diffusion coefficient equation [eqn. (27)] for real systems

No.	Substance	σ/nm	(ε/k)/K	NDP	AAD (%)
1	Argon	0.3196	76.9	56	7.55
2	Krypton	0.3459	56.5	40	9.80
3	Xenon	0.3674	106.5	71	7.44
4	Carbon disulfide	0.4315	69.0	29	4.06
5	Methane	0.3360	102.0	59	6.46
6	Carbon tetrachloride	0.5299	119.2	27	7.96
7	Fluoromethane	0.3327	181.1	57	6.56
8	Chloromethane	0.3765	229.0	42	7.28
9	Chlorotrifluoromethane	0.4370	137.9	66	3.33
10	Isopentane	0.5402	100.1	22	8.75
11	Sulfur hexafluoride	0.4536	124.5	43	6.85
12	Cyclopentane	0.5150	100.2	21	6.59
13	Cyclohexane	0.5530	100.2	39	9.84
14	Trimethylamine	0.4953	46.0	23	8.54

Lennard-Jones chain (LJC)[7] models. The LJ and LJC models give AADs within 8% for all the substances studied in this work.

Comparison of the calculated results with the experimental data for xenon[35] at 343 K is plotted in Fig. 7. The corrected self-diffusion coefficient equation [eqn. (27)] represents the experimental data quite well in the whole density range for xenon at 343 K. The logarithm of the self-diffusion coefficient for methane as a function of temperature and pressure is shown in Fig. 8. In the high temperature region, the corrected self-diffusion coefficient equation gives good results, but when the temperature becomes low and pressure becomes high, eqn. (27) overestimates the self-diffusion coefficient for methane. This trend is different from that of the LJ and LJC models. At high density, the LJ and LJC models generally underestimate the self-diffusion coefficient for real fluids. However, the absolute deviations at high density from the LJ and LJC models are smaller than those of the SW model. The LJC model generally gives the best result among the three models. Considering the wide ranges of temperature and pressure, the calculation results of the SW model for these substances are satisfactory.

From the calculation of the real systems, we found that the self-diffusion coefficient is much more sensitive to the hard-core diameter parameter σ than to the well depth parameter ε. The hard-core diameter parameter σ should represent an equivalent molecular size of real substances. In Fig. 9, the hard-core diameter parameter listed in Table 3 is plotted

against the critical volume V_c. From Fig. 9, one can conclude that the value of parameter σ is proportional to $V_c^{4/3}$. This result is comparable to that obtained from viscosity data for a Lennard-Jones fluid.[47]

Conclusion

The real systems studied were investigated by the statistical theory of a dense fluid of molecules interacting with a square-well potential. The self-diffusion coefficient equation derived by the Chapman–Enskog method of solution was corrected. The correction functions for the friction coefficient due to the hard-core repulsive and attractive potentials were obtained by using the expression of Speedy[4] and the molecular dynamics simulation data[17-19] for the square-well fluid, respectively. The equilibrium radial distribution functions required in the calculation were proposed in this work. They can be obtained with the explicit analytic equations of Chang and Sandler,[22,23] and the approximation given in this work. With these structural data for the square-well fluid, the corrected self-diffusion coefficient equation [eqn. (27)] represents the molecular dynamics simulation data[17-19] with average absolute deviation of 4.64%. The equation obtained in this work has been compared with the original equation obtained by the Chapman–Enskog method and the expression proposed by Liu et al.,[5] and it gives the best results for the square-well fluid. The corrected self-diffusion coefficient equation [eqn. (27)] was used to calculate the self-diffusion coefficients for 14 simple substances over wide temperature and pressure ranges. The equation represents the self-diffusion coefficients for these systems with acceptable accuracy and the average absolute deviations are smaller than 10%.
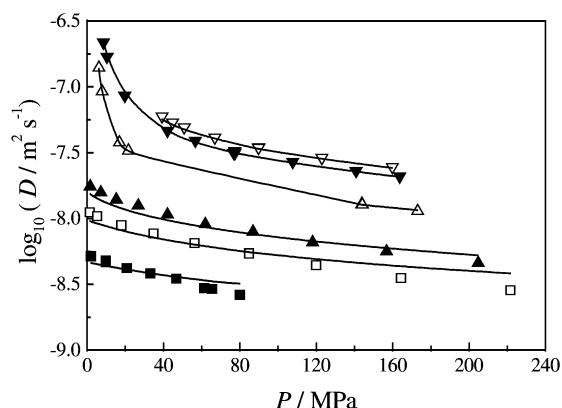
Acknowledgements

Fig. 8 The logarithm of the self-diffusion coefficient of methane as a function of temperature and pressure. Solid lines represent the results calculated with eqn. (27). Symbols denote the experimental data:[37] ■, 110.00 K; □, 140.00 K; ▲, 160.00 K; △, 223.15 K; ▼, 298.15 K; ▽, 323.15 K.
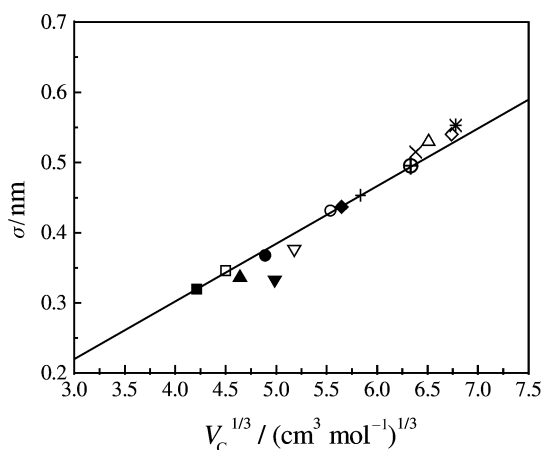

Fig. 9 The hard-core diameter parameter as a function of the critical volume: ■, Ar; □, Kr; ●, Xe; ○, CS_2; ▲, CH_4; △, CCl_4; ▼, CH_3F; ▽, CH_3Cl; ◆, $CClF_3$; ◇, i-C_5H_{12}; ×, C_5H_{10}; +, SF_6; *, C_6H_{12}; ⊕, $(CH_3)_3N$.

Appendix

List of symbols

AAD	average absolute deviation
a_i	constants in eqns. (8) and (9)
D	self-diffusion coefficient
D_0	self-diffusion coefficient at very low densities
$f(\rho^*)$	correction function for friction coefficient
$g(\sigma)$	radial distribution function at $\sigma + 0$
$g(\lambda\sigma)$	radial distribution function at $\lambda\sigma + 1$
I	integral of eqn. (6)
J	integral of eqn. (4)
k	Boltzmann constant
M	molar mass
m	mass of a molecule
NDP	number of data points
P	pressure
r	distance between two particles
T	absolute temperature
t_i	functions in eqns. (8) and (9)
$u(r)$	pair potential
V_c	critical volume
x	reduced distance
y	variable in eqn. (4)

Greek letters

α, β	constants in eqn. (11)
ε	well depth parameter

η	reduced density
λ	well width parameter
ρ	number density
σ	hard-core diameter
Ξ	quantity represented by eqn. (3)
ξ	friction coefficient

Superscripts

cal	calculated value
E	Enskog
exp	simulated or experimental value
HS	hard-sphere fluid

Subscripts

R	repulsive potential
SW	square-well fluid
S	attractive potential
*	reduced quantity

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