Lennard–Jones Chain Model for Self-Diffusion of *n*-Alkanes

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The Lennard–Jones chain model, which was developed from the equation for the self-diffusion coefficient in a Lennard–Jones fluid and the molecular dynamics simulation data of a tangent hard-sphere chain fluid, is used to calculate the self-diffusion coefficient of *n*-alkanes. *n*-Alkanes are characterized by a Lennard–Jones segment diameter, a segment–segment interaction energy, and a chain length expressed as the number of segments. The equation represents the experimental self-diffusion coefficients with an average absolute deviation of 3.93% for 16 *n*-alkanes covering wide ranges of temperature and pressure. The correlated results are compared with those of the rough Lennard–Jones model. A generalized version of the Lennard–Jones chain model is presented which requires only the carbon number in order to predict *n*-alkane self-diffusivity.

KEY WORDS: diffusivity; effective hard-sphere diameter; friction coefficient; Lennard–Jones chain model; *n*-alkane; rough Lennard–Jones model; self-diffusion coefficient.

1. INTRODUCTION

The transport properties of fluids are of considerable importance in the design of chemical process plants, and, in particular, the diffusion coefficient of fluids is a primary variable in mass transfer calculations. Diffusion refers to the net transport of material within a single phase in the absence of mixing (either by mechanical means or by convection) [1]. In this paper, only the diffusion resulting from concentration gradients will be discussed.

The self-diffusion coefficients of gases at low densities may be calculated from the Enskog theory and its modifications [2, 3]. Usually,

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molecular dynamics (MD) simulations for simple spherical fluids, such as hard sphere (HS) and Lennard–Jones (LJ) fluids have been employed to generate equations [4–6] for the self-diffusion coefficient. A connection between real and simple model fluids can be made by using Chandler's rough hard-sphere theory [7, 8]. The self-diffusion coefficient of the shorter n-alkanes can be fairly characterized by these models, but for the longer alkanes, the rotation–translation coupling parameter becomes very small and decreases significantly with falling temperature [9]. Much effort has been made to obtain a method for the correlation and prediction of the diffusivity for the longer n-alkanes. For example, Sun et al. [10] proposed a correlation for the rotation–translation coupling parameter as a function of temperature and carbon number of n-alkanes. Salim and Trebble [11] modified the interacting-sphere model [5] by introducing a multiple hard-sphere term into the probability function of molecular collisions.

In recent years, there has been much interest in understanding the dynamics of n-alkanes by molecular simulations. Mondello et al. [12, 13] have simulated the self-diffusion coefficients for n-alkanes ($6 \leqslant n \leqslant 66$) with nontangent spheres with model potentials. The models for the interactions they used were united atom (UA) models. They found the symmetric UA model of Padilla and Toxvaerd [14], and the optimized symmetric UA model of Paul et al. [15] fit the available experimental data quite well. There have been computer simulations using both Monte Carlo and molecular dynamics for freely jointed tangent spheres with model potentials [16, 17], which are useful for describing fluid phase thermodynamics [18–20]. Although the UA models are more realistic than the tangent-sphere models, they have more intramolecular interaction parameters. The freely jointed tangent-sphere model potentials often contain only three interaction parameters. This made it easier to develop an analytical expression between the studied properties and the interaction parameters.

We have recently developed a tangent Lennard–Jones chain (LJC) model from the equation of self-diffusion in a LJ fluid [6] and the molecular dynamics simulation data for a tangent hard-sphere chain (HSC) fluid [16]. This allows us to model n-alkanes as chains of tangent Lennard–Jones segments and to obtain a new method for the correlation and prediction of the diffusion coefficient of n-alkanes over wide ranges of temperature and pressure.

2. THEORY

The self-diffusion coefficient D in a fluid can be expressed as [21]

$$D = kT/\xi \tag{1}$$

where k is the Boltzmann constant, T is the absolute temperature, and ξ is the friction coefficient.

For a LJ fluid, the friction coefficient can be written as [6, 21]

$$\xi_{LJ} = \xi_H + \xi_S \tag{2}$$

where ξ_H represents the friction coefficient due to the repulsive portion of the potential and ξ_S is that due to the attractive one. Ruckenstein and Liu [6] have determined the hard-core friction coefficient and soft friction coefficient by using MD simulation results of the HS and LJ fluids.

$$\xi_H = \frac{kT}{D_0} \frac{g(\sigma_e)}{f(\rho^*)} \tag{3}$$

$$\xi_S = \frac{kT}{D_0} \frac{\alpha_1}{T^{*1.5}} \tag{4}$$

where $\alpha_1 = 0.4$, $T^* = kT/\varepsilon$, $g(\sigma_e)$ is the hard-sphere radial distribution function at contact, D_0 is the self-diffusion coefficient at very low gas densities, ρ^* is the reduced density, ε is the LJ segment energy, σ_e is the effective hard-sphere diameter (EHSD), and $f(\rho^*)$ is the correction function for a HS fluid.

The self-diffusion coefficient for a dilute gas composed of hard spheres is given by

$$D_0 = \frac{3}{8\rho\sigma_e^2} \left(\frac{kT}{\pi m}\right)^{1/2} \tag{5}$$

where m is the mass of single spherical molecule and ρ is the number density.

The hard-sphere radial distribution function at contact can be obtained from the Carnahan–Starling equation

$$g(\sigma_e) = \frac{1 - 0.5\eta}{(1 - \eta)^3} \tag{6}$$

where $\eta = \pi\rho^*/6 = \pi\rho\sigma_e^3/6$.

The correction function $f(\rho^*)$ has the form [6]

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

Various expressions have been obtained theoretically for the EHSD σ_e. Ruckenstein and Liu [6] have tested them by using a large number of MD simulation data. They found that the Boltzmann EHSD with the parameters obtained by Ben-Amotz and Herschbach [22] leads to the best agreement with the diffusion data. The Boltzmann EHSD is given by

$$\sigma_e = 1.1532\sigma_{LJ}\left[1 + \left(\frac{T^*}{0.527}\right)^{1/2}\right]^{-1/6} \tag{8}$$

where σ_{LJ} is the LJ segment diameter. It should be pointed out that, for hard-sphere or hard-sphere chain fluids, σ_e is equal to the hard-sphere diameter σ.

From Eqs. (1)–(4), the self-diffusion coefficient for a LJ fluid can be obtained:

$$D_{LJ} = D_0 \left/ \left(\frac{g(\sigma_e)}{f(\rho^*)} + \frac{\alpha_1}{T^{*1.5}}\right)\right. \tag{9}$$

Our Lennard–Jones chain model is a straightforward modification of the self-diffusion coefficient equation for the LJ fluid. A long-chained LJ molecule containing N LJ segments of diameter σ_{LJ} and mass m was assumed to be a single LJ molecule of diameter σ'_{LJ} and mass m'. Then the values of σ_e and m in Eqs. (5)–(7) may be replaced by σ'_e and m', which are calculated as follows [11]:

$$\sigma_e'^3 = N\sigma_e^3 \tag{10}$$

$$m' = Nm \tag{11}$$

which preserve the total volume and mass of molecules. Therefore, for a LJC fluid, D_0 and ρ^* can be expressed as

$$D_{0C} = \frac{3\sigma}{8\rho^* N^{1/6}}\left(\frac{kT}{\pi m}\right)^{1/2} \tag{12}$$

$$\rho^* = \rho N\sigma_e^3 \tag{13}$$

Analogous to the LJ fluid, the friction coefficient for a LJC fluid may be written as

$$\xi_{LJC} = \xi_{HSC} + \xi_{aC} \tag{14}$$

where ξ_{HSC} represents the friction coefficient due to the hard-core repulsive potential and the chain formation, and ξ_{aC} is that due to the attractive one.

We assume that the attractive friction coefficient of the LJC fluid is the same as that of a LJ fluid. That is,

$$\xi_{\text{aC}} = \frac{kT}{D_{0\text{C}}} \frac{\alpha_1}{T^{*1.5}} \tag{15}$$

ξ_{HSC} can be obtained from the diffusion coefficient of the HSC fluid by

$$\xi_{\text{HSC}} = kT/D_{\text{HSC}} \tag{16}$$

where D_{HSC} is the self-diffusion coefficient for the HSC fluid.

Recently, Yu and Gao [23] have proposed an equation for the self-diffusion coefficient of the HSC fluid. The equation is

$$D_{\text{HSC}} = D_{0\text{C}} F(N, \rho^*)/g(\sigma) \tag{17}$$

where $g(\sigma)$ can be calculated from Eqs. (6) and (13). The correction function $F(N, \rho^*)$ in the above equation was obtained by using MD simulation results of Smith et al. [16] in the density range $0.191 \leqslant \rho^* \leqslant 0.955$. The obtained equation has the form

$$F(N, \rho^*) = f(\rho^*) \exp[-0.06356(N-1) - (0.05212\gamma + 1.9709\gamma^2)\,\rho^*] \tag{18}$$

where $\gamma = (N-1)/N$. Equation (17) predicts the self-diffusion coefficients for the HSC fluid of chain length $N = 2, 4, 8,$ and 16 with the absolute average deviation (AAD) of 3.95%.

From Eqs. (1) and (14)–(17), one can obtain the self-diffusion coefficient equation for the LJC fluid. That is

$$D_{\text{LJC}} = D_{0\text{C}} \left/ \left[\frac{g(\sigma_{\text{e}})}{F(N, \rho^*)} + \frac{\alpha_1}{T^{*1.5}} \right] \right. \tag{19}$$

3. RESULTS AND DISCUSSION

The Lennard–Jones chain model outlined above was tested on *n*-alkanes from CH_4 to $C_{154}H_{310}$. Table I lists the *n*-alkanes considered, the data sources for the self-diffusion coefficients, the number of data points (*NDP*), and the temperature T and pressure P ranges involved. Densities of methane, ethane, and propane were calculated from equations proposed by Younglove and Ely [30], densities of *n*-hexane and *n*-octane from the same references as the self-diffusion coefficients, and densities of *n*-heptane and higher *n*-alkanes from the Hudlestone equation [31]. The values of the critical properties of *n*-alkanes up to *n*-$C_{16}H_{34}$ were extracted from a compilation by Reid et al. [1]. Critical temperatures and critical pressures for

Table I. Database of the Self-Diffusion Coefficients for the *n*-Alkanes Studied in this Work

Component	T_c (K)	M	T (K)	P (MPa)	NDP	Ref.
Methane	190.4	16.043	110.0–454.0	1.5–221.6	104	24, 25
Ethane	305.4	30.070	136.0–454.0	25.–200.0	65	24
Propane	369.8	44.094	112.0–453.0	Sat.–200.0	95	24
n-Hexane	507.5	86.178	223.2–333.2	0.1–393.8	59	26
n-Heptane	540.3	100.205	185.6–371.2	0.1	11[a]	27
n-Octane	568.8	114.232	248.2–348.1	0.1–360.8	43	28
n-Nonane	594.6	128.259	222.1–422.0	0.1	11[a]	27
n-Decane	617.7	142.286	247.9–440.2	0.1	11[a]	27
n-$C_{12}H_{26}$	658.2	170.340	264.2–434.8	0.1	11[a]	27
n-$C_{14}H_{30}$	693.0	198.394	279.4–436.2	0.1	11[a]	27
n-$C_{16}H_{34}$	717.0	226.448	291.9–434.3	0.1–279.2	36	27, 29
n-$C_{18}H_{38}$	748.0	254.504	301.9–438.8	0.1	11[a]	27
n-$C_{30}H_{62}$	848.0	422.822	356.5–469.0	0.1–600.0	63	9
n-$C_{50}H_{102}$	942.7	703.360	375.0–473.0	0.1–550.0	46	9
n-$C_{78}H_{158}$	1020.5	1096.113	403.0–473.0	0.1–450.0	35	9
n-$C_{154}H_{310}$	1134.1	2162.155	412.0–473.0	0.1–350.0	24	9

[a] The data points were calculated from the Arrhenius equation, with the parameters given in Ref. 27.

n-alkanes longer than *n*-$C_{16}H_{34}$ were estimated from a molecular weight-dependent equation given by Sigmund and Trebble [32].

$$T_c = -50.6 + 155.4 \ln M - \frac{18820}{M} + \left(\frac{785}{M}\right)^2 \tag{20}$$

$$V_c = 10^{-6}(48 + 4.07M - 2340/M) \tag{21}$$

where T_c is the critical temperature, V_c is the critical volume in $m^3 \cdot mol^{-1}$, and M is the molecular weight.

In Tables II and III, the average absolute deviation (AAD) is defined as

$$AAD = \frac{100}{NDP} \sum_{i=1}^{NDP} |(D_i^{cal} - D_i^{exp})/D_i^{exp}| \tag{22}$$

and the standard deviation (SD) is calculated from

$$SD = 100 \left[\frac{1}{NDP-1} \sum_{i=1}^{NDP} \left(\frac{D_i^{cal} - D_i^{exp}}{D_i^{exp}}\right)^2 \right]^{1/2} \tag{23}$$

where D_i^{cal} is the calculated diffusion coefficient and D_i^{exp} is the experimental value.

Table II. Fit Results of the LJC Model and Comparison with the RLJ Model

Component	N	σ_{LJ} (10^{-10} m)	ε/k (K)	NDP	AAD (%)	
					LJC	RLJ
Methane	1.077	3.570	140.38	104	3.80	3.14
Ethane	1.561	3.609	155.36	65	3.63	4.02
Propane	2.578	3.425	113.91	95	7.04	11.29
n-Hexane	2.021	4.524	199.41	59	2.30	3.34
n-Heptane	2.085	4.701	205.78	11	3.00	3.58
n-Octane	2.119	4.892	213.16	43	3.45	3.32
n-Nonane	2.145	5.072	220.12	11	2.65	3.63
n-Decane	2.166	5.233	226.46	11	4.80	2.77
n-C$_{12}$H$_{26}$	2.287	5.474	228.54	11	1.49	2.67
n-C$_{14}$H$_{30}$	2.373	5.702	231.90	11	1.74	2.91
n-C$_{16}$H$_{34}$	3.898	5.122	147.08	36	6.76	5.20
n-C$_{18}$H$_{38}$	4.002	5.294	148.46	11	5.71	2.81
n-C$_{30}$H$_{62}$	9.692	4.842	69.48	63	5.34	7.14
n-C$_{50}$H$_{102}$	15.912	5.001	47.05	46	5.39	6.27
n-C$_{78}$H$_{158}$	24.998	5.113	32.42	35	3.20	13.65
n-C$_{154}$H$_{310}$	40.893	5.535	22.02	24	2.62	10.27
Total				636	3.93	5.36

Table III. Results of the LJC Model for Self-Diffusion Coefficients with Parameters from Eqs. (24)–(28)

Alkane	NDP	AAD (%)	SD (%)
Methane	104	3.85	5.35
Ethane	65	4.01	5.63
Propane	95	6.91	8.81
n-Hexane	59	4.05	5.44
n-Heptane	11	16.89	18.00
n-Octane	43	10.76	14.36
n-Nonane	11	5.05	6.09
n-Decane	11	6.03	6.87
n-C$_{12}$H$_{26}$	11	7.00	8.28
n-C$_{14}$H$_{30}$	11	9.47	11.64
n-C$_{16}$H$_{34}$	36	8.24	10.16
n-C$_{18}$H$_{38}$	11	9.66	11.61
n-C$_{30}$H$_{62}$	63	5.34	6.77
n-C$_{50}$H$_{102}$	46	6.27	8.34
n-C$_{78}$H$_{158}$	35	6.91	7.84
n-C$_{154}$H$_{310}$	24	3.40	4.78
Total	636	7.12	8.75

In this work, n-alkanes were modeled as tangent LJC fluids. The LJC model contains three parameters: σ_{LJ}, ε/k, and N. Because 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 energy parameter ε/k, the values for ε/k may be set in accordance with some reasonable trends. In the present study, the relation between the energy parameter and the critical temperature, which was obtained from viscosity data by Chung et al. [33], was modified and employed. The energy parameter can be calculated from

$$\varepsilon/k = T_C/1.2593N \tag{24}$$

where a chain molecular energy was assumed to be the sum of the energies for all the LJ segments in the molecule. The other two parameters were regressed for each component by using the standard deviation as an objective function.

Table II lists the fit results of the LJC model. From this table, one can see that the LJC model provides an accurate correlation for all n-alkanes. For almost all the n-alkanes, the AAD is smaller than the experimental uncertainty. The reported measurement precision was $\pm 5\%$ [24]. The chain length N in Table II is smaller than the carbon number in a molecule. This is because the realistic chain molecule has a *trans-gauche* barrier and is not completely flexible. It can also been seen from Table II that the values of the LJ segment diameter for n-alkanes longer than n-hexane are between 4.5×10^{-10} and 5.7×10^{-10} m. These values are larger than that of the CH_3 or CH_2 group. In the work of Mondello et al. [13], the diameter of the CH_3 or CH_2 group has a value of 4.010×10^{-10} m. These results indicate that the tangent LJC model leads to more dynamically flexible molecules than the realistic n-alkanes.

For comparison, the AAD from the rough Lennard–Jones model (RLJ) [6] with three parameters is also listed in Table II. In the calculation, the same objective function was used to determine the three adjustable parameters for the RLJ model. The two parameter RLJ model was not included because high deviations, larger than 50%, were found when it is used to correlate the self-diffusion coefficients for n-alkanes longer than triacontane. The LJC and RLJ models give almost the same AAD for methane, because methane is not too far from a single LJ molecule. For longer n-alkanes, the LJC model shows superiority compared to the RLJ model and shows a reduction of 1% or more in the AAD.

Figures 1–4 present the isothermal pressure dependence of the self-diffusion coefficients for n-$C_{30}H_{62}$, n-$C_{50}H_{102}$, n-$C_{78}H_{158}$, and n-$C_{154}H_{310}$, respectively. From these figures, it can be seen that at low temperatures,
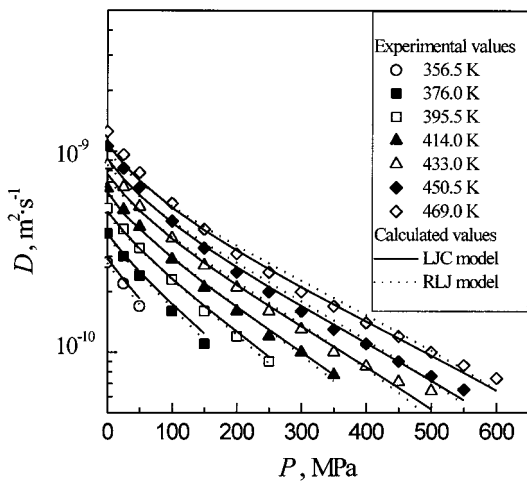
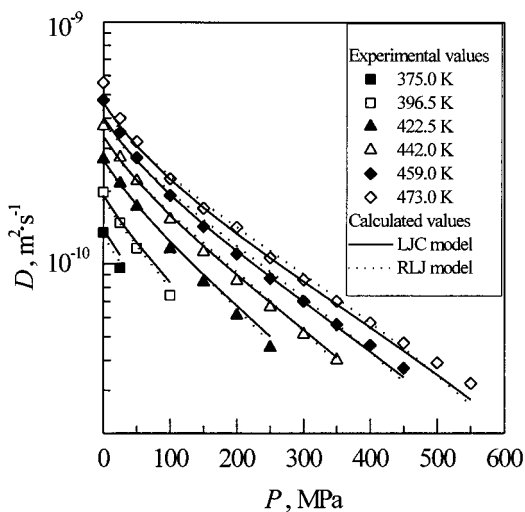**Fig. 1.** Isothermal pressure dependence of self-diffusion coefficients in triacontane.

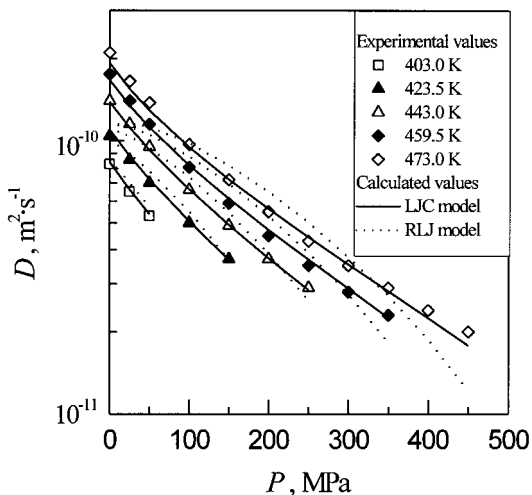**Fig. 2.** Isothermal pressure dependence of self-diffusion coefficients in pentacontane.

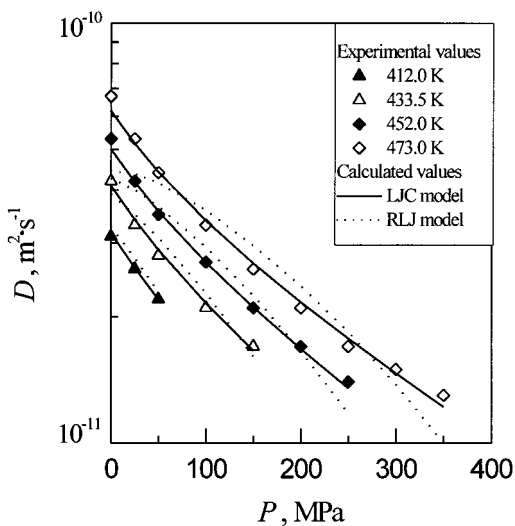**Fig. 3.** Isothermal pressure dependence of self-diffusion coefficients in n-$C_{78}H_{158}$.

Fig. 4. Isothermal pressure dependence of self-diffusion coefficients in n-$C_{154}H_{310}$.

almost the same good agreement between the calculated and the experimental values is obtained for LJC and RLJ models, but at high temperatures, the RLJ model yields much larger deviations from the experimental self-diffusion coefficients. Good agreement between the calculated and the experimental self-diffusion coefficients can be obtained from the LJC model over the entire range of temperature and pressure for these long chain molecules.

For engineering applications, it is important to generalize functions for all the model parameters. Based on the analyses of the parameters listed in Table II, the following equations were generated and were correlated against carbon number (n_C) in a molecule. For CH_4–C_3H_8,

$$\sigma_{LJ} = 10^{-10}(3.443 + 1.850n_C^{-3}) \, m \tag{25}$$

$$N = 0.2697 + 0.7495n_C \tag{26}$$

for C_6H_{14}–$C_{154}H_{310}$,

$$\sigma_{LJ} = 10^{-10}(6.417 + 36.54n_C^{-1} - 15.034n_C^{-1/2} - 43.064n_C^{-3}) \, m \tag{27}$$

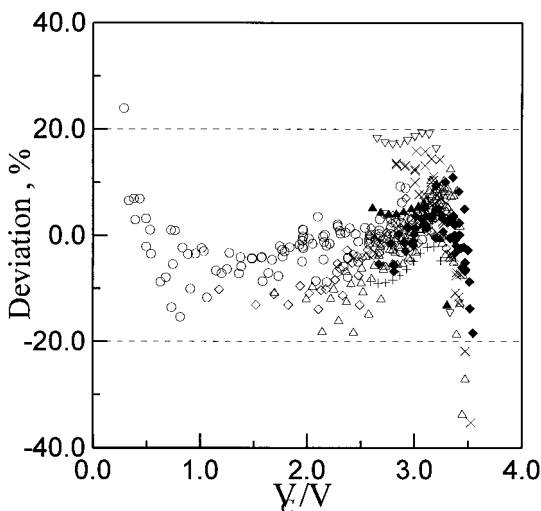$$N = -10.360 + 0.139n_C + 9.986n_C^{-1/2} + 2.510n_C^{1/2} \tag{28}$$

Fig. 5. Percentage deviations $[100(D_{cal} - D_{exp})/D_{exp}]$ of calculated self-diffusion coefficients from Eq. (19) utilizing generalized Eqs. (24)–(28) from experimental data for shorter *n*-alkanes at different reduced densities: ○, CH_4; ◇, C_2H_6; △, C_3H_8; ◆, *n*-C_6H_{14}; ▽, *n*-C_7H_{16}; ×, *n*-C_8H_{18}; ▲, *n*-C_9H_{20}; +, *n*-$C_{10}H_{22}$.

The equations need to be broken off at propane because *trans* and *gauche* conformations begin to appear at *n*-butane. It is not the molecule as a whole that undergoes a diffusive displacement but, due to the increasing flexibility, the contribution of segmental movements becomes more dominant. When the LJC model parameters from Eqs. (24)–(28) are used to calculate self-diffusion coefficients, the predicted errors are shown in Table III. Figures 5 and 6 give the percentage deviations in the self-diffusion coefficients for 16 *n*-alkanes calculated from the generalized parameters. For 636 data points, only 9 points have deviations which are larger than $\pm 20\%$. In the book of Reid et al. [1], the correlation of Hayduk and Minhas is recommended to calculate the diffusion coefficients for normal paraffins up to C_{32}, but the temperature range covered in their correlation is small and it is not suitable for the estimation of the self-diffusion coefficients for *n*-alkanes under high pressure. Considering the wide ranges of temperature and pressure involved and the large number of data points from different authors used in this work, the prediction results of the LJC model are acceptable.
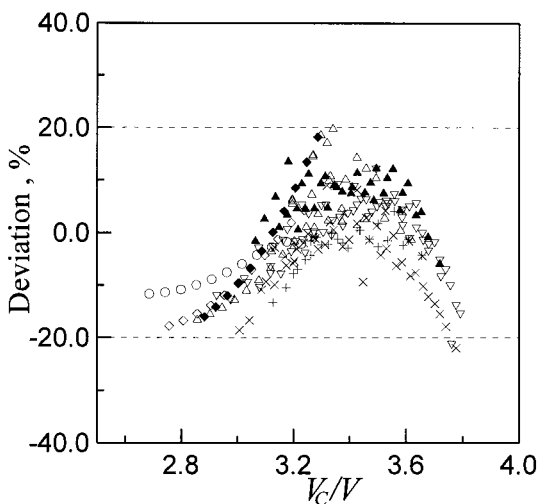

Fig. 6. Percentage deviations $[100(D_{cal} - D_{exp})/D_{exp}]$ of calculated self-diffusion coefficients from Eq. (19) utilizing generalized Eqs. (24)–(28) from experimental data for longer *n*-alkanes at different reduced densities: $\bigcirc$, *n*-$C_{12}H_{26}$; $\diamondsuit$, *n*-$C_{14}H_{30}$; $\triangle$, *n*-$C_{16}H_{34}$; $\blacklozenge$, *n*-$C_{18}H_{38}$; $\triangledown$, *n*-$C_{30}H_{62}$; $\times$, *n*-$C_{50}H_{102}$; $\blacktriangle$, *n*-$C_{78}H_{158}$; $+$, *n*-$C_{154}H_{310}$.

4. CONCLUSIONS

The Lennard–Jones chain model, which was developed from the Lennard–Jones model and molecular dynamics simulations of a tangent hard-sphere chain fluid, was tested with a large number of diffusion data for long-chained normal alkanes over wide ranges of temperature and pressure. The segment–segment interaction energy parameter ε/k is estimated from the critical temperature. Comparison of the correlation results for the self-diffusion coefficients of n-alkanes shows that the Lennard–Jones chain model is superior to the rough Lennard–Jones model with three adjustable parameters. Generalized parameters σ_{LJ} and N were proposed as a function of carbon number only. This allows one to make acceptable predictions regarding the self-diffusion coefficients of n-alkanes.

APPENDIX

As an example, we estimate the self-diffusion coefficient of n-hexane at 298.15 K and 0.1 MPa. Data: from Table I, $M = 86.178$ g $\cdot$ mol^{-1} = 0.086178 kg $\cdot$ mol^{-1}; from Ref. 26, at 298.15 K and 0.1 MPa, density $d = 7.598$ mol $\cdot$ dm^{-3} = 7.598×10^3 mol $\cdot$ m^{-3}; then number density $\rho = 4.5763 \times 10^{27}$ m^{-3}. From Table II, $N = 2.021$, $\sigma_{LJ} = 4.524 \times 10^{-10}$ m, and $\varepsilon/k = 199.41$ K; then $T^* = 1.4952$.

From Eqs. (8) and (13), $\sigma_e = 4.4254 \times 10^{-10}$ m, $\rho^* = 0.8016$, $\eta = 0.4197$. From Eqs. (6), (7), and (18), $g(\sigma_e) = 4.0434$, $f(\rho^*) = 1.0843$, and $F(N, \rho^*) = 0.6648$.

The mass of an LJ segment can be calculated from the molecular weight. That is,

$$m = M/(N_A \cdot N) \tag{A1}$$

where N_A is Avogadro's constant. Considering the gas constant $R = kN_A$, the following equation can be obtain from Eq. (12):

$$D_{0C} = \frac{3\sigma_e N^{1/3}}{8\rho^*} \left(\frac{RT}{\pi M}\right)^{1/2} \tag{A2}$$

From Eq. (A2), $D_{0C} = 2.505 \times 10^8$ m$^2 \cdot$ s^{-1}. From Eq. (19), $D = 3.98 \times 10^{-9}$ m$^2 \cdot$ s^{-1}. The experimental self-diffusion coefficient for n-hexane at 298.15 K and 0.1 MPa from Ref. 26 is 4.18×10^{-9} m$^2 \cdot$ s^{-1}, error = -4.8%.

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