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Self-diffusion coefficient equation for polyatomic fluid

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Abstract

An equation for the self-diffusion coefficient in a polyatomic fluid is presented as a sum of three friction coefficient terms: the temperature-dependent hard-sphere contribution, the chain contribution and the soft contribution. This equation has been developed by using the molecular dynamics simulation data for the HS chain fluid and the expression for the Lennard–Jones (LJ) fluid proposed by Ruckenstein and Liu. The real nonspherical compounds are modeled as chains of tangent LJ segments. The segment diameter σ_{LJ}, segment–segment interaction energy $\varepsilon_{\mathrm{LJ}}$ and chain length N (the number of segments) are obtained from the experimental diffusion data. The equation reproduces the experimental self-diffusion coefficients with an average absolute deviation (AAD) of 3.72% for 22 polyatomic compounds (1081 data points) over wide ranges of temperature and pressure. The results have been compared with that of the rough LJ (RLJ) equation. To minimize the number of the fitting parameters, the energy parameter $\varepsilon_{\mathrm{LJ}}$ is estimated using a correlation obtained from viscosity data. The equation with two parameters gives an AAD of 4.72%. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Model; Self-diffusion coefficient; Friction coefficient; Lennard–Jones chain; Polyatomic fluid

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1. Introduction

The diffusion coefficients of dense fluids and their mixtures are required in many engineering calculations involving mass transfer. A detailed study of diffusion is also very important for the development of our understanding of molecular motions and interactions in these systems. For monatomic gases at low densities, diffusion coefficients may be calculated at any temperature using exact kinetic theory [1]. However, no formal theory may be used to evaluate diffusion coefficients for monatomic fluids at high densities or polyatomic fluids in terms of a realistic description of the molecular interactions. Simple semitheoretical methods based on statistical mechanics (such as

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hard-sphere and square-well theories) appear to be the most promising for engineering use. An extensive review of diffusion coefficient prediction and correlation methods has been given by Liu et al. [2], which discussed the abundance of literature and compared several diffusion models.

Molecular dynamics simulations for hard-sphere (HS), square-well (SW) or Lennard–Jones (LJ) fluids were often employed to generate equations [3–5] for the self-diffusion coefficient of monatomic fluids. Because no quantitative and analytical theoretical expression is available to estimate the diffusion coefficients of LJ fluids, the effective hard-sphere diameter (EHSD) method [6,7] was applied. Ruckenstein and Liu [8] compared the six EHSD expressions and found that the Boltzmann EHSD with the parameters obtained by Ben-Amotz and Herschbach [9] leads to the best agreement with the diffusion data. For polyatomic fluids, Chandler's rough hard-sphere theory (RHS) [10] can be used as a connection between real and simple model fluids. For example, Sun et al. [11] presented analytical expressions for the transport properties of the n-alkanes by combining the rough hard-sphere theory with the molecular dynamics results for the LJ fluids reported by Heyes [6], and Hammonds and Heyes [12]. The translational–rotational coupling factor of the RHS theory may depend on both temperature and density [3], and for long chain molecules, it may be very small [13]. Furthermore, there is no expression for this factor available for the real fluids. All these limited the use of the theory.

In the studies of equilibrium properties, the real near-sphere and nonsphere compounds are frequently described as flexible homonuclear chainlike molecules. One of these approaches is the statistical associating fluid theory (SAFT) [14–16]. It has been extensively tested against computer simulations [17,18] and experimental results [19–21]. In the theories of transport properties, however, seldom have researchers considered the real fluids as chain molecules. Only Salim and Trebble [22] modified the interacting sphere model by introducing a multiple hard-sphere to the probability function of molecular collision.

In this work, the real compounds are described as freely tangent Lennard–Jones chain (LJC) molecules. A new equation for D_{HSC} is proposed here based on the molecular dynamics simulations carried out by Smith et al. [23]. An expression for D_{LJC} is also obtained on the basis of the friction coefficient of the LJ fluid given by Ruckenstein and Liu [8]. The equation is used to correlate the self-diffusion coefficients for 22 compounds. The correlated results are compared with that of the rough Lennard–Jones (RLJ) [8] type equation.

2. Background theory

2.1. Self-diffusion coefficient equation for the HSC fluid

Self-diffusion coefficient for a dilute gas composed of hard spheres is given by:

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

For dense gases, the well-known Enskog equation for a hard-sphere fluid is:

$$D_{\mathrm{E}} = \frac{D_0}{g(\sigma)} = \frac{3}{8\rho\sigma^2}\left(\frac{kT}{\pi m}\right)^{1/2}\frac{1}{g(\sigma)}, \tag{2}$$

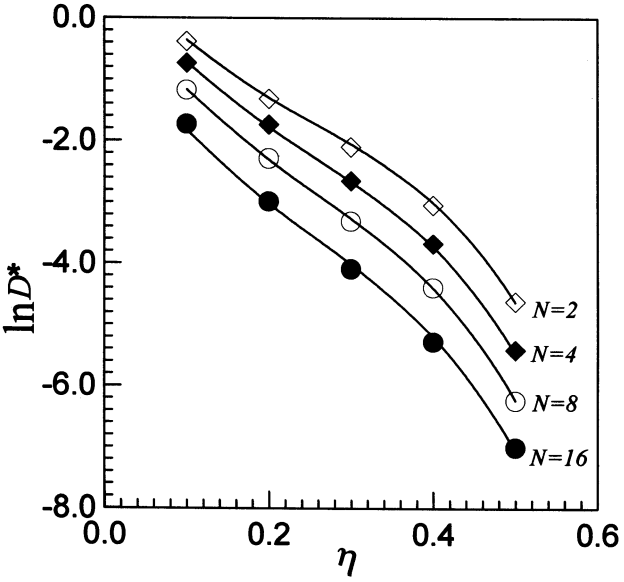

Fig. 1. Reduced self-diffusion coefficients of the hard-sphere chain fluids. Symbols refer to the MD simulation results; solid lines refer to the fitted values.

where the radial distribution function at contact can be calculated from Carnahan–Starling equation [24]:

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

Comparing with the molecular dynamics simulation data, Eq. (2) is valid only at low densities. In the moderate- and high-density ranges, a correction factor have been obtained using the molecular dynamics simulation data by Ruckenstein and Liu [8]. Then the self-diffusion coefficient of hard-sphere fluid can be expressed as:

$$D_{\mathrm{HS}} = D_{\mathrm{E}} f(\rho^*) = D_0 f(\rho^*)/g(\sigma), \tag{4}$$

where:

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

For a chain molecule containing N hard-spheres of diameter σ and mass m, we assumed its self-diffusion coefficient at dilute gas condition is the same as that of a single hard-sphere of diameter σ' and mass m' [22], i.e.:

$$D_{0\mathrm{C}} = \frac{3}{8\rho\sigma'^2}\left(\frac{kT}{\pi m'}\right)^{1/2}, \tag{6}$$

where σ' and m' can be calculated as follows:

$$\sigma'^3 = N\sigma^3, \tag{7}$$

$$m' = Nm, \tag{8}$$

Table 1
Database of the self-diffusion coefficients for the compounds studied in this work

No.	Compounds	Formula	M	T (K)	P (MPa)[a]	Data Ref.
1	methane	CH_4	16.043	110.0–323.2	1.5–221.6	[26]
2	n-hexane	C_6H_{14}	86.178	223.2–333.2	0.1–393.8	[27]
3	n-hexadecane	$C_{16}H_{34}$	226.448	298.2–348.2	0.1–279.2	[28]
4	isopentane	C_5H_{12}	72.151	298.0–328.0	0.1–200.0	[29]
5	cyclopentane	C_5H_{10}	70.135	298.0–328.0	0.1–200.0	[29]
6	cyclohexane	C_6H_{12}	84.162	313.0–383.0	0.1–214.0	[30]
7	ethylene	C_2H_4	28.054	123.2–298.2	2.0–272.2	[31]
8	carbon disulfide	CS_2	76.131	268.2–313.2	0.1–385.1	[32]
9	benzene	C_6H_6	78.114	303.0–433.0	0.1–454.4	[33]
10	toluene	C_7H_8	92.134	248.2–348.2	0.1–360.8	[34]
11	chloromethane	CH_3Cl	50.488	186.0–440.0	sat–200.0	[35][b]
12	dichloromethane	CH_2Cl_2	84.933	186.0–406.0	sat–200.0	[35][b]
13	chloroform	$CHCl_3$	119.378	217.0–397.0	sat–150.0	[35][b]
14	carbon tetrachloride	CCl_4	153.823	283.2–328.2	0.1–147.5	[36]
15	fluoromethane	CH_3F	34.033	153.0–440.0	sat–200.0	[37]
16	fluoroform	CHF_3	70.014	142.0–433.0	sat–200.0	[38]
17	perfluorocyclobutane	C_4F_8	200.028	323.0–473.0	5.0–190.0	[39]
18	chlorotrifluoromethane	$CClF_3$	104.459	303.2–348.2	3.7–188.4	[40]
19	tetramethylsilane	$Si(CH_3)_4$	88.224	298.0–373.0	4.5–450.0	[33]
20	pyridine	C_5H_5N	79.101	303.2–423.2	0.1–500.0	[41]
21	acetonitrile	C_2H_3N	41.053	253.2–343.2	0.1–303.6	[42][b]
22	carbon dioxide	CO_2	44.011	223.0–450.0	1.0–200.0	[43][c][44][c]

[a] Where sat refers to the saturated pressure.
[b] Densities were estimated by the Hankinson–Brobst–Thomson method [45].
[c] Densities were calculated from the equation given by Pitzer and Schreiber [46].

which preserve the total volume and mass of molecules. From Eqs. (6)–(8), the following equation can be obtained:

$$D_{0C} = \frac{3\sigma}{8\rho^* N^{1/6}} \left(\frac{kT}{\pi m} \right)^{1/2}, \tag{9}$$

where:

$$\rho^* = \rho N \sigma^3, \tag{10}$$

Analogous to the self-diffusion coefficient equation for a hard-sphere fluid, the self-diffusion coefficient of hard-sphere chain fluid can be expressed as:

$$D_{HSC} = D_{0C} F(N, \rho^*) / g(\sigma), \tag{11}$$

where the radial distribution function at contact should be the value of the hard sphere chain fluid. In this work, it is replaced by the value of the hard sphere fluid for simplification, and is calculated from Eq. (3). The volume fraction η is defined as:

$$\eta = \frac{\pi}{6} \rho^* = \frac{\pi}{6} \rho N \sigma^3. \tag{12}$$

The correction function $F(N,\rho^*)$ in Eq. (11) can be obtained by using MD simulation results. Smith et al. [23] used equilibrium molecular dynamics to simulate fluids containing molecules modeled as chains of tangent hard spheres. The self-diffusion coefficients are calculated for chains of length 2, 4, 8, and 16 at the reduced densities ρ^* ranging from 0.191 to 0.955 using a mean-square displacement approach. By analyzing the MD simulation data of Smith et al. [23], we found the function $F(N,\rho^*)$ has the form:

$$F(N,\rho^*) = f(\rho^*)\exp\left[-0.06356(N-1) - 0.05212\left(\frac{N-1}{N}\right)\rho^* - 1.9709\left(\frac{N-1}{N}\right)^2\rho^*\right]. \tag{13}$$

When the chain length N equals to 1, Eq. (11) reduces to the self-diffusion coefficient equation for a hard-sphere fluid. For the MD simulation data given by Smith et al. [23], Eq. (11) represents the self-diffusion coefficients for the HSC fluid of length $N = 2$, 4, 8, and 16 with the average absolute deviation (AAD) of 3.95%. Fig. 1 presents the simulation data along with the calculated values of Eq. (11). From Fig. 1, one can see that the self-diffusion coefficient equation obtained in this work can give good results in all the ranges of densities.

Table 2
The parameters of the LJC equation and the average absolute deviations from the LJC equation and the RLJ equation

No.	Compounds	N	σ_{LJ} (nm)	ε_{LJ}/k (K)	NDP	AAD%	
						Present	RLJ
1	methane	1.081	0.3630	103.30	59	2.24	2.09
2	n-hexane	2.021	0.4524	199.48	59	2.29	3.34
3	n-hexadecane	4.409	0.7593	0.37	25	1.83	2.45
4	isopentane	1.164	0.5087	469.34	22	5.71	5.71
5	cyclopentane	1.365	0.4565	473.24	21	4.29	4.37
6	cyclohexane	1.356	0.5027	316.12	39	2.06	2.13
7	ethylene	1.562	0.3563	86.03	63	4.61	6.00
8	carbon disulfide	2.071	0.3616	68.25	29	0.97	1.07
9	benzene	1.667	0.4468	160.42	35	4.14	4.37
10	toluene	2.002	0.4509	107.66	54	2.26	3.20
11	chloromethane	2.608	0.3507	10.17	42	3.32	2.63
12	dichloromethane	2.851	0.5369	0.11	43	4.47	6.30
13	chloroform	2.572	0.4246	10.39	39	3.36	3.97
14	carbon tetrachloride	2.115	0.4362	93.11	27	2.45	2.68
15	fluoromethane	2.162	0.4678	0.12	57	6.40	7.56
16	fluoroform	2.378	0.4825	0.17	75	3.70	5.32
17	perfluorocyclobutane	1.292	0.5429	132.38	59	3.70	3.74
18	chlorotrifluoromethane	1.005	0.4631	254.14	66	1.90	1.88
19	tetramethylsilane	2.526	0.4290	147.18	42	4.56	6.52
20	pyridine	1.899	0.4973	9.34	55	8.04	9.10
21	acetonitrile	2.705	0.4333	1.16	65	2.22	6.52
22	carbon dioxide	1.001	0.3660	235.56	105	7.29	7.52
	total				1081	3.72	4.48

2.2. Self-diffusion coefficient equation of the LJC fluid

The relationship between the self-diffusion coefficient and the friction coefficient [25] is:

$$D = kT/\xi. \tag{14}$$

According to Rice and Gray [25], the friction coefficient of a LJ fluid can be written as $\xi_{LJ} = \xi_{HS} + \xi_a$, where the hard core friction coefficient, ξ_{HS}, can be calculated from the self-diffusion coefficient of hard-sphere fluid:

$$\xi_{HS} = kT/D_{HS} = \frac{kT}{D_0}\frac{g(\sigma)}{f(\rho^*)}, \tag{15}$$

and the attractive friction coefficient, ξ_a, can be expressed in terms of the intermolecular attractive potential, $u(r)$, and the radial distribution function, $g(r)$, through the following equation [8,25]:

$$\xi_a = -\frac{(\pi m\beta)^{1/2}\rho}{2(2\pi)^2}\int_0^\infty s^3 U(s)G(s)\mathrm{d}s, \tag{16}$$

where $U(s)$ and $G(s)$ are the spatial Fourier transforms of $u(r)$ and $g(r)$, respectively. Using the numerical data on the radial distribution function of the LJ fluid, Ruckenstein and Liu [8] found that the attractive friction coefficient of the LJ fluid can be approximately written as:

$$\xi_a = \frac{kT}{D_0}\frac{\alpha_1}{T^{*1.5}}, \tag{17}$$

where α_1 is a constant which has a value of 0.4.

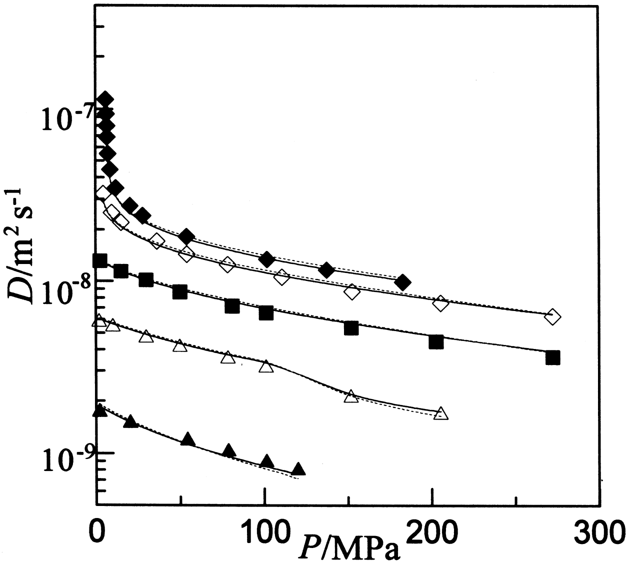

Fig. 2. Self-diffusion coefficients as a function of temperature and pressure for ethylene. solid line refers to the results of the LJC equation; dashed line refers to the results of the RLJ equation; Symbols refer to the experimental values: ▲, 123.15 K; △, 173.15 K; ■, 223.15 K; ◇, 273.15 K; ◆, 298.15 K.

The self-diffusion coefficient equation of a LJ fluid can be obtained using the EHSD method. Various expressions have been obtained theoretically for the EHSD σ_e. They have been tested using a large number of MD simulation data by Ruckenstein and Liu [8]. The Boltzmann EHSD with the parameters given by Ben-Amotz and Herschbach [9] leads to the best agreement with the diffusion data of the LJ fluid. The expression of Boltzmann EHSD is:

$$\sigma_B^*(T^*) = 1.1532\left[1+\left(\frac{T^*}{0.527}\right)^{1/2}\right]^{-1/6}. \tag{18}$$

The EHSD is calculated by:

$$\sigma_e = \sigma_{LJ}\sigma_B^*(T^*) = 1.1532\,\sigma_{LJ}\left[1+\left(\frac{T^*}{0.527}\right)^{1/2}\right]^{-1/6}. \tag{19}$$

Therefore, the hard core friction coefficient for the LJ fluid can be calculated by replacing σ in Eq. (15) by the EHSD σ_e. The equation for self-diffusion in the LJ Fluid can be obtained from Eqs. (14), (15) and (17), i.e.:

$$D_{LJ} = \frac{kT}{\frac{kT}{D_0}\left(\frac{g(\sigma_e)}{f(\rho^*)}+\frac{\alpha_1}{T^{*1.5}}\right)}. \tag{20}$$

For the LJC fluid, the friction coefficient can be modified as:

$$\xi_{LJC} = \xi_{HS} + \xi_C + \xi_{aC} = \xi_{HSC} + \xi_{aC}, \tag{21}$$

where ξ_{HSC} can be obtained from the equation for the self-diffusion in the HSC fluid, i.e.:

$$\xi_{HSC} = kT/D_{HSC} = \frac{kT}{D_{0C}}\frac{g(\sigma)}{F(N,\rho^*)}. \tag{22}$$

Assuming the attractive friction coefficient of a LJC fluid can be obtained from that of the LJ fluid by replacing D_0 in Eq. (15) by D_{0C}, the following expression can be obtained:

$$\xi_{aC} = \frac{kT}{D_{0C}}\frac{\alpha_1}{T^{*1.5}}. \tag{23}$$

From Eqs. (14), (21)–(23), the equation of the self-diffusion coefficient for the LJC fluid can be obtained:

$$D_{LJC} = \frac{kT}{\frac{kT}{D_{0C}}\left(\frac{g(\sigma_e)}{F(N,\rho^*)}+\frac{\alpha_1}{T^{*1.5}}\right)}. \tag{24}$$

The radial distribution function, $g(\sigma_e)$, is given by Eq. (3) and $F(N,\rho^*)$ by Eq. (12). It should be pointed out that in Eqs. (3) and (12), the reduced density ρ^* should be calculated by replacing σ in Eq. (10) by σ_e. Therefore:

$$\rho^* = \rho N{\sigma_e}^3 = \rho N\sigma_{LJ}^3\left[\sigma_B^*(T^*)\right]^3. \tag{25}$$

The comparison between the present LJC Eq. (24) and the RLJ equation will be made in Section 3 by using the experimental self-diffusion coefficients of real compounds. The RLJ equation of Ruckenstein and Liu [8] is:

$$D_{\mathrm{RLJ}} = A_{\mathrm{D}} D_{\mathrm{LJ}} = \frac{A_{\mathrm{D}} kT}{\frac{8}{3} \rho \sigma_{\mathrm{e}}^{2} (\pi mkT)^{1/2} \left[\frac{g(\sigma_{\mathrm{e}})}{f(\rho^{*})} + \frac{\alpha_1}{T^{*1.5}} \right]}. \tag{26}$$

3. Results and discussion

Because we did not find any simulation data for Lennard–Jones chain fluid, the LJC equation has not been tested against molecular dynamics simulation data. In this work, a certain amount of self-diffusion coefficient data for the real polyatomic compounds have been used to test the LJC equation. The data sources, the temperature and pressure ranges of the self-diffusion coefficients for 22 substances are listed in Table 1. The substances studied include paraffin, halogenated paraffins, olefins, aromatics, heterocycles and nitriles. The substances were chosen only when self-diffusion coefficients at different temperatures and pressures are available. Because the density data of chloromethane, dichloromethane, chloroform and acetonitrile are not available from the same

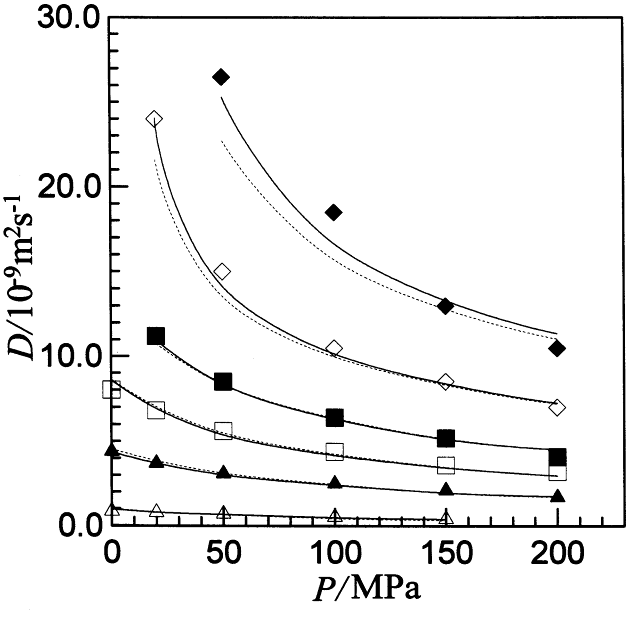

Fig. 3. Self-diffusion coefficients as a function of temperature and pressure for fluoroform. Solid lines refer to the results of the LJC equation; dashed lines refer to the results of the RLJ equation; symbols refer to the experimental value: △, 142 K; ▲, 208 K; □, 250 K; ■, 291 K; ◇, 353 K; ◆, 433 K.

reference as the self-diffusion coefficient, they were estimated by using the Hankinson–Brobst–Thomson method [45].

The LJC equation contains three parameters: N, σ_{LJ} and $\varepsilon_{\mathrm{LJ}}$. They can be determined from diffusion coefficient data by the least squares regress method. The obtained parameters along with the AADs in the self-diffusion coefficient are listed in Table 2. The average absolute deviations is defined as:

$$\mathrm{AAD} = \frac{1}{\mathrm{NDP}} \sum_{i=1}^{\mathrm{NDP}} \left|\left(D_i^{\mathrm{cal}} - D_i^{\mathrm{exp}}\right)/D_i^{\mathrm{exp}}\right| \times 100\%. \tag{27}$$

As seen from Table 2, Eq. (24) provides accurate correlation for almost all the substances studied in this work. For most compounds, the AAD is comparable to the experimental uncertainty. The total AAD for 22 substances is 3.72%.

The LJC equation has been compared with the RLJ equation. The results of the RLJ equation were calculated by the authors using three adjusted parameters: A_{D}, σ_{LJ} and $\varepsilon_{\mathrm{LJ}}$. The three parameter RLJ equation gives less deviations than the one or two parameter models [2,8]. The AADs of the RLJ equation are also listed in Table 2. From Table 2, one can see that for spherical and near-spherical molecules (such as methane, carbon tetrachloride, etc.), the LJC equation and RLJ equation give almost the same AAD, but for nonspherical chain molecules, the LJC equation gives better results.

In Fig. 2, the self-diffusion coefficients for ethylene at different temperatures are plotted against pressure. At high temperature region, both the LJC and RLJ equations give good results, but when the

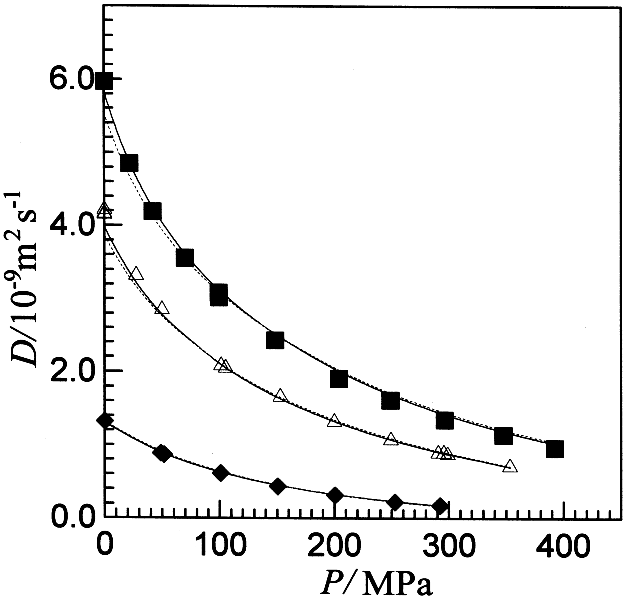

Fig. 4. Self-diffusion coefficients as a function of temperature and pressure for n-hexane. Solid lines refer to the results of the LJC equation; dashed lines refer to the results of the RLJ equation; symbols refer to the experimental values: ◆, 223.15 K; △, 298.15 K; ■, 333.15 K.

temperature becomes low and the pressure becomes high, the RLJ equation yields lower values compared with the experimental values.

The self-diffusion coefficients as a function of temperature and pressure for fluoroform, n-hexane and acetonitrile are shown in Figs. 3–5, respectively. As shown in these figures, The LJC equation developed in this work can represent the experimental self-diffusion coefficients for nonspherical molecules with good accuracy. The LJC equation often gives better results than that of the RLJ equation for nonspherical polyatomic fluid.

Although the LJC equation with three adjustable parameters gives very accurate correlation results for the substances considered, the values obtained for the energy parameter of n-hexadecane, dichloromethane, fluoromethane, fluoroform, pyridine and acetonitrile are very small and unreasonable. The values of the parameters greatly depend on the self-diffusion coefficient data used. In the calculation, one can see that for the LJC fluid, the diffusion coefficient is much more sensitive to the segment diameter σ_{LJ} and the chain length N than to the segment energy parameter $\varepsilon_{\mathrm{LJ}}$. From the results of Ruckenstein and Liu [8], the energy parameter should depend on the critical temperature in a simple manner. Analogous to the LJ fluid, the relation obtained from viscosity data [45] is employed to determine the energy parameter. Assuming the molecular energy is the sum of all the LJ segment energies, one can obtain:

$$N(\varepsilon_{\mathrm{LJ}}/k) = T_c/1.2593. \tag{28}$$

The other two parameters should depend on the molecular size and shape.

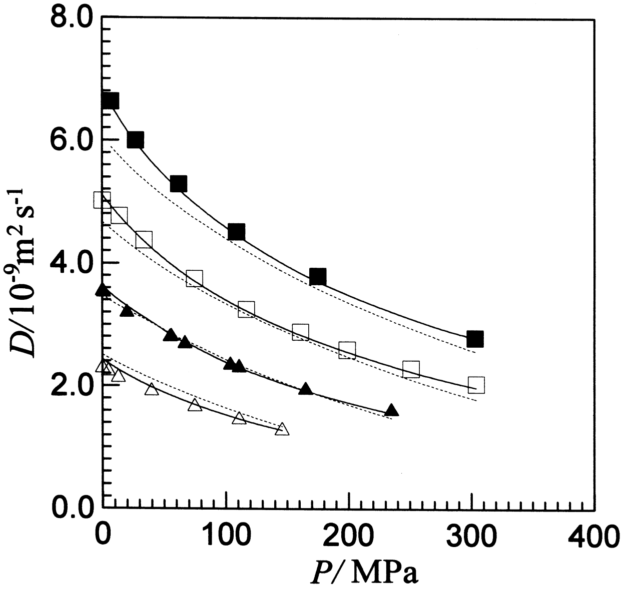

Fig. 5. Self-diffusion coefficients as a function of temperature and pressure for acetonitrile. Solid lines refer to the results of the LJC equation; dashed lines refer to the results of the RLJ equation; symbols refer to the experimental value: △, 253.2 K; ▲, 283.2 K; □, 313.2 K; ■, 343.2 K.

Table 3
Calculated results from the LJC equation with two adjustable parameters

No.	Compounds	N	σ_{LJ} (nm)	ε_{LJ}/k (K)	T_c (K)	NDP	AAD%
1	methane	1.102	0.3547	137.20	190.4	59	3.02
2	n-hexane	2.021	0.4524	199.41	507.5	59	2.31
3	n-hexadecane	4.911	0.4784	116.74	722.0	25	5.83
4	isopentane	1.480	0.4817	247.03	460.4	22	5.93
5	cyclopentane	1.571	0.4469	258.65	511.7	21	4.42
6	cyclohexane	1.351	0.5026	325.34	553.5	39	2.06
7	ethylene	1.326	0.3653	169.12	282.4	63	5.06
8	carbon disulfide	1.846	0.3517	237.45	552.0	29	1.18
9	benzene	1.585	0.4414	281.66	562.2	35	4.22
10	toluene	1.813	0.4458	259.21	591.8	54	3.46
11	chloromethane	1.956	0.3278	169.01	416.3	42	3.33
12	dichloromethane	1.888	0.3627	214.51	510.0	43	8.33
13	chloroform	1.893	0.3923	225.01	536.4	39	4.52
14	carbon tetrachloride	2.017	0.4231	219.05	556.4	27	2.68
15	fluoromethane	1.369	0.3293	182.72	315.0	57	8.12
16	fluoroform	1.636	0.3430	145.28	299.3	75	5.36
17	perfluorocyclobutane	1.102	0.5510	279.95	388.5	59	4.08
18	chlorotrifluoromethane	1.000	0.4657	239.82	302.0	66	2.10
19	tetramethylsilane	2.533	0.4297	140.64	448.6	42	4.52
20	pyridine	1.634	0.4206	301.31	620.0	55	10.17
21	acetonitrile	2.303	0.3232	188.09	545.5	65	5.89
22	carbon dioxide	1.000	0.3655	241.48	304.1	105	7.29
	total					1081	4.72

Table 3 listed the calculation results from the LJC equation with two adjustable parameters. In Table 3, the critical temperatures were taken from Reid et al. [45]. From this table one can see that the values for the parameters become more reasonable though the total AAD increases by 1.00%. The diameters of the LJ segment are in the range of 0.3–0.5 nm. The big and long chain molecules have big values of chain length N. These trends in the values for the parameters of the LJC equation make good physical sense. The LJC equation with two parameters also provides accurate results for the compounds studied. Considering the wide ranges of temperature and pressure, the calculation results are satisfactory.

4. Conclusion

In this work, an expression for the diffusion coefficient of a hard-sphere chain fluid was obtained by using the molecular dynamics simulations of Smith et al. [23]. Based on this expression, an equation of self-diffusion coefficient for the tangent Lennard–Jones chain (LJC) fluid was developed by the effective hard-sphere diameter (EHSD) method and including the soft friction coefficient. The Boltzmann EHSD with the parameters obtained by Ben-Amotz and Herschbach [9] was adopted. The real polyatomic substances were treated as freely tangent LJC molecules. The equation was used to calculate the self-diffusion coefficients for 22 polyatomic substances over wide temperature and pressure ranges, and the total AAD is 3.72%. The equation have been compared with the rough LJ (RLJ) equation given by Ruckenstein and Liu [8]. It gives better results than that of RLJ equation for nonspherical polyatomic fluids. When the energy parameters was estimated from the critical temperature, it was found that the diffusion data for all compounds, including polar molecules, can also be represented accurately with the LJ equation in which only two parameters had to be obtained from the experimental data.

List of symbols

AAD	Average absolute deviation defined by Eq. (27)
A_D	Translational-rotational factor
D	Self-diffusion coefficient, m^2/s
$F(N,\rho^*)$	Correction function for HSC fluid defined by Eq. (13)
$f(\rho^*)$	Correction function for HS fluid defined by Eq. (5)
$G(s)$	Spatial Fourier transforms of $g(r)$
$g(r)$	Radial distribution function
$g(\sigma)$	Radial distribution function at contact
k	Boltzmann constant
M	Molecular mass, g/mol
m	Mass of a segment, kg
N	Chain length
NDP	Number of data points
R	Universal gas constant, 8.3144 J/mol K
s	Parameter in Fourier transform
T	Absolute temperature, K
T^*	Reduced temperature, $T^* = kT/\varepsilon$
$U(s)$	Spatial Fourier transforms of $u(r)$
$u(r)$	Segment–segment potential, J

Greek Letters

α_1	Parameter in Eq. (17)
ε	Lennard–Jones segment energy, J
η	$\eta = \pi\rho\sigma^3/6$ for the HS fluid; $\eta = \pi\rho\sigma^3/6$ for the LJC and real fluids
ρ	Number density, nm^{-3}
ρ^*	Reduced density, $\rho^* = \rho\sigma^3$ for the HS fluid, $\rho^* = \rho\sigma_e{}^3$ for the LJC and real fluids
σ	Segment diameter, nm
σ_e	Effective hard-sphere diameter, nm
σ_B^*	Ratio of effective hard-sphere diameter and LJ segment diameter
ξ	Friction coefficient

Subscripts

a	Attractive
B	Boltzmann effective hard-sphere diameter
C	Chain
c	critical state

E	Enskog
e	Effective hard-sphere diameter
HS	Hard sphere
LJ	Lennard–Jones
LJC	Lennard–Jones chain
RLJ	Rough Lennard–Jones
0	Hard-sphere fluid at very low gas densities
0C	Chain fluid at very low gas densities

Superscripts

*	Reduced quantity
cal	Calculated value
exp	Experimental value

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