

Revised Equation of State for Two-Center Lennard-Jones Fluids

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The equation of state for two-center Lennard-Jones fluids originally proposed by Mecke et al. [*Int. J. Thermophys.* **18**:683–698 (1997); Erratum, *Int. J. Thermophys.* **19**:1495 (1998)] has been revised to extend its applicability to large molecular elongations. The equation of state is written in the form of a generalized augmented van der Waals equation for the Helmholtz energy, $F = F_H + F_A$, where F_H accounts for the hard-body interaction and F_A for the attractive dispersion forces. The revised EOS is constructed on the basis of previously published simulation data for 2CLJ fluids with reduced elongations $L = 0.0, 0.22, 0.3292, 0.505, \text{ and } 0.67$ and results from new extensive simulations for two-center Lennard-Jones fluids with $L = 0.8$ and 1.0 . The revised equation of state provides a very good description of the fluid state behavior over a wide range of temperatures and pressures as well as of the vapor-liquid equilibrium phase behavior for the two-center Lennard-Jones fluids with L ranging from 0.0 to 1.0 .

KEY WORDS: equation of state; molecular simulation; thermodynamic properties; two-center Lennard-Jones fluid; vapor-liquid equilibria.

1. INTRODUCTION

Two-center Lennard-Jones (2CLJ) fluids might be viewed as some of the simplest models of fluids with non-spherical molecules. In a series of papers [1–3], a physically based equation of state (EOS) was developed for 2CLJ fluids of molecules with short and moderate reduced elongations L .

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The EOS is written in the form of a generalized augmented van der Waals equation for the Helmholtz energy, $F = F_H + F_A$, where F_H accounts for the hard-body interactions and F_A for the attractive dispersion forces. The hard-body term F_H was represented by the expression due to Boublík and Nezbeda [4] based on the scaled particle theory with a temperature dependence of the packing fraction resulting from the hybrid Barker–Henderson perturbation theory [5]. The construction of the attractive contribution F_A was accomplished with the Setzmann–Wagner optimization procedure [6] on the basis of virial coefficients and critically assessed computer simulation data for 2CLJ fluids with L ranging from 0.0 to 0.67 [3].

Since the original EOS was fitted to simulation data for the 2CLJ fluids with $L \leq 0.67$, its accuracy abruptly deteriorates for $L > 0.67$ as was shown by Lísal et al. [7]. Hence, the purpose of this work is to extend the applicability of the original EOS to 2CLJ fluids with $L > 0.67$. We generated new computer simulation data for 2CLJ fluids with $L = 0.8$ and 1.0 in the single-fluid phase and vapor-liquid coexistence regions, see Lísal et al. [7] for details. In this paper, we use these new simulation data together with the previously published simulation data for the 2CLJ fluids with $L = 0.0, 0.22, 0.3292, 0.505,$ and 0.67 [3] to revise the original EOS for the 2CLJ fluids and develop an EOS valid for the entire range of elongations up to $L = 1.0$.

2. FUNCTIONAL FORM OF THE EQUATION OF STATE

We consider a 2CLJ fluid characterized by the energy and size parameters ε and σ , respectively, and by the reduced elongation $L = l/\sigma$; l is the distance between the interaction sites. We denote all quantities in reduced units, such as the reduced temperature $T^* = kT/\varepsilon$, the reduced density $\rho^* = \rho\sigma^3$, the reduced pressure $p^* = p\sigma^3/\varepsilon$, and the reduced residual internal energy $u^* = U/(N\varepsilon)$; k is Boltzmann's constant and N is the number of molecules.

The 2CLJ-EOS [3] is written as

$$F(T^*, \rho^*, L) = F_H(T^*, \rho^*, L) + F_A(T^*, \rho^*, L) \quad (1)$$

The hard-body term F_H is taken from Boublík and Nezbeda [4] as

$$\frac{F_H}{NkT} = (\alpha_p^2 - 1) \ln(1 - \eta) + \frac{(\alpha_p^2 + 3\alpha_p) \eta - 3\alpha_p \eta^2}{(1 - \eta)^2} \quad (2)$$

where α_p is the anisotropy parameter of a pseudocritical point (a critical point given by the perturbation theory (PT) [8]) and η is the packing fraction; α_p is a function of L and is represented [3] by

$$\alpha_p = P_1 + P_2 L^2 + P_3 L^{7/2} + P_4 L^4 \quad (3)$$

η depends linearly on ρ^* and is given by a relation developed by Sager et al. [1] and later modified by Mecke et al. [3] as

$$\eta = \rho^* \frac{(\eta/\rho)_p}{a + (1-a)(T^*/T_p^*)^\gamma} \quad (4)$$

In Eq. (4), $a = 0.67793$, $\gamma = 0.3674$, T_p^* is the temperature of a pseudocritical point, and $(\eta/\rho)_p$ is the ratio of density and packing fraction of a pseudocritical point. T_p^* and $(\eta/\rho)_p$ are functions of L , and they are represented [3] by

$$T_p^* = \frac{1}{4} \sqrt{\frac{P_5 + P_6 L}{1 + P_7 L + P_8 L^2}} \quad \text{for } L = 0.0$$

$$\sqrt{\frac{P_5 + P_6 L}{1 + P_7 L + P_8 L^2}} \quad \text{for } L > 0.0 \quad (5)$$

$$(\eta/\rho)_p = P_9 + P_{10} L^2 + P_{11} L^{5/2} + P_{12} L^4 \quad (6)$$

respectively. We refer readers to the original paper by Mecke et al. [3] for additional details.

For the attractive term F_A , Mecke et al. [3] have made an ansatz of the form,

$$\frac{F_A}{NkT} = \sum_i c_i \left(\frac{T^*}{T_p^*} \right)^{m_i} \left(\frac{\rho^*}{\rho_p^*} \right)^{n_i} \alpha_p^{o_i} \exp \left[p_i \left(\frac{\rho^*}{\rho_p^*} \right)^{q_i} \right] \quad (7)$$

where ρ_p^* is the density of a pseudocritical point. ρ_p^* is a function of L and is represented [3] by

$$\rho_p^* = \frac{P_{13} + P_{14} L}{1 + P_{15} L + P_{16} L^2} \quad (8)$$

The coefficients c_i as well as the exponents m_i , n_i , o_i , p_i , and q_i are determined by the optimization procedure of Setzmann–Wagner [6] (see the next section).

3. DATA AND OPTIMIZATION PROCEDURE

We start with coefficients P_1 - P_{16} of Eqs. (3), (5), (6), and (8). These equations represent L -dependence of the pseudocritical anisotropy parameter, the pseudocritical temperature, the pseudocritical ratio of density and packing fraction, and the pseudocritical density, and they are obtained from the fit of the PT results for 2CLJ fluids [8]. In the original EOS, P_1 - P_{16} were fitted to the PT results for the 2CLJ fluids with $L \leq 0.67$. Hence, we performed the additional PT study for the 2CLJ fluids with $L > 0.67$, and evaluated new values of α_p , T_p^* , $(\eta/\rho)_p$, and ρ_p^* for the 2CLJ fluids with $L > 0.67$. We used these new values together with the values of α_p , T_p^* , $(\eta/\rho)_p$, and ρ_p^* for the 2CLJ fluids with $L \leq 0.67$ to obtain a new set of coefficients P_1 - P_{16} . New coefficients P_1 - P_{16} are listed in Table I.

In the original EOS, Mecke et al. [3] used critically assessed computer simulation data (pressure-volume-temperature and internal energies) for the 2CLJ fluids with $L = 0.0, 0.22, 0.3292, 0.505, \text{ and } 0.67$ to construct the attractive term F_A . Simulation data covered fluid phase regions in the range of $0.4 \leq T^*/T_p^* \leq 5.0$ and $0.0 \leq \rho^*/\rho_p^* \leq 3.1$. In addition, they also utilized explicitly calculated second virial coefficients as well as VLE data of

Table I. Revised Coefficients P_1 - P_{16} for the Correlation Eqs. (3), (5), (6), and (8)

i	P_i
1	1.0
2	0.5296092
3	-0.4531784
4	0.4421075
5	34.037352
6	17.733741
7	0.53237307
8	12.860239
9	0.5256
10	3.2088804
11	-3.1499114
12	0.43049357
13	0.31258137
14	1.2240569
15	3.7974509
16	6.5490937

Lotfi et al. [9] and Kriebel et al. [10]. Since the critical point of the Lennard-Jones fluid is known with high accuracy, Mecke et al. [3] constrained the original EOS to

$$\left(\frac{\partial p}{\partial \rho}\right)_{T_C, \rho_C, L_{LJ}} = 0 \quad \left(\frac{\partial^2 p}{\partial \rho^2}\right)_{T_C, \rho_C, L_{LJ}} = 0 \quad (9)$$

with $T_C^* = 1.328$, $\rho_C^* = 0.3107$, and $L_{LJ} = 0.0$ [2].

Table II. Coefficients c_i and Exponents m_i , n_i , o_i , p_i , and q_i for the Attractive Contribution to the Helmholtz Energy $F_A/(NkT)$ Given in the Form of Eq. (7)

i	c_i	m_i	n_i	o_i	p_i	q_i
1	$-0.64211055047 \times 10^{-1}$	-1.50	2.00	-3.00	0.0	0.0
2	$0.17682583145 \times 10^{-2}$	-1.50	5.00	-2.00	0.0	0.0
3	$-0.62963373291 \times 10^{+0}$	-1.00	1.00	0.00	0.0	0.0
4	$-0.35320115512 \times 10^{+0}$	-1.00	1.00	1.00	0.0	0.0
5	$0.11339264270 \times 10^{+2}$	-1.00	2.00	-3.00	0.0	0.0
6	$-0.33311941616 \times 10^{+2}$	-1.00	2.00	-2.00	0.0	0.0
7	$0.37022843830 \times 10^{+2}$	-1.00	2.00	-1.00	0.0	0.0
8	$-0.18683743554 \times 10^{+2}$	-1.00	2.00	0.00	0.0	0.0
9	$0.34566448842 \times 10^{+1}$	-1.00	2.00	1.00	0.0	0.0
10	$-0.11216048862 \times 10^{-5}$	-1.00	10.00	-3.00	0.0	0.0
11	$0.69315597535 \times 10^{+0}$	-0.50	1.00	-3.00	0.0	0.0
12	$-0.95242644353 \times 10^{+0}$	-0.50	1.00	-2.00	0.0	0.0
13	$0.13303429920 \times 10^{-1}$	-0.50	3.00	-1.00	0.0	0.0
14	$-0.17518819492 \times 10^{-4}$	-0.50	9.00	-3.00	0.0	0.0
15	$0.30942693727 \times 10^{-5}$	-0.50	10.00	-2.00	0.0	0.0
16	$0.44671277084 \times 10^{-1}$	0.00	1.00	0.00	0.0	0.0
17	$-0.84065404026 \times 10^{+0}$	0.00	2.00	-3.00	0.0	0.0
18	$0.12662354443 \times 10^{+1}$	0.00	2.00	-2.00	0.0	0.0
19	$-0.43706789738 \times 10^{+0}$	0.00	2.00	-1.00	0.0	0.0
20	$0.34751432401 \times 10^{-5}$	0.00	9.00	0.00	0.0	0.0
21	$-0.52988956334 \times 10^{-6}$	0.00	10.00	2.00	0.0	0.0
22	$0.37399304905 \times 10^{-1}$	-3.00	1.00	-2.00	-1.0	1.0
23	$-0.32905342462 \times 10^{+0}$	-2.00	1.00	0.00	-1.0	1.0
24	$0.63121341882 \times 10^{-1}$	-2.00	3.00	0.00	-1.0	1.0
25	$-0.20913100716 \times 10^{-2}$	-2.00	6.00	1.00	-1.0	1.0
26	$-0.26852824281 \times 10^{-1}$	-1.00	3.00	2.00	-1.0	1.0
27	$0.70733527178 \times 10^{-1}$	0.00	3.00	-1.00	-1.0	1.0
28	$0.58291227149 \times 10^{-1}$	-4.00	1.00	-3.00	-1.0	2.0
29	$-0.76337837062 \times 10^{-1}$	-4.00	1.00	0.00	-1.0	2.0
30	$-0.37502524667 \times 10^{-1}$	-4.00	2.00	-3.00	-1.0	2.0
31	$0.19201247728 \times 10^{-2}$	-4.00	6.00	-2.00	-1.0	2.0
32	$-0.76922623587 \times 10^{-1}$	0.00	1.00	-3.00	-1.0	2.0
33	$0.12939011597 \times 10^{+0}$	0.00	1.00	1.00	-1.0	2.0
34	$-0.37539710780 \times 10^{-1}$	0.00	1.00	3.00	-1.0	2.0

To extend the applicability of the original EOS to $L > 0.67$, we generated simulation data for 2CLJ fluids with $L = 0.8$ and 1.0 that cover fluid phase regions in the range of $0.4 \leq T^*/T_p^* \leq 5.0$ and $0.0 \leq \rho^*/\rho_p^* \leq 3.1$. In addition, we calculated second virial coefficients for the 2CLJ fluids with $L = 0.8$ and 1.0 by a non-product algorithm [11] and VLE data for the 2CLJ fluids with $L = 0.8$ and 1.0 by the Gibbs ensemble Monte Carlo (GEMC) method [12]. Further, VLE data for the 2CLJ fluid with $L = 0.8$ have been determined using the NpT ensemble with a test particle [13] and for the 2CLJ fluid with $L = 1.0$ have been determined by the GEMC method [14], and we have used them.

The original data sets for the 2CLJ fluids with $L = 0.0, 0.22, 0.3292, 0.505, \text{ and } 0.67$ and the new data for the 2CLJ fluids with $L = 0.8$ and 1.0 were utilized by the optimization procedure of Setzmann–Wagner [6]. In the Setzmann–Wagner procedure, a “bank of terms” is created by prescribed sets for the exponents $m_i, n_i, o_i, p_i, \text{ and } q_i$ in Eq. (7). From this bank of terms, the most effective elements are selected by an algorithm which combines a stepwise regression analysis with elements of an evolutionary optimization method. Table II contains the exponents $m_i, n_i, o_i, p_i, \text{ and } q_i$ and coefficients c_i obtained by this procedure for the attractive contribution to the Helmholtz energy F_A given in the form of Eq. (7). It is worth noting that the optimization procedure results in the same number of terms for the revised and original EOS.

4. RESULTS AND DISCUSSION

First, we compare how the revised and original EOS reproduce data used for construction. For that purpose, we define standard deviations,

$$\text{STD}_{pvT} = \left(\frac{1}{n} \sum_{i=1}^n \frac{(p_{i,\text{EOS}} - p_{i,\text{SIM}})^2}{\Delta p_{i,\text{SIM}}^2} \right)^{1/2} \quad (10)$$

$$\text{STD}_u = \left(\frac{1}{n} \sum_{i=1}^n \frac{(u_{i,\text{EOS}} - u_{i,\text{SIM}})^2}{\Delta u_{i,\text{SIM}}^2} \right)^{1/2} \quad (11)$$

where n denotes the number of state points, $p_{i,\text{EOS}}$ and $u_{i,\text{EOS}}$ are the results from the EOS, while the simulation results are denoted by $p_{i,\text{SIM}}$ and $u_{i,\text{SIM}}$ together with their statistical uncertainties $\Delta p_{i,\text{SIM}}$ and $\Delta u_{i,\text{SIM}}$. Table III shows how these standard deviations are distributed over molecular elongations L . We can see from Table III that (i) the standard deviations for the revised EOS are distributed quite uniformly over L , i.e., accuracy of the revised EOS does not depend on L , (ii) the revised EOS yields almost the same accuracy as the original EOS for $L < 0.67$, and (iii) the original EOS badly

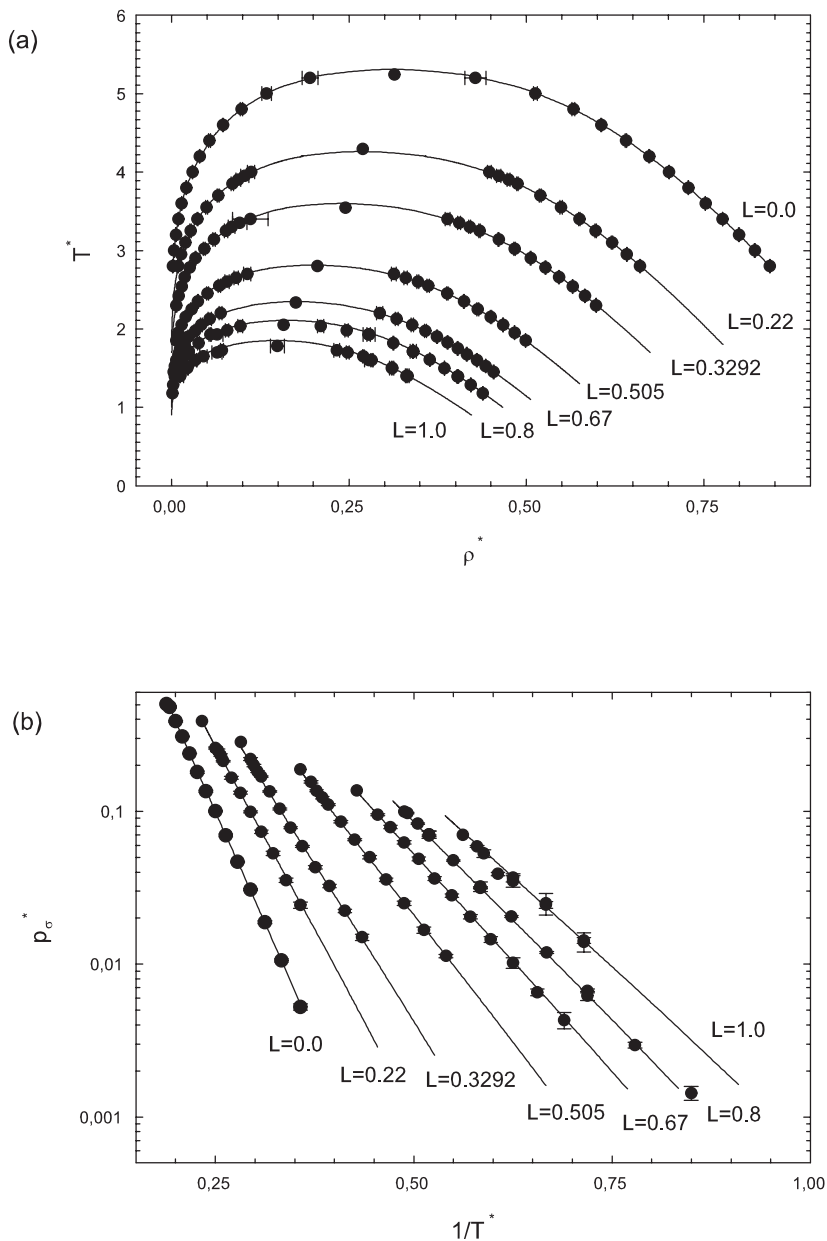


Fig. 1. (a) Vapor-liquid coexistence curves and (b) vapor pressure for the 2CLJ fluids with different reduced molecular elongations L (—, the revised EOS; ●, simulation results [9, 10, 13, 14]).

Table III. Standard Deviations of the Pressure STD_{pvT} and of the Internal Energy STD_u Obtained from the Original EOS [3] and the Revised EOS for Several Reduced Elongations L

L	STD_{pvT}		STD_u	
	Original EOS	Revised EOS	Original EOS	Revised EOS
0	1.87	1.93	1.57	1.67
0.22	1.84	1.98	1.54	2.12
0.3292	1.99	2.12	2.00	2.03
0.505	1.94	2.07	1.77	2.13
0.67	2.04	2.21	1.88	1.93
0.8	> 10	2.08	> 10	1.93
1	> 50	2.11	> 50	1.86

deteriorates for $L > 0.67$. Overall, the revised EOS reproduces the data with $STD_{pvT} = 1.96$ and $STD_u = 2.07$, and these standard deviations are only slightly larger than those from the original EOS, namely $STD_{pvT} = 1.75$ and $STD_u = 1.93$.

Second, we calculated VLE for 2CLJ fluids with $L = 0.0, 0.22, 0.3292, 0.505, 0.67, 0.8,$ and 1.0 using the revised EOS and compared them with results from the original EOS [3] (for the cases of $L \leq 0.67$) and from the simulations [9, 10, 13, 14] in Figs. 1–3. In the case of the 2CLJ with $L = 1.0$, we also calculated VLE using the soft-SAFT EOS [15]. We used the Kolafa and Nezbeda EOS [16], and the Mecke et al. EOS [2] to describe monomers and the Johnson et al. [17] expression for the contact value of the radial distribution function. In this case, we have found that (i) use of the Kolafa and Nezbeda EOS [16] and the Mecke et al. EOS [2] gives nearly identical results and (ii) VLE from the soft-SAFT EOS agree very well with VLE results from both the revised EOS and GEMC simulations, and differences cannot be seen within the scale of Fig. 1.

Figure 1 demonstrates the dependence of the coexistence densities and vapor pressures on reduced elongations L . Figures 2 and 3 then show in detail the quality of the revised EOS to describe VLE with deviation plots of the vapor pressure and coexistence densities for two different elongations, namely: $L = 0.505$ (Fig. 2) and $L = 1.0$ (Fig. 3). From Fig. 2, we can see that the accuracy of the revised EOS is very close to that of the original EOS and also that both EOS are able to describe VLE almost within statistical uncertainties of the pseudo-experimental data. In Fig. 3 we do not plot deviations from the original EOS since the original EOS is off by more than 100%. Figure 3 shows that the revised EOS is able to describe the VLE almost within statistical uncertainties of the pseudo-experimental data also for $L = 1.0$. (For $L = 0$ the revised equation fits the coexisting densities

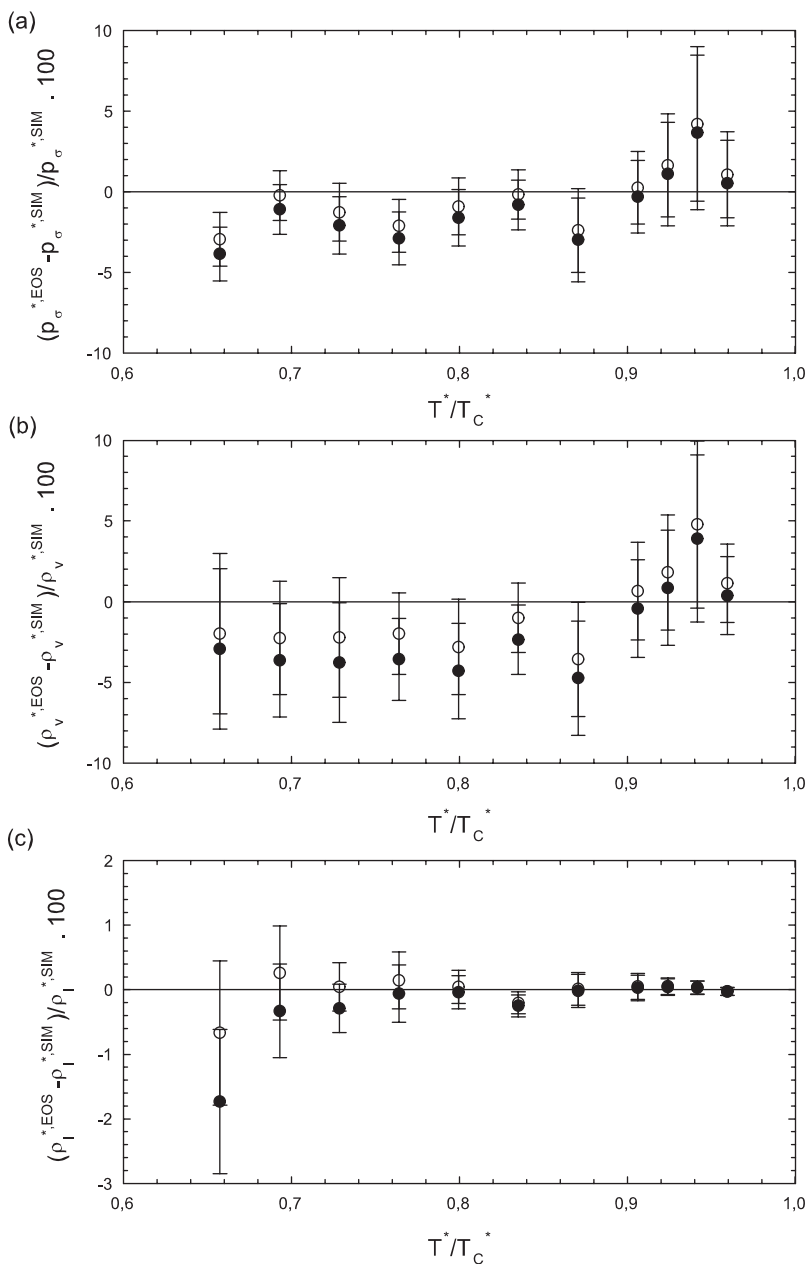


Fig. 2. Deviation plots of the vapor pressure and coexistence densities obtained from the revised EOS (●) and original EOS (○) [3] in comparison with the simulation results [10] for the 2CLJ fluid with $L = 0.505$.

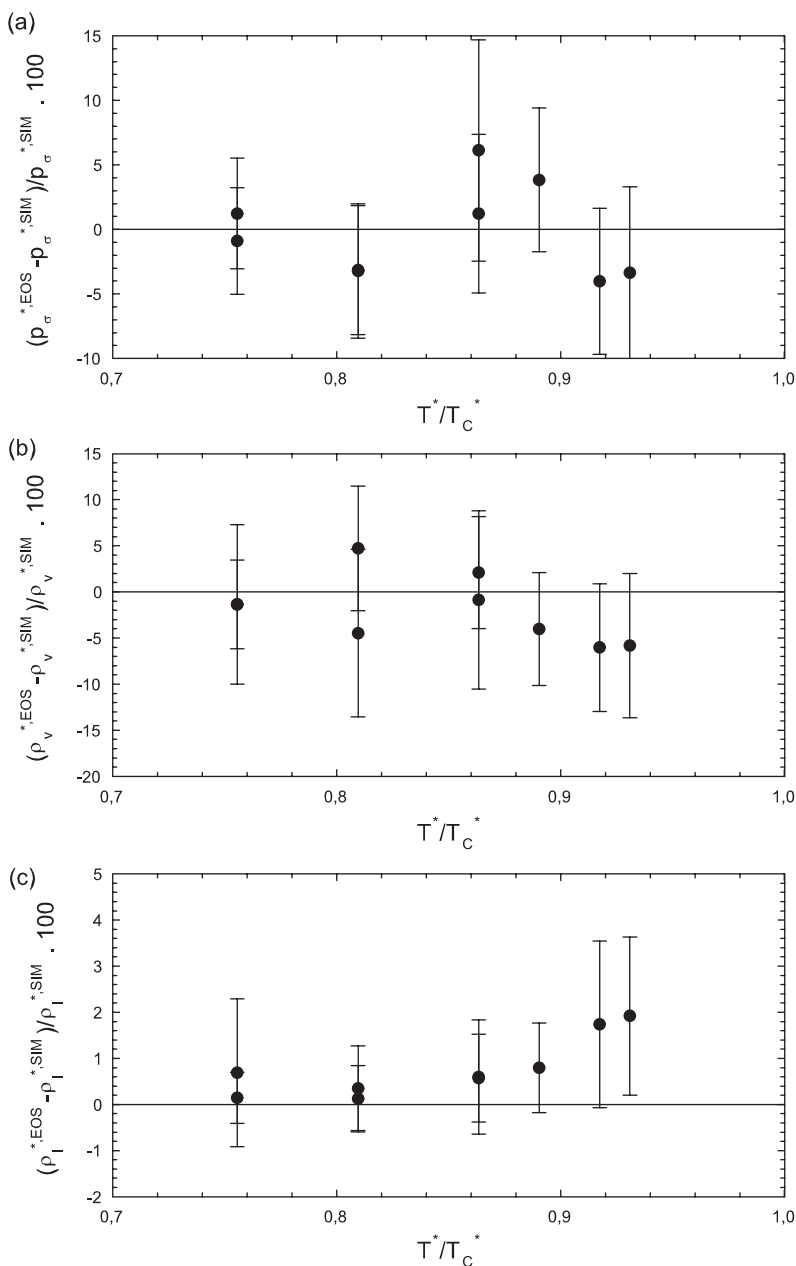


Fig. 3. Deviation plots of the vapor pressure and coexistence densities obtained from the revised EOS (●) in comparison with the simulation results [14] for the 2CLJ fluid with $L = 1.0$.

and vapor pressures within the uncertainties of the simulations and with results almost identical to the original EOS.) Corresponding conclusions can then be drawn for intermediate elongations (not shown in the figures).

Figures 1 to 3 indicate small discrepancies between the simulation and EOS results in the vicinity of the critical point. This is caused by three factors: (i) the EOS does not explicitly constrain the critical point, (ii) van der Waals-type EOS are in principle not able to precisely capture the near-critical behavior, and (iii) simulation data in the vicinity of the critical point are subject to large errors. Nevertheless, the revised EOS captures reasonably well the critical-point coordinates as is demonstrated in Fig. 4, in which we compare the critical-point parameters from the simulations [9, 10, 13, 14] and from the revised EOS for different molecular elongations.

Finally, we added to the revised EOS the dipolar term F_D [18] and calculated VLE for dipolar 2CLJ fluids with square of reduced dipole moments $\mu^{*2} = 9$ and 12 for molecular elongations of $L = 0.8$ and 1.0. The calculated VLE are compared with simulation results [7] in Figs. 5 and 6. In our previous paper [7], we showed that the original EOS with the dipolar term failed to describe VLE for dipolar 2CLJ fluids with $L > 0.67$. From Figs. 5 and 6, we can see that use of the revised EOS combined with the F_D term dramatically improves the description of these highly dipolar

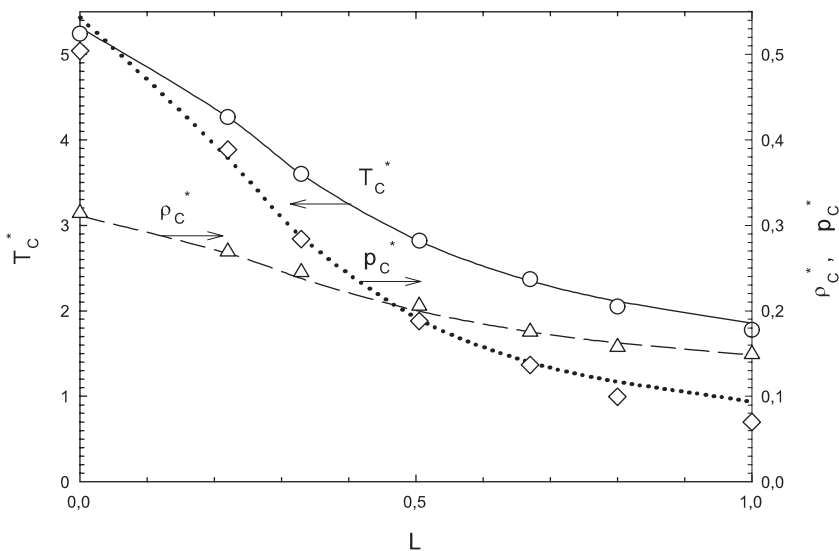


Fig. 4. Critical-point parameters for the 2CLJ fluids as a function of reduced molecular elongations L . Lines correspond to the revised EOS and marks correspond to simulation results [9, 10, 13, 14].

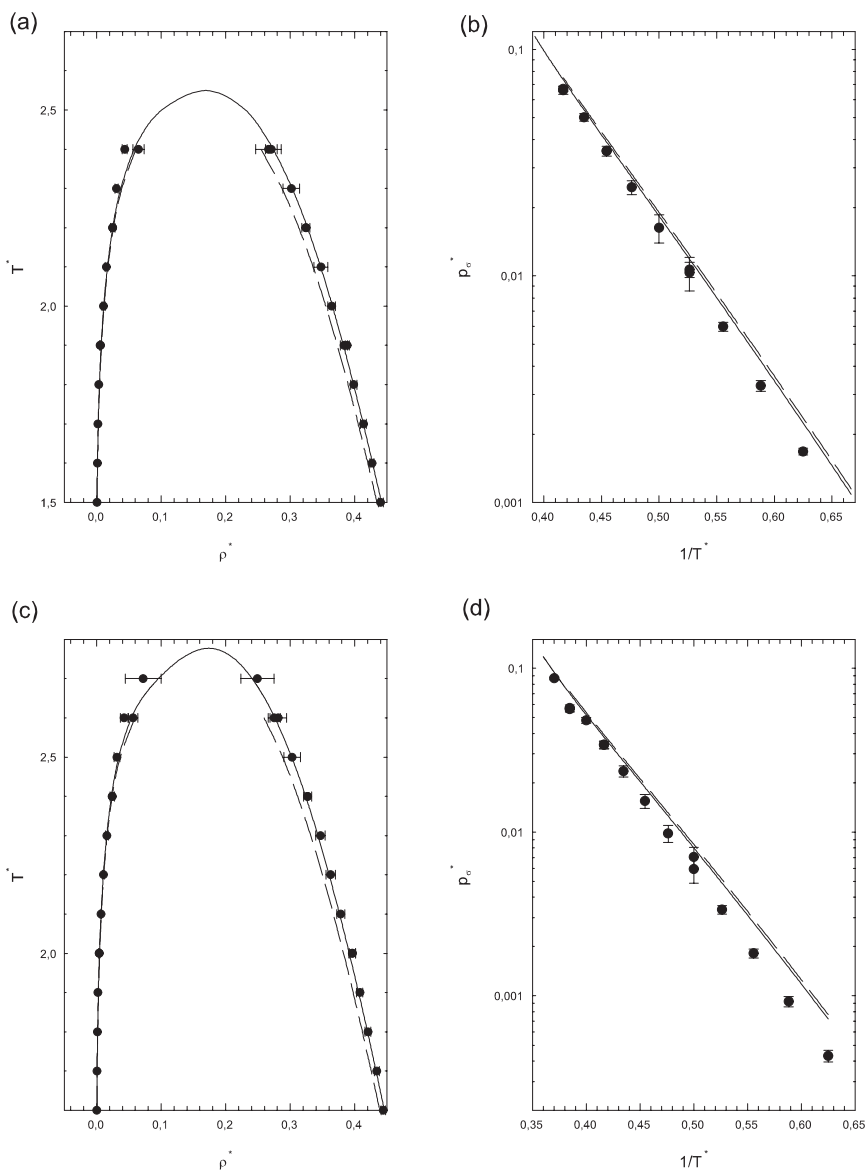


Fig. 5. Vapor-liquid coexistence curves and vapor pressures for dipolar 2CLJ fluids with the reduced molecular elongation $L = 0.8$ and square of reduced dipole moments $\mu^{*2} = 9$ (a, b) and $\mu^{*2} = 12$ (c, d) (—, the revised EOS combined with the dipolar term F_D [18]; ---, the original EOS [3] combined with the dipolar term F_D [18]; ●, simulation results [7]).

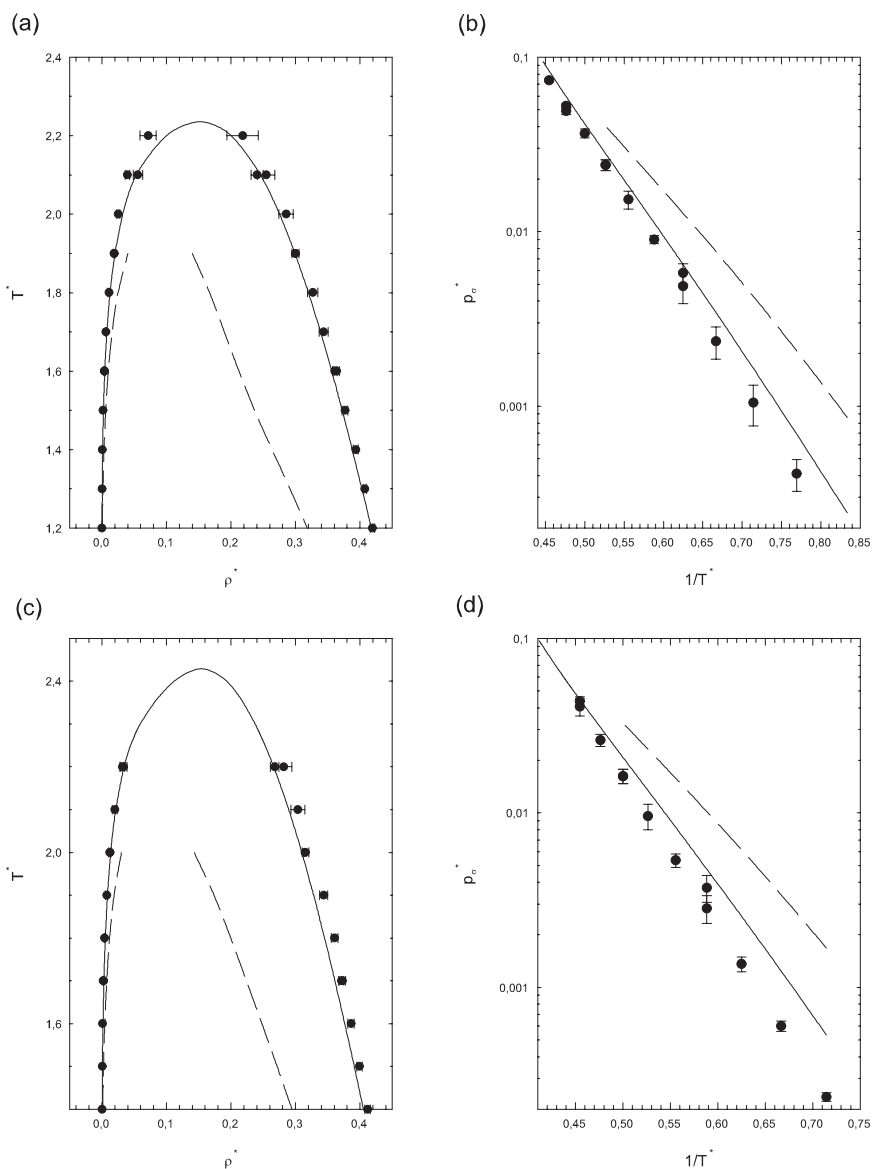


Fig. 6. Vapor-liquid coexistence curves and vapor pressures for dipolar 2CLJ fluids with the reduced molecular elongation $L = 1.0$ and square of reduced dipole moments $\mu^{*2} = 9$ (a, b) and $\mu^{*2} = 12$ (c, d) (—, the revised EOS combined with the dipolar term F_D [18]; ---, the original EOS [3] combined with the dipolar term F_D [18]; ●, simulation results [7]).

2CLJ fluids. In the case of dipolar 2CLJ fluids with $L = 0.8$ (Fig. 5), simulation coexistence densities are clearly represented within statistical uncertainties. In the case of dipolar 2CLJ fluids with $L = 1.0$ (Fig. 6), simulation coexistence densities are about 2% higher than coexistence densities given by the revised EOS combined with the F_D term. In both cases, the revised EOS combined with the F_D term slightly overestimates vapor pressures. These discrepancies must be primarily caused by the F_D term, since the revised EOS alone represents the VLE of (nonpolar) 2CLJ fluids with $L = 0.8$ and 1.0 within statistical uncertainties of the simulation data. The F_D term was originally constructed so as to be independent of L ; nevertheless, Müller et al. [19] showed that F_D is weakly dependent on L at large dipole moments. One may also note that the coexistence curves in Figs. 5 and 6 exhibit a somewhat unusual shape in the vicinity of the critical point, similar to the behavior observed by Kriebel et al. [20] for the Stockmayer fluid.

5. CONCLUSIONS

A revised equation of state for two-center Lennard-Jones fluids has been developed, based on previously published simulation data for 2CLJ fluids with reduced elongations $L = 0.0, 0.22, 0.3292, 0.505,$ and 0.67 and on results of recent extensive simulations for 2CLJ fluids of molecules with elongations $L = 0.8$ and 1.0 . The revised EOS yields a very good description of the 2CLJ model fluid state behavior over a wide range of temperatures and pressures as well as of the vapor-liquid equilibrium phase behavior for the 2CLJ fluids made up of molecules with L ranging from 0.0 to 1.0. With an added dipolar term, the revised EOS leads also to substantial improvement in the description of both the state and phase behavior of the dipolar 2CLJ fluids (with square of reduced dipole moments $\mu^{*2} = 9$ and 12) made up of molecules with large elongations (up to $L = 1.0$).

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