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# Self-diffusion coefficient of two-center Lennard-Jones fluids: Molecular simulations and free volume theory

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A comprehensive investigation is conducted to study the thermodynamics, structure, and mean free volume of rigid two-center Lennard-Jones fluids through Monte Carlo simulations. For a large number of states, the self-diffusion coefficient is computed using the following two different approaches: the equilibrium molecular dynamics simulation method and the modified Cohen–Turnbull theory. The effects of the bond elongation on different thermophysical properties are studied. The generic van der Waals theory, which has recently been extended to rigid polyatomic fluids [A. Eskandari Nasrabad and R. Laghaei, *J. Chem. Phys.* **125**, 154505 (2006)], is used to compute the mean free volume needed in the modified Cohen–Turnbull theory. The effective site diameter is computed using the virial minimization method and the results are applied within the generic van der Waals theory. The Gibbs ensemble Monte Carlo simulation technique is applied to determine the location of the fluid phase envelope. The *NVT* Monte Carlo simulation method is then utilized to compute the equation of state and the correlation functions appearing in the generic van der Waals theory. It appears that the logarithm of the mean free volume versus density is almost linear at  $\rho > \rho_c$  independent of the bond length, which suggests a universal behavior. The self diffusion coefficient results of the modified Cohen–Turnbull theory are analyzed in detail. © 2009 American Institute of Physics. [DOI: 10.1063/1.3054139]

## I. INTRODUCTION

Diffusion process as the translocation of particles due to thermal fluctuations is one of the basic and ubiquitous phenomena in nature.<sup>1–3</sup> Apart from its scientific importance, diffusion is of enormous practical relevance for industry. Compared to other transport properties, experimental data on diffusion coefficients are scarce because of the technical difficulties of these measurements. On the other hand, different molecular dynamics (MD) simulation techniques in conjunction with the Einstein or Green–Kubo relations have become standard tools to compute the transport properties.<sup>4,5</sup> It has been shown that both methods are mathematically equivalent.<sup>6</sup> The results of computer simulations for a model potential serve as a testing ground for various theoretical methods. The thermophysical properties of two-center Lennard-Jones (2CLJ) fluids have been studied in the past via computer simulations<sup>7–14</sup> and theory.<sup>15–19</sup> Although the transport coefficients for the spherical potential models have been reported by several authors,<sup>20–26</sup> the relevant data for two-center model fluids are not abundant in the literature. In the present work, the self-diffusion coefficient of the 2CLJ model fluid is computed using the Green–Kubo approach within the equilibrium MD simulation method over a wide range of densities and temperatures. The influences of the bond length on the subject are explored.

From the theoretical standpoint, the diffusion coefficient of gases at low densities is well understood via the Chapman–Enskog theory for a long time.<sup>27</sup> For dense gases

and liquids, the mechanism of diffusion has been studied through the recent developments of the mode-coupling theories.<sup>28</sup> As an alternate method, the diffusion coefficient can be computed using a free volume theory. Cohen and Turnbull proposed a theory, which relates the mean free volume of a system to its diffusion constant.<sup>29</sup> Efforts have been made to establish a molecular Cohen–Turnbull theory in which the diffusion coefficient is obtained based on a sufficient knowledge at the molecular level such as the interaction potential, the effective diameter, and the pair correlation function.<sup>30–32</sup> A critical analysis has recently been made for the self-diffusion coefficient results of this modified Cohen–Turnbull theory for the Mie(14,7) model fluid.<sup>25</sup>

The generic van der Waals (GvdW) theory<sup>32,33</sup> has been used to compute the mean free volume needed in the modified Cohen–Turnbull theory.<sup>25,31,32,34</sup> This theory is a reformulation of the statistical mechanical virial equation based on a separation of the repulsion and attraction parts of the interaction potential.<sup>32,33</sup> The theory has been used to compute the GvdW parameters and the mean free volume of LJ,<sup>24,31,32,34,35</sup> argon (with an *ab initio* forcefield),<sup>36</sup> Mie(14,7),<sup>37</sup> and carbon disulfide<sup>38</sup> fluids.

In this paper, Monte Carlo (MC) and MD simulations are used to study the thermodynamics, structure, mean free volume, and self-diffusion coefficient of 2CLJ fluids over a wide range of densities and temperatures. To explore the effects of the bond elongation on different properties, the three bond lengths of 0.5, 0.75, and 1.0 are considered. The Gibbs ensemble MC simulation technique is used to obtain the fluid phase envelope and the *NVT* Monte Carlo (*NVT*-MC) simulation method is applied to compute the equation of state and

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the correlation functions. The effective site diameter is calculated using the virial minimization method and the results are utilized within the GvdW theory. The self-diffusion coefficient is then computed through the modified Cohen–Turnbull theory and the results are compared with those from MD simulations. The behavior of different quantities with respect to the density and temperature is studied and discussed.

## II. THEORETICAL BASIS

### A. GvdW theory and effective site diameter

The GvdW theory has recently been extended to rigid polyatomic molecules.<sup>38</sup> For a system of rigid polyatomic particles obeying the site-site interaction potential, the GvdW equation is given by<sup>38</sup>

$$(p^* + \bar{A}^* \rho^{*2})(v^* - \bar{B}^*) = T^*, \quad (1)$$

where  $p^* = p\sigma^3/\epsilon$  is the reduced pressure with  $\sigma$  being the site diameter and  $\epsilon$  being the potential well-depth,  $\rho^* = \rho\sigma^3$  is the reduced density,  $v^* = v/\sigma^3$  is the reduced specific volume,  $T^* = k_B T/\epsilon$  is the reduced temperature with  $k_B$  being the Boltzmann constant, and  $\bar{A}^* = \bar{A}/\sigma^3\epsilon$  and  $\bar{B}^* = \bar{B}/\sigma^3$  are the GvdW parameters. The statistical mechanical relations for the  $\bar{A}$  and  $\bar{B}$  parameters have been given in Ref. 38. The reduced effective site diameter  $\bar{\delta}_{\alpha\beta}^* = \bar{\delta}_{\alpha\beta}/\sigma$ , which gives the effective diameter between site  $\alpha$  in one molecule and site  $\beta$  in another, is used in the GvdW parameter  $\bar{A}^*$  and  $\bar{B}^*$  expressions.<sup>38</sup> The effective site diameter  $\bar{\delta}_{\alpha\beta}^*$  is obtained by solving the following equation:<sup>38</sup>

$$\left( \frac{\partial \bar{I}(r_{\alpha\beta}^*)}{\partial r_{\alpha\beta}^*} \right)_{r_{\alpha\beta}^* = \bar{\delta}_{\alpha\beta}^*} = 0, \quad (2)$$

with  $\bar{I}(r_{\alpha\beta}^*)$  being

$$\bar{I}(r_{\alpha\beta}^*) = r_{\alpha\beta}^{*2} \frac{d\phi^*(r_{\alpha\beta}^*)}{dr_{\alpha\beta}^*} \langle \mathbf{e}_{\alpha\beta} \cdot \mathbf{R}_{12}^* \rangle_{\Omega} g(r_{\alpha\beta}^*), \quad (3)$$

where  $r_{\alpha\beta}^* = r_{\alpha\beta}/\sigma$  is the reduced distance between site  $\alpha$  and  $\beta$  on two different molecules,  $\phi^*(r_{\alpha\beta}^*) = \phi(r_{\alpha\beta})/\epsilon$  is the reduced site-site interaction potential,  $\mathbf{e}_{\alpha\beta}$  is a unit vector between sites  $\alpha$  and  $\beta$  on two molecules,  $\mathbf{R}_{12}^*$  is a vector between centers of mass of two molecules,  $\langle \dots \rangle_{\Omega}$  denotes the average over the molecular orientations, and  $g(r_{\alpha\beta}^*)$  is the site-site pair correlation function. In what follows, for the sake of simplicity, the asterisk in reduced quantities is removed.

The hat symbol in  $\bar{A}$ ,  $\bar{B}$ , and  $\bar{\delta}_{\alpha\beta}$  indicates that these quantities have contributions from the site-site interaction force and the bond force [the bracket term in Eq. (3)]. It is obvious that the intermolecular forces are responsible for the excluded volume of particles. To compute the excluded volume, Eq. (3) should be replaced with the following relation, which has contributions from the site-site forces (for a detailed discussion on this issue, see Ref. 39),

$$I(r_{\alpha\beta}) = r_{\alpha\beta}^3 \frac{d\phi(r_{\alpha\beta})}{dr_{\alpha\beta}} g(r_{\alpha\beta}). \quad (4)$$

Upon using the above relation, the following equation for the excluded volume is obtained

$$B(\rho, T) = \sum_{\alpha\beta=1}^N B_{\alpha\beta}(\rho, T) \left[ 1 + \rho \sum_{\alpha\beta=1}^N B_{\alpha\beta}(\rho, T) \right]^{-1}, \quad (5)$$

where  $N$  is the number of interaction sites on molecule and  $B_{\alpha\beta}$  is given by

$$B_{\alpha\beta}(\rho, T) = -\frac{2\pi}{3T} \int_0^{\delta_{\alpha\beta}} dr_{\alpha\beta} I(r_{\alpha\beta}). \quad (6)$$

In the above relation, the effective site diameter  $\delta_{\alpha\beta}$ , which has only the intermolecular contribution, is given by

$$\left( \frac{\partial I(r_{\alpha\beta})}{\partial r_{\alpha\beta}} \right)_{r_{\alpha\beta} = \delta_{\alpha\beta}} = 0. \quad (7)$$

The above relation gives rise to  $\delta_{\alpha\beta}$ , which is the value of  $r_{\alpha\beta}$  where  $I(r_{\alpha\beta})$  is minimum with respect to  $r_{\alpha\beta}$ . The free volume is then obtained using the relation

$$v_f(\rho, T) = v - B(\rho, T). \quad (8)$$

The results of this work for the free volume are given in the following sections.

### B. Green–Kubo formalism and modified Cohen–Turnbull theory

For diffusion coefficients, the Green–Kubo formula is an integral of the velocity autocorrelation function of center of mass<sup>5,6</sup>

$$D = \frac{1}{3N} \int_0^\infty \left\langle \sum_{i=1}^N \mathbf{v}_i(0) \cdot \mathbf{v}_i(t) \right\rangle dt, \quad (9)$$

where  $\mathbf{v}_i$  is the velocity of center of mass of  $i$ th particle,  $t$  is the time, and  $\langle \dots \rangle$  denotes the ensemble average. In this work, the equilibrium MD simulation method is used to compute the velocity autocorrelation function and diffusion coefficient.

Diffusion coefficient can be obtained by making use of the modified Cohen–Turnbull theory.<sup>25,32</sup> According to this theory, the (reduced) diffusion coefficient is computed via<sup>32</sup>

$$D = D_0 \exp\left(-\alpha \frac{v_c}{v_f}\right), \quad (10)$$

where  $D_0$  is the (reduced) Chapman–Enskog diffusion coefficient for a spherical particle with the effective molecular diameter  $\delta_M$  at low densities<sup>27</sup>

$$D_0 = \frac{3}{8\rho\delta_M^2} \sqrt{\frac{T}{\pi m}}, \quad (11)$$

$\alpha$  is the overlap parameter ( $\alpha \approx 1.0$ ), and  $v_c$  is the critical volume. For a system of 2CLJ particles,  $m=2$ . As the virial minimization method has not been extended to compute the effective molecular diameter, in this work, the MD simulation results at very low densities are used to compute it.

The critical volume of a spherical particle can be calculated via<sup>32</sup>

$$v_c = \frac{\pi}{6}(\delta - \Delta r_0)^3, \quad (12)$$

where  $\Delta r_0$  is a distance between the zero potential and zero force of the interaction potential. Upon using the above relation, the overlap parameter is unity ( $\alpha=1.0$ ) and Eq. (10) is capable of predicting the diffusion coefficient.<sup>25,32</sup> The above relation can be extended to 2CLJ particles by adding the critical volumes of each interaction site

$$v_{c,M} = \sum_{i=1}^2 \frac{\pi}{6} r_{i,c}^3 - \bar{v}_{1,2}, \quad (13)$$

where  $r_{i,c} \equiv \delta_i - \Delta r_{i,0}$  is the critical diameter of the  $i$ th interaction site and  $\bar{v}_{1,2}$  is the overlapping volume between two critical spheres.

### III. COMPUTATION DETAILS

The thermodynamic properties of the coexisting fluid phases were computed using the *NVT* Gibbs ensemble MC simulation technique.<sup>40</sup> MC simulations were performed using 500 particles in a cubic box (or two cubic boxes in Gibbs ensemble MC) with standard periodic boundary conditions and minimum image convention.<sup>4</sup> About 10 000 MC cycles were carried out to achieve equilibrium conditions and additional 50 000 cycles to collect the ensemble averages. Each simulation cycle consists of 500 random displacements of the center of mass, 500 random rotations for both types of simulations and also one volume change, and 100–600 particle transfer trial moves for the Gibbs ensemble MC simulation.<sup>41</sup> For the displacement, rotation, and volume change attempts, the maximum trial moves were adjusted every 100 MC steps to give an average acceptance ratio of 50%. The potential cutoff distance was set to half the box length and standard relations<sup>4</sup> were used to compute the corrections on energy and pressure.

Equilibrium MD simulations were carried out in constant *NVT* ensemble with 500 particles. In the present work, a harmonic bond potential was used

$$\phi(l) = \frac{1}{2}k(l - l_e)^2, \quad (14)$$

where  $k$  is the reduced force constant,  $l$  is the bond length, and  $l_e$  is the reduced bond length at equilibrium ( $(\phi(l))_{l=l_e} = 0$ ). It has been shown<sup>39</sup> that the thermophysical properties of flexible 2CLJ fluids are essentially the same as those for the rigid 2CLJ by taking  $k \geq 1600$ . In this work, the bond spring constant  $k=3000$  is chosen, which is the value taken by Johnson *et al.*<sup>42</sup> and by Reis *et al.*<sup>43</sup>

The system was coupled to a heat bath according to the weak coupling method<sup>44</sup> to control the temperature with a coupling time constant of 1.0 in reduced unit ( $t^* = t\sigma\sqrt{\epsilon/m}$ ). The velocity Verlet algorithm was used to integrate the equations of motion in a time step equal to 0.005 (in reduced units) and a potential cutoff distance  $r^* = r/\sigma = 4.0$  was taken in all simulation runs. The convergence of the integral in Eq. (9) was assured by taking a sufficient number of the time

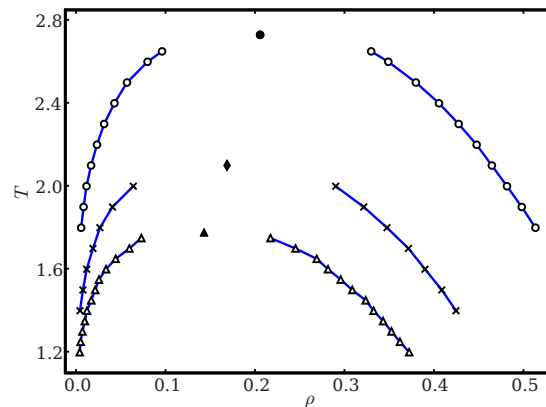


FIG. 1. (Color online) Orthobaric densities for 2CLJ fluids. The simulation results for  $l=0.5$  ( $\circ$ ),  $0.75$  ( $\times$ ), and  $1.0$  ( $\triangle$ ) are plotted. The predicted critical points are indicated with the filled symbols. The solid lines connect the simulation results.

steps. The first  $5 \times 10^4$  time steps were taken to reach the equilibrium condition in all simulations. For low density limit ( $\rho=0.01$  and  $0.02$ ), the next  $4 \times 10^6$  time steps, and for the higher densities, the next  $5 \times 10^5$  time steps were used to collect the ensemble averages. The sampling algorithm described by Rapaport<sup>5</sup> was used to compute the autocorrelation functions. In this algorithm, sets of different time origins are created in the course of the production run, which are simultaneously sampled.

### IV. RESULTS AND DISCUSSION

Tables with the numerical results of Gibbs ensemble MC simulations and also tables with the computed diffusion constant results of MD simulations are presented in the supplementary material in the electronic archive of this journal.<sup>45</sup>

#### A. Thermodynamics and structure

The Gibbs ensemble MC simulation results for the orthobaric densities and the vapor pressure are plotted in Figs. 1 and 2, respectively. A scaling law was used to estimate the critical temperature<sup>41</sup>

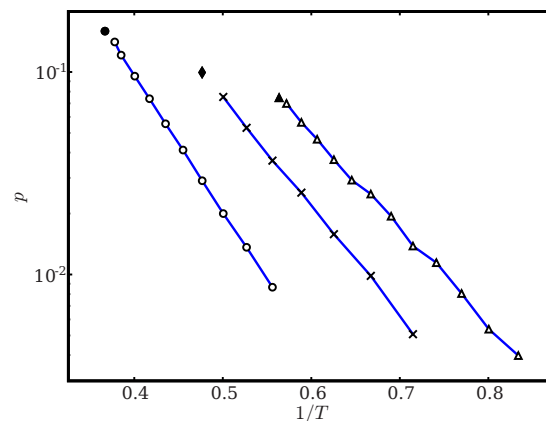


FIG. 2. (Color online) Vapor pressure for 2CLJ fluids. The symbols are the same as Fig. 1.

TABLE I. Critical parameters for 2CLJ fluids.

	$l_e$		
	0.5	0.75	1.0
$T_c$	2.730	2.100	1.776
$\rho_c$	0.2052	0.1682	0.1426
$p_c$	0.160	0.101	0.075
$\bar{\delta}_c$	0.9740	0.9824	0.9894
$\delta_c$	0.9756	0.9844	0.9915
$\bar{A}_c$	21.98	21.22	21.20
$\bar{B}_c$	2.356	2.939	3.505
$B_c$	2.192	2.712	3.239
$v_{f,c}^a$	2.680	3.232	3.776

<sup>a</sup> $v_{f,c}=v_c-B_c$  with  $v_c$  being the critical volume.

$$\rho_l - \rho_v = b(T_c - T)^\beta, \quad (15)$$

where indices  $l$  and  $v$  denote the liquid and vapor phases, respectively, and  $\beta \approx 0.32$  is the nonclassical critical exponent. The critical temperatures  $T_c$  and  $b$  were calculated by a least-squares fit to the density-temperature results. The critical density  $\rho_c$  was subsequently computed based on the law of rectilinear diameters<sup>41</sup>

$$\frac{\rho_l + \rho_v}{2} = \rho_c + A(T - T_c). \quad (16)$$

For each system, a separate NVT-MC simulation was performed with the computed critical density and temperature as input to compute the critical effective diameter, the critical pressure, the critical GvdW parameters, and the critical free volume. Table I collects the properties of the critical points for the systems with different bond lengths.

A plot of the logarithm of the pressure versus  $1/T$  in Fig. 2 is almost linear for all three systems. It is seen in Figs. 1 and 2 that by a raise in the bond length  $T_c$ ,  $\rho_c$ , and  $p_c$  decrease. By increasing the bond length from 0.5 to 1.0,  $T_c$ ,  $\rho_c$ , and  $p_c$  decrease by 34.9%, 30.5%, and 53.1%, respectively.

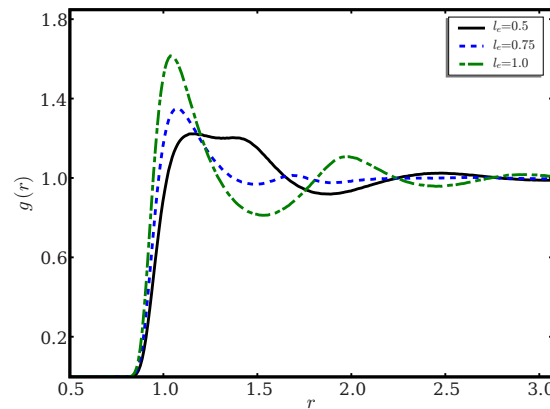
The NVT-MC and MD simulation results of this work for the equation of state of the system with  $l_e=1.0$  at  $T=4.0$  are given in Table II. The MD simulation results of

TABLE II. A comparison between the results of this work and the literature for a system with  $l_e=1.0$  at  $T=4.0$ .

$\rho$	$p$ (MC)	$p$ (MD)	$p$ (MD) <sup>a</sup>	$D$	$D^b$
0.05	0.205	0.204	0.202	3.289	3.313
0.10	0.44	0.44	0.44	1.550	1.550
0.15	0.76	0.75	0.76	0.954	...
0.20	1.23	1.23	1.23	0.650	...
0.25	2.00	2.00	2.00	0.465	0.476
0.30	3.32	3.30	3.31	0.333	...
0.35	5.49	5.47	5.52	0.240	0.241
0.40	9.07	8.99	8.99	0.170	0.169
0.45	14.68	14.54	14.60	0.118	0.118
0.50	23.21	22.96	22.9	0.080	...

<sup>a</sup>Reference 42.

<sup>b</sup>Reference 43.

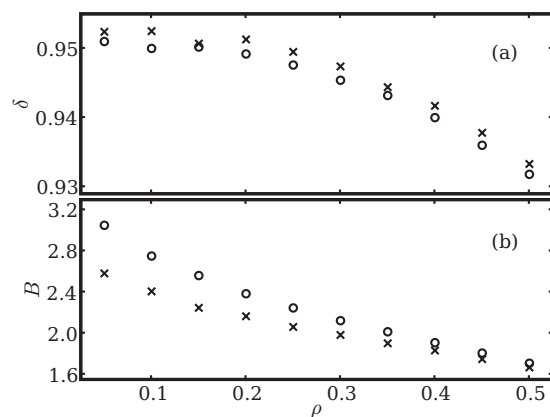
FIG. 3. (Color online) Site-site pair correlation function for 2CLJ fluids at  $\rho=0.4$  and  $T=4.0$  for different bond elongations.

Johnson *et al.*<sup>42</sup> are also included in the table. A close agreement is seen over the whole density range.

As the 2CLJ particles are homonuclear, the  $\alpha\beta$  subscript is dropped in site-site quantities. In Fig. 3, the site-site pair correlation function  $g(r)$  is shown at  $\rho=0.4$  and  $T=4.0$  as a function of the bond length. By an increase in  $l_e$ , the intensity of the first peak in  $g(r)$  increases, its maximum shifts towards the smaller values of  $r$ , and the oscillations become more pronounced.

The results of this work for the effective site diameter  $\delta$  and  $\bar{\delta}$  are given in Fig. 4(a) for a system with  $l_e=1.0$  at  $T=4.0$ . The difference between the two quantities is relatively small. Both  $\delta$  and  $\bar{\delta}$  are decreasing functions of the density, which is similar to the effective diameter of simple fluids.<sup>32,36,37</sup> The GvdW parameters  $B$  and  $\bar{B}$  are given in the same figure (panel b) at the same states. The  $B$  parameter is smaller than  $\bar{B}$  over the whole density range and the difference between the two quantities is larger at lower densities.

The density and bond length dependences of the effective site diameter are given in Fig. 5 at  $T=3.0$  (a) and 6.0 (b). The effective site diameter is a decreasing function of the density and bond length. By increasing the density, the difference between the effective site diameters with different bond lengths increases.

FIG. 4. (a) Effective site diameter and (b) GvdW parameter  $B$  for 2CLJ fluids with bond length 1.0 at  $T=4.0$ . In panel a,  $\bar{\delta}$  (○) and  $\delta$  (×) and in panel b,  $\bar{B}$  (○) and  $B$  (×) are shown.



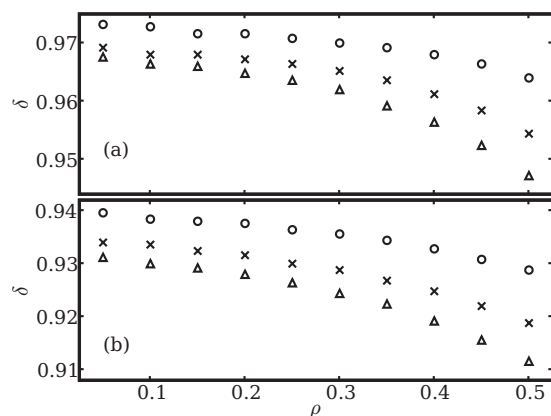


FIG. 5. Effective site diameter  $\delta$  for 2CLJ fluids with bond lengths 0.5 (○), 0.75 (×), and 1.0 (△) at (a)  $T=3.0$  and (b)  $T=6.0$ .

The GvdW theory was used to compute the mean free volume and the results are given in Fig. 6 at  $T=4.0$  (a) and 6.0 (b) for all three bond lengths. As expected, at the same state, the free volume decreases with a raise in the bond length. It is also seen that the logarithm of the free volume is almost a linear function of the density at  $\rho > \rho_c$  independent of the bond elongation. This is similar to the previous observations for simple fluids,<sup>36,37</sup> which suggests that this behavior is universal. We can see that the bond length has an effect on the slope of the line.

## B. Diffusion coefficient

To the best of the author's knowledge, the only report on the self-diffusion coefficient of diatomic fluids in condensed phase is from Krynicki *et al.*<sup>46</sup> They measured the diffusion constant of nitrogen in the liquid phase along the coexisting line. Due to this scarcity of experimental data, we use the results of MD simulations to examine the capability of the modified Cohen–Turnbull theory.

To compute the diffusion coefficient from the theory, the effective molecular diameter  $\delta_M$  has to be known as a function of temperature. This can be obtained using the MD simulation results at very low density. For this purpose, MD simulations were performed at the densities of  $\rho=0.01$  and 0.02 for all the bond elongations. The results are presented in

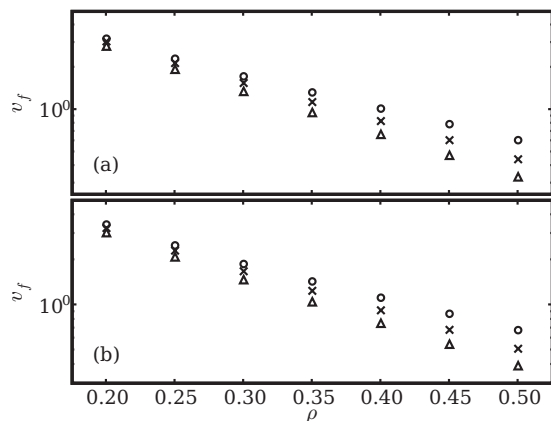


FIG. 6. Density dependence of  $v_f$  for 2CLJ fluids with bond lengths 0.5 (○), 0.75 (×), and 1.0 (△) at (a)  $T=4.0$  and (b) 6.0.

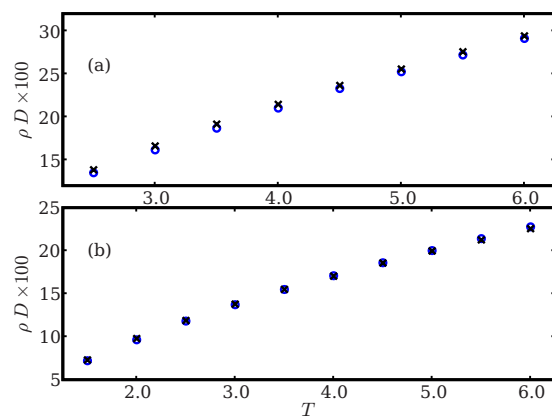


FIG. 7. (Color online) Diffusion coefficient for 2CLJ fluids with bond lengths (a) 0.5 and (b) 1.0. The MD simulation results are shown at  $\rho=0.01$  (○) and 0.02 (×).

Fig. 7 for the bond lengths of 0.5 and 1.0. The Chapman–Enskog relation [Eq. (11)] indicates that the diffusion constant of simple fluids at very low densities is proportional to the inverse density. The results of MD simulations in Fig. 7 confirm that the product  $\rho D$  is almost independent of the density over a large temperature range. The computed diffusion coefficients were used to obtain the effective molecular diameter  $\delta_M$  using Eq. (11) and the results are given in Fig. 8. As expected, the temperature has a large influence on the effective molecular diameter.

Reis *et al.*<sup>43</sup> used the Einstein relation to compute the diffusion coefficient of 2CLJ fluids with  $l_e=1.0$  through the equilibrium MD simulation method. Their results at  $T=4.0$  are compared with the results of this work in Table II. A close agreement is seen over the entire density range.

The computed effective molecular diameter, free volume, and critical volume were used in modified Cohen–Turnbull formula (10) to compute the diffusion coefficient. We use the average absolute deviation (AAD) to show the deviation of the modified Cohen–Turnbull theory results from the MD simulation ones

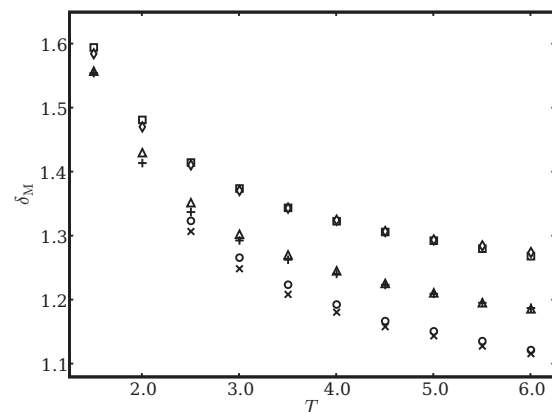


FIG. 8. Molecular effective diameter for 2CLJ fluids. The results are, respectively, shown at isochors of 0.01 and 0.02 for the bond lengths of 0.5 (○, ×), 0.75 (△, +), and 1.0 (□, ◇).

TABLE III. AAD in Eq. (17) for 2CLJ fluids.

$l_e=0.5$			$l_e=0.75$			$l_e=1.0$		
$T$	$N_p$	AAD	$T$	$N_p$	AAD	$T$	$N_p$	AAD
2.5	3	22.6	2.0	5	11.6	1.5	5	33.6
3.0	10	12.2	3.0	10	6.0	2.0	10	14.2
4.0	10	5.6	4.0	10	3.2	4.0	10	7.2
6.0	10	1.8	6.0	10	4.9	6.0	10	9.6
All	33	8.0	All	35	5.7	All	35	13.7

$$\text{AAD} = \frac{100}{N_p} \sum_{i=1}^{N_p} \left| 1 - \frac{D_{i,\text{theory}}}{D_{i,\text{MD}}} \right|, \quad (17)$$

where  $N_p$  is the number of the state points. The AADs are given in Table III. Figure 9 shows the results of MD simulations and the Cohen–Turnbull theory in the  $\rho$ - $\rho D$  projection. The results in the figure confirm that although there are discrepancies between the results of the two methods in the liquid phase, there is an excellent agreement in the higher isotherms. The AADs for all three bond lengths in the liquid phase are larger than the supercritical region. Among three bond lengths studied in this work, the system with  $l_e=1.0$  shows the largest AADs in the liquid and supercritical regimes. With respect to the fact that real diatomic fluids have bond lengths much smaller than 1.0 (e.g., the reduced bond length for nitrogen<sup>47</sup> and oxygen<sup>48</sup> are 0.33 and 0.40, respectively), it is expected that the modified Cohen–Turnbull theory is capable of reproducing reliable results for the diffusion coefficient of real diatomic fluids at high temperatures.

The temperature dependence of the diffusion coefficient is given in Fig. 10 for the results of both methods and all bond lengths. In almost all the isochors studied in this work, a crossover is seen between the results of the two methods, in

which at lower temperatures, the modified Cohen–Turnbull theory underestimates the MD simulation results and at higher temperatures, this trend is inverted.

## V. CONCLUDING REMARKS

An extensive study was presented for the thermodynamics, structure, and self-diffusion coefficient of 2CLJ fluids by making use of atomistic simulations and theory. The effects of the bond elongation on different properties were studied. The location of the fluid phase envelope was determined by applying the Gibbs ensemble MC simulation technique. The correlation functions were then computed utilizing the *NVT*-MC simulation method. The Green–Kubo formalism was used through the equilibrium MD simulation scheme to compute the self-diffusion coefficient over a wide range of densities and temperatures. Furthermore, the modified Cohen–Turnbull theory was employed to determine the diffusion coefficient, and the effective site diameter and the mean free volume needed for this purpose were obtained via the virial minimization method and the GvdW theory. A plot of the logarithm of the free volume versus density is almost linear at  $\rho > \rho_c$  for all three bond elongations, which is consistent with the previous studies for simple spherical fluids and can be considered as a universal behavior. The temperature dependence of the effective molecular diameter was computed using the  $D_0$  relation and the MD simulation results at very low densities. A detailed analysis was given for the diffusion coefficient results of the theory. The system with  $l_e=1.0$  shows the largest AAD among the three systems

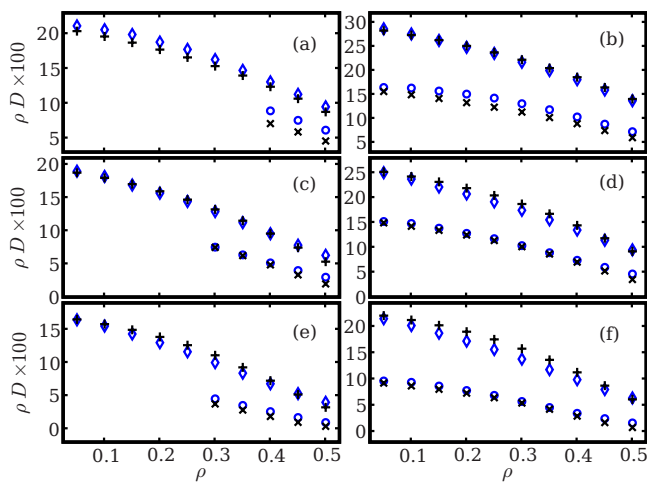


FIG. 9. (Color online) Density dependence of  $\rho D$  for 2CLJ fluids. The MD simulation and modified Cohen–Turnbull results are, respectively, shown for the bond length of 0.5 at  $T=2.5$  ( $\circ$ ,  $\times$ ) (a), 4.0 ( $\diamond$ ,  $+$ ) (a), 3.0 ( $\circ$ ,  $\times$ ) (b), and 6.0 ( $\diamond$ ,  $+$ ) (b); for the bond length of 0.75 at  $T=2.0$  ( $\circ$ ,  $\times$ ) (c), 4.0 ( $\diamond$ ,  $+$ ) (c), 3.0 ( $\circ$ ,  $\times$ ) (d), and 6.0 ( $\diamond$ ,  $+$ ) (d); and for the bond length of 1.0 at  $T=1.5$  ( $\circ$ ,  $\times$ ) (e), 4.0 ( $\diamond$ ,  $+$ ) (e), 2.0 ( $\circ$ ,  $\times$ ) (f), and 6.0 ( $\diamond$ ,  $+$ ) (f).

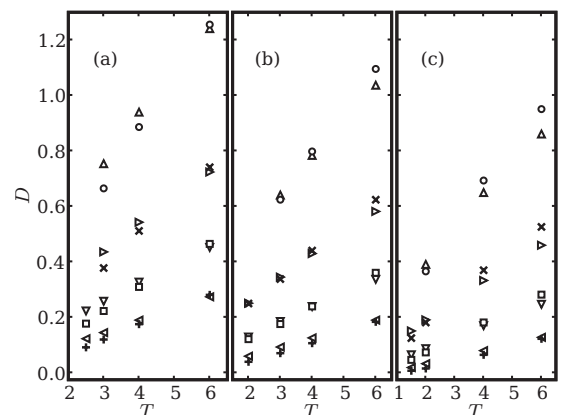


FIG. 10. Temperature dependence of diffusion coefficient for 2CLJ fluids with the bond lengths of (a) 0.5, (b) 0.75, and (c) 1.0. The MD simulation and modified Cohen–Turnbull results are, respectively, given at  $\rho=0.2$  ( $\circ$ ,  $\triangle$ ), 0.3 ( $\times$ ,  $\triangleright$ ), 0.4 ( $\square$ ,  $\nabla$ ), and 0.5 ( $+$ ,  $\triangleleft$ ).

studied in this work. For all three systems, the AAD for the liquid phase is larger than the ones in the supercritical region. An excellent agreement is seen between the results of the theory and simulations at high temperatures for the systems with  $l_e=0.5$  and  $0.75$ . As the real diatomic fluids have a (reduced) bond length closer to  $0.5$ , it is expected that the modified Cohen–Turnbull theory gives reliable results for diffusion coefficients of real systems especially at high temperatures.

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