

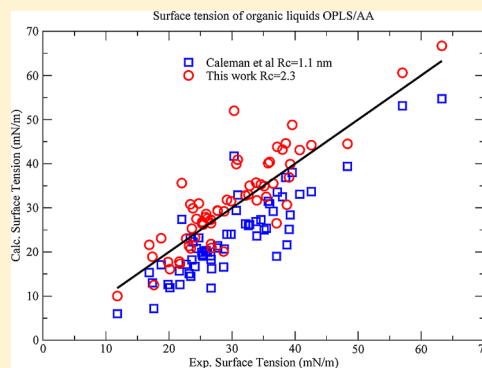
Surface Tension of Organic Liquids Using the OPLS/AA Force Field

Rafael A. Zubillaga,[†] Ariana Labastida,[†] Bibiana Cruz,[†] Juan Carlos Martínez,[†] Enrique Sánchez,[‡] and José Alejandro^{*,†}

[†]Departamento de Química, Universidad Autónoma Metropolitana-Iztapalapa, Av. San Rafael Atlixco 186, Col. Vicentina, 09340 México D.F., México

[‡]Colegio de Ciencia y Tecnología, Universidad Autónoma de la Ciudad de México, Plantel Casa Libertad, Calzada Ermita Iztapalapa s/n, 09620 México D. F., México

ABSTRACT: Molecular dynamics simulations are performed to obtain the surface tension of 61 organic liquids using the OPLS/AA (all-atom optimized potential for liquid simulations). The force field parameters are the same as those recently used (Caleman et al. *J. Chem. Theory Comput.* **2012**, *8*, 61) to determine several thermodynamic properties of 146 organic liquids. The correct evaluation of surface tension using slab simulations of liquids requires one to properly take into account the long-range interactions (Trukhymchuk and Alejandro *J. Chem. Phys.* **1999**, *111*, 8510). In addition, the liquid density from slab simulations has to be the same as that obtained in liquid simulations at constant temperature and pressure. The new results of surface tensions from this work improve those reported by Caleman et al. The OPLS/AA force field gives good surface tensions compared with experimental data for most of the systems studied in this work, although it was developed to simulate liquids.



1. INTRODUCTION

Molecular interactions play a key role in the description of physicochemical properties of matter. During the past two decades, new and efficient computer simulation methods combined with fast computers have helped in the understanding of the effect that such interactions have on atomistic simulations. Several nonpolarizable force fields such as OPLS/AA,¹ GAFF (Generalized Amber force field),² and CHARMM³ have been developed. The parameters of different groups of atoms, which can be used to describe the interaction with more complex molecules, have been determined. Recently, Caleman et al.⁴ performed molecular dynamics simulations to make a force field benchmark of organic liquids using the OPLS/AA and GAFF models, mainly under ambient conditions. They obtained the liquid density, enthalpy of vaporization, heat capacities, surface tension, isothermal compressibility, volumetric expansion coefficient, and dielectric constant. They found, when the simulation results were compared with experimental data, large and systematic deviations for the surface tension and dielectric constant. The other properties were in reasonably good agreement. The parameters for the OPLS/AA force field were obtained in simulations of liquids; therefore it is not surprising that the surface tension deviates from experimental data. The difference of dipole moments in the vapor and in the liquid phases of organic molecules suggests that a polarizable force field might be required to reproduce the interfacial properties, in particular surface tension.

The parametrization of a polarizable force field useful for a large number of organic molecules is a difficult task. The simulation of the liquid–vapor interface with a slab geometry requires the use of a parallelepiped cell where the system is

inhomogeneous; i.e., two regions of vapor surround a liquid phase. There are several factors that have to be taken into account to calculate accurate surface tensions.^{5–7} Before including polarization, it is justified to analyze if the OPLS/AA force field fails to reproduce the experimental surface tension because some of those factors were not properly included in the simulation.

If the slab geometry is used to simulate the liquid–vapor interface, the maximum number of reciprocal vectors⁵ has to be $k_z^{\max} = (L_z/L_x)k_x^{\max}$ (where L_z is the longest direction of the simulation cell and L_x^2 gives the surface area) when the Ewald sum is applied to calculate the electrostatic interactions. The standard long-range corrections for the Lennard-Jones (LJ) interactions on the components of the pressure tensor, because of the inhomogeneity of the system, cannot be included during the simulations. In simulations of the liquid–vapor interface, some approaches have been proposed to include long-range corrections^{8,9} based on the density profiles of the system. Expressions for binary mixtures were reported by Goujon et al., see refs 8 and 9. The density profile of the system is needed to apply this method, and the equations for systems with more than two components are complex. The Ewald sum method to calculate the long-range behavior of dispersion interactions¹⁰ is a better option to perform simulations because it requires a small truncation distance and maximum number of reciprocal vectors in every spatial direction. The density profile is not needed. The Ewald method has been implemented using the Particle Mesh Ewald technique to speed up the calculations,

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and it has been applied with success to calculate coexistence densities and the surface tension of molecular systems including hydrocarbons^{11,12} and water.¹³ In these cases, the simulations were carried out using small truncation distances. The method is general, and it can easily be applied to simulate multi-component systems at the liquid–vapor interface. When these approaches are not used, the slab simulations have to be conducted using large values for truncation distance. The surface tension increases when the cutoff distance increases. The truncation distance for the LJ interactions has to be^{6,14} in the range of 5.5σ to 7σ , where σ is related to the sphere diameter. Finally, the surface area (L_x^2) has a strong effect on surface tension due to finite size effects^{7,13} and oscillations are observed. Large surface areas are needed to obtain reliable results.

The main goal of this work is to calculate the surface tension of 61 organic liquids using the same molecular geometries and the OPLS/AA force field parameters reported by Caleman et al.⁴ and available on the Web at <http://virtualchemistry.org>. Simulations at constant density/temperature (NVT) and constant temperature/pressure (NPT) were also carried out to obtain the liquid density under ambient conditions. These results were compared with those from slab simulations to check consistency between both methods. It is found that the surface tensions of previous calculations are not correct because of the use of a small truncation distance. The liquid density of slab simulations with a truncation distance of 1.1 nm, used by Caleman et al., is smaller than that obtained using the NPT simulations.

2. FORCE FIELD AND SIMULATION DETAILS

The interaction between atoms in different molecules or within the same molecule but separated by three or more bonds, according with the OPLS/AA force field,¹ is defined in terms of LJ and Coulomb models:

$$u_{ij}(r_{ij}) = \left[4\epsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] + \frac{1}{4\pi\epsilon_0} \frac{q_i q_j}{r_{ij}} \right] f_{ij} \quad (1)$$

where r_{ij} is the distance between atoms i and j , q_i is the electric charge on site i , ϵ_0 is the permittivity of the vacuum, ϵ_{ij} and σ_{ij} are the LJ parameters of the ij pair. The factor f_{ij} in eq 1 is 1.0 and 0.5 for intermolecular and 1–4 intramolecular interactions, respectively. The cross interactions for LJ contributions are obtained using the geometric mixing rules

$$\sigma_{ij} = (\sigma_{ii}\sigma_{jj})^{1/2}; \quad \epsilon_{ij} = (\epsilon_{ii}\epsilon_{jj})^{1/2} \quad (2)$$

The molecules are rigid on bond distances, but they have intramolecular degrees of freedom on bending and torsional angles. The force field parameters for all the molecules studied in this work were taken from the Web page <http://virtualchemistry.org/gmld.php>. More information about the force field and simulations was published recently by van der Spoel et al.¹⁵

The slab simulations to obtain the surface tension were performed using the GROMACS software suite¹⁶ at a constant number of molecules, volume, and temperature (NVT). Initially, N molecules, with a density close to the liquid branch of the phase boundaries, were allocated in the middle of a parallelepiped cell of dimensions $L_x = L_y$ and $L_z = 3L_x$. The value of L_x was at least 4.6 nm, which gives a surface area large enough to avoid finite size effects on surface tension.⁷ Thus, the

initial set up consists of a liquid phase surrounded by two empty regions, in which the simulation evolves as the molecules move from the liquid to the empty regions until the system is equilibrated. Periodic boundary conditions were applied in all three directions. The equations of motion were solved using the leapfrog algorithm with a time step of 2 fs. The bond distance was kept constant using the LINCS algorithm for all the molecules. The Berendsen thermostat is applied with a parameter of 0.5 ps. The temperature of 298.15 K was chosen to compare our results with those reported by Caleman et al.⁴ The electrostatic forces were handled using the Ewald sums method.¹⁷ The short-range interactions for the LJ and Coulomb potentials were truncated from 1.1 nm (R_c/σ_{\max} around 3) to 3.0 nm (R_c/σ_{\max} around 8.5), where σ_{\max} is the largest value of σ of all the sites on the molecule. That range of distances includes the value suggested by Truckymchuk and Alexandre.⁶ The simulation results with a truncated distance of 1.1 nm are compared directly with those obtained by Caleman et al.⁴ The error in the Ewald part was 10^{-6} . The long corrections on LJ potential were not applied, and a switching function was not used to smooth the potential at the cutoff distance. The particle mesh Ewald (PME) method¹⁷ was used to evaluate the long-range Coulombic interactions with a grid space of 0.12 nm and a spline of order 4. It was checked that the number of reciprocal vectors followed the relation $k_z^{\max} = (L_z/L_x)k_x^{\max}$.

The surface tension was calculated by^{10,18}

$$\gamma = 0.5L_z[\langle P_{zz} \rangle - 0.5(\langle P_{xx} \rangle + \langle P_{yy} \rangle)] \quad (3)$$

where L_z is the length of the simulation cell in the longest direction and $P_{\alpha\alpha}$ ($\alpha = x, y, z$) are the diagonal components of the pressure tensor. The factor 0.5 outside the squared brackets takes into account the fact that the system has two interfaces.

The systems were equilibrated using 1 million time steps; it was checked that the average values of P_{xx} and P_{yy} were the same, within the simulation error. The average properties were obtained at least for additionally 2 million steps. At the end of the slab simulations, the density profile, liquid density, and surface tension were obtained.

3. SURFACE TENSION RESULTS

Some simulations were performed to check consistency between the liquid density obtained by the NPT method (500 molecules) applied on a liquid phase and the liquid density obtained using the slab geometry (1000 or 2048 molecules) in the NVT simulations. The long-range corrections of the LJ potential were added to the energy and pressure in the NPT simulations, but they were not included in the slab simulations. The truncation distance in NPT simulations was 1.1 nm, the same used by Caleman et al. The value of the liquid densities using NPT simulations was systematically higher than that obtained with the slab method at the same truncation distance. For instance, the density from slab simulations of pyrimidine was 1071.2 kg m^{-3} in comparison with 1091 kg m^{-3} obtained with NPT simulations. This latter value is in good agreement with 1094.5 kg m^{-3} reported by Caleman et al. When the slab simulation was performed at the liquid–vapor interface with a truncation distance of 2.3 nm, the value of the liquid density was 1092.1 kg m^{-3} , in good agreement with NPT simulations. The average density profile ($\rho(z) = N(z)/\Delta V$ where $\Delta V = (L_x^2 L_z/800)$ is the volume of one slab) of the

system for truncation distances of 1.1 and 2.3 nm is shown in Figure 1.

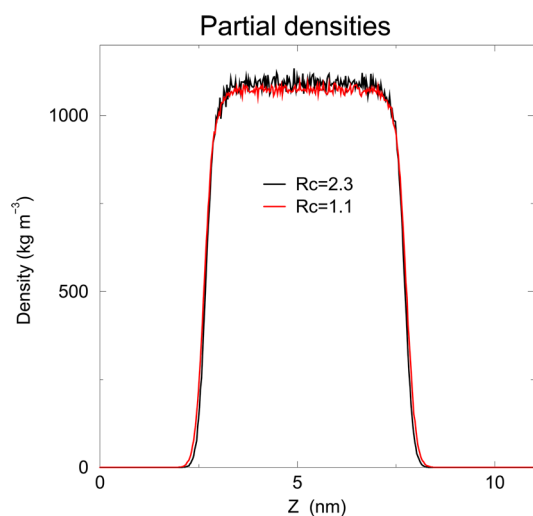


Figure 1. Density profile of pyrimidine at 298.15 K using truncation distances of 1.1 and 2.3 nm for the dispersion forces.

Several factors affect the surface tension of the liquid–vapor interface when the slab geometry is applied in a simulation as described in the Introduction. In this work, large surface areas and the Ewald sums method, with an adequate number of reciprocal vectors to treat the electrostatic interactions, have been used. To analyze the effect that truncation distance has on surface tension, the organic solvents methanamide, pyrimidine, 2-iodopropane, and methoxymethane are chosen because they have different numbers of atoms that interact with the Lennard-Jones potential and because they cover a wide range of surface tension values, from 10 mN/m for methoxymethane to 62 mN/m for methanamide. The simulations are performed at 298.15 K using 2048 molecules within a noncubic simulation cell with dimensions of at least $L_x = L_y = 6$ nm and $L_z = 2L_x$. The

truncation distance is varied from 1.1 to 3.0 nm. The density of the liquid branch at the liquid–vapor interface, obtained from slab simulations for different systems, are shown in the left panel of Figure 2 as a function of R_c/σ_{\max} . The atom type and σ_{\max} value in nm are (C, 0.375) for methanamide, (C, 0.355) for pyrimidine, (I, 0.367) for 2-iodopropane, and (C, 0.35) for methoxymethane. The density value converges at R_c/σ_{\max} around 5.5. The density results are also given in Table 1.

The results of surface tension are shown in the right panel of Figure 2. The numerical values are given in Table 1. The results obtained in this work using $R_c = 1.1$ nm are in good agreement with those reported by Coleman et al. for all the molecules, see Figure 2. The surface tension increases as R_c/σ_{\max} increases. This work shows that in order to calculate accurate surface tensions of organic liquids, when the slab geometry is used to simulate the liquid–vapor interface, the value of R_c/σ_{\max} has to be between 6 and 7. The same conclusion was found for the pure LJ fluid.^{6,14} Table 1 also contains results for simulations using 1000 molecules, $L_x = 2.6$ nm, $L_z = 3L_x$, and $R_c = 2.3$ nm. The surface tension values for the two surface areas are the same within the simulation error. Therefore, simulations for 61 organic liquids are performed at the liquid–vapor interface using the smaller system and surface area with $R_c = 2.3$ nm.

The surface tension results from this work are shown in Figure 3, and the numerical values are given in Tables 2 and 3. They are compared with experimental data and with those reported by Coleman et al. The new results are in much better agreement with experimental data for most of the systems. The name of the molecule and the reference number were taken from the Web page <http://virtualchemistry.org/gmld.php>.

The OPLS/AA force field fails to reproduce the dielectric constant, ϵ , for most of the organic liquids.⁴ Several NPT simulations were performed at 298.15 K on pyrimidine to analyze the effect that truncation distance has on dielectric constant. The results ($R_c/\text{nm}, \epsilon$) are (1.1, 8.5), (2.3, 9.2), and (3.0, 9.4). The result reported by Coleman et al. was (1.1, 8.8). The dielectric constant is not affected by truncation. The

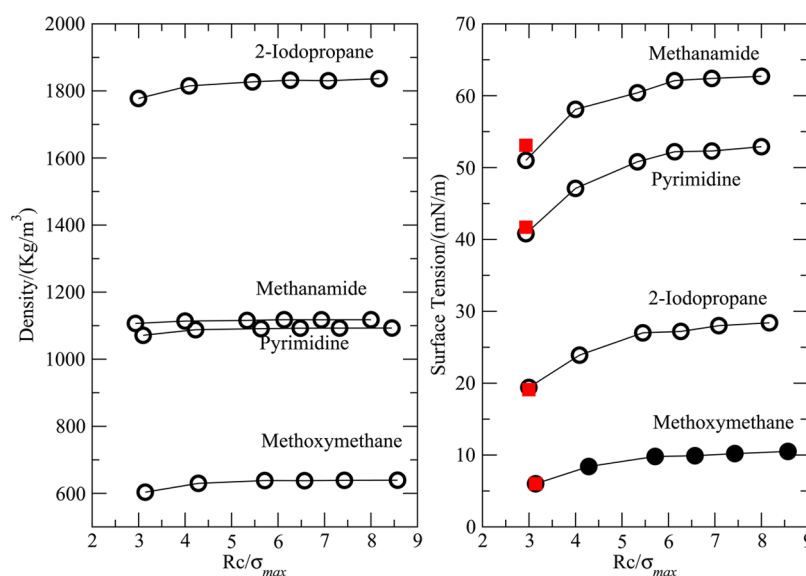


Figure 2. Liquid density (left panel) and surface tension (right panel) as a function of dimensionless truncation distance R_c/σ_{\max} for several systems obtained using slab simulations in the NVT ensemble. The results from this work and those reported by Coleman et al.⁴ are shown with open circles and filled red squares, respectively.

Table 1. Surface Tension of Organic Liquids As a Function of R_c at 298.15 K^a

system	R_c	R_c/σ_{\max}	γ	γ_{Caleman}	ρ	ρ_{Caleman}
methoxymethane	1.1	3.14	6.0	6.0	603.5	
	1.5	4.29	8.4		629.9	
	2.0	5.71	9.8		638.2	
	2.3 ^b	6.57	10.0		637.8	
	2.3	6.57	9.9		637.9	
	2.6	7.43	10.2		638.9	
2-iodopropane	3.0	8.57	10.5		639.3	
	1.1	3.00	19.4	19.1	1777.4	1848.2 ^c
	1.5	4.10	23.9		1814.9	
	2.0	5.45	27.0		1826.8	
	2.3 ^b	6.27	27.3		1829.3	
	2.3	6.27	27.2		1831.9	
pyrimidine	2.6	7.08	28.0		1830.3	
	3.0	8.17	28.4		1836.5	
	1.1	3.10	40.8	41.7	1071.2	1094.5 ^c
	1.5	4.23	47.1		1087.9	
	2.0	5.63	50.8		1091.0	
	2.3 ^b	6.48	51.0		1092.1	
methanamide	2.3	6.48	52.2		1092.4	
	2.6	7.32	52.3		1092.8	
	3.0	8.45	52.9		1092.9	
	1.1	2.93	51.0	53.1	1106.6	1122.1 ^c
	1.5	4.00	58.1		1113.7	
	2.0	5.33	60.4		1115.6	
	2.3 ^b	6.13	60.6		1117.7	
	2.3	6.13	62.1		1117.8	
	2.6	6.93	62.4		1117.6	
	3.0	8.00	62.7		1117.8	

^aThe atom type and σ_{\max} value in nm are (C, 0.35) for methoxymethane, (I, 0.367) for 2-iodopropane, (C, 0.355) for pyrimidine, and (C, 0.375) for methanamide. The simulation error is estimated to be around 1 mN m⁻¹. The units are nm for distance, mN m⁻¹ for surface tension, and kg m⁻³ for density. ^bResults with 1000 molecules and $L_x = 4.6$ nm. ^cThe density results reported by Caleman et al. and obtained using NPT simulations

problem seems to be related with the charge distribution on the molecule.

4. CONCLUSIONS

Accurate calculation of thermodynamic, transport, and structural properties is needed to determine the efficiency of force fields in molecular simulations. The OPLS/AA model is a nonpolarizable force field where the parameters have been developed to simulate liquids including all of the atoms. It is believed that polarizable force fields are required to obtain surface tensions and dielectric constants in good agreement with experimental data. The results previously reported by Caleman et al. for 146 molecular systems, using the OPLS/AA force field model, suggested that nonpolarizable models are not good enough to reproduce the surface tension and dielectric constant. In a recent work we have found¹⁹ that the experimental dielectric constant, surface tension, and several density anomalies of water can be reproduced with a nonpolarizable force field. We have found in this work that surface tension obtained using the OPLS/AA force field gives good agreement with experimental data for most of the 61 molecular systems once R_c/σ_{\max} is between 6 and 7 to calculate the long-range interactions of the dispersion forces. The good

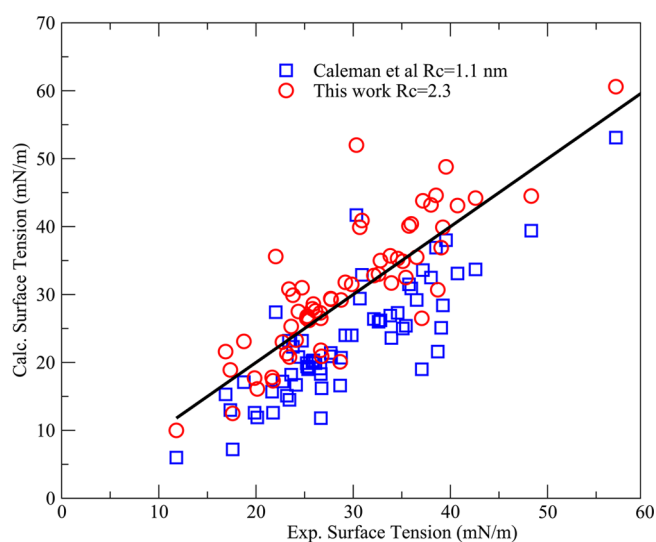


Figure 3. Correlation between experimental results of surface tension and those calculated in this work using the OPLS/AA force field with a truncation distance of 2.3 nm (open circles). The results obtained by Caleman et al.⁴ using a truncation distance of 1.1 nm (open squares) are also shown. The error bars are less than symbols' size. The statistics (Caleman, this work) are RMSD (7.8, 5.4), the correlation coefficient R^2 (76%, 76%), and the % mean deviation between simulation results and experimental data (24, 14).

Table 2. Surface Tension, in mN m⁻¹, of Organic Liquids Obtained in This Work^a

Name	T	γ_{Exp}	γ	γ_{Caleman}
1. chloroform	298.15	26.67	21.8	11.8
2. dichloro(fluoro)methane	300.00	17.60	12.5	7.2
3. dibromomethane	298.15	39.05	36.9	25.1
8. methanamide	298.15	57.03	60.6	53.1
9. nitromethane	298.15	36.53	35.5	29.2
13. 1,1-dichloroethene	298.15	21.66	17.8	15.7
15. acetonitrile	298.15	28.66	20.1	16.6
16. 1,2-dibromoethane	298.15	39.55	48.8	38.0
19. methyl formate	298.15	24.36	27.5	20.8
20. bromoethane	298.15	23.62	25.3	18.2
24. N-methylformamide	298.15	38.52	44.6	36.9
25. nitroethane	298.15	32.13	32.8	26.4
26. methoxymethane	298.08	11.80	10.0	6.0
32. 2-aminoethanol	298.15	48.32	44.5	39.4
35. 1,3-dioxolan-2-one	312.15	63.28	66.7	54.7
36. propanenitrile	298.15	26.75	20.9	16.2
38. 1,3-dichloropropane	298.15	33.93	31.7	23.6
40. propan-2-one	298.15	22.72	23.0	17.2
41. methyl acetate	298.15	24.73	31.0	23.2
42. 1,3-dioxolane	298.15	32.61	33.0	26.0
43. 2-iodopropane	298.15	26.62	27.3	19.1
44. 1-bromopropane	298.15	25.26	26.8	19.4
45. N,N-dimethylformamide	298.15	35.74	40.1	31.5
47. 1-nitropropane	298.15	29.85	31.5	24.0
49. dimethoxymethane	298.15	18.75	23.1	17.1
51. propane-1-amine	298.15	21.75	17.3	12.6
52. propane-2-amine	298.15	17.36	18.9	13.0
55. butane-1-thiol	298.15	25.22	26.5	19.9
60. N-ethylethanamine	298.15	19.85	17.7	12.6

^aThe results are compared with experimental and simulation data reported by Caleman et al.⁴ Blue font indicates that the calculated value differs more than 10% from the experimental ones; a red font indicates that it differs by more than 25%. The index numbers and the names of the molecular systems are the same as those used by Caleman et al.⁴ The temperature units are Kelvins. The simulation error is estimated to be less than 1 mN m⁻¹.

Table 3. Surface Tension, in mN m^{-1} , of Organic Liquids Obtained in This Work^a

Name	T	γ_{Exp}	γ	γ_{Caleman}
61. butan-1-amine	298.15	23.44	20.8	14.5
62. 2-methylpropan-2-amine	298.15	16.87	21.6	15.3
64. pyrimidine	298.15	30.33	51.0	41.7
66. thiophene	298.15	30.68	39.9	29.4
68. ethenyl acetate	298.15	22.03	35.6	27.4
71. 1,4-dichlorobutane	298.15	35.42	32.5	25.4
74. ethyl acetate	298.15	23.39	30.8	23.2
76. thiolane	298.15	33.82	35.7	26.9
77. 1-bromobutane	298.15	25.90	28.6	20.3
78. 1-chlorobutane	298.15	23.18	21.3	15.1
79. pyrrolidine	298.15	37.06	26.5	19.0
83. cyclopentanone	298.15	32.80	35.0	26.2
85. pentane-2,4-dione	298.15	30.90	40.9	32.9
88. ethyl propanoate	298.15	23.80	29.9	22.3
90. pentan-1-ol	298.15	25.36	26.4	19.0
99. fluorobenzene	298.15	26.66	26.5	18.3
103. benzenethiol	298.15	38.70	30.7	21.6
107. cyclohexanone	298.15	34.57	35.3	27.3
109. hexan-2-one	298.15	25.45	26.2	19.3
119. benzaldehyde	298.15	38.00	43.2	32.5
120. toluene	298.15	27.73	29.3	20.9
121. methoxybenzene	298.15	35.10	34.9	25.0
122. phenylmethanol	298.15	35.97	40.4	30.9
128. heptan-2-one	298.15	26.12	27.6	19.9
131. methyl benzoate	298.15	37.17	43.8	33.6
133. ethylbenzene	298.15	28.75	29.2	20.7
139. N-butylbutan-1-amine	298.15	24.12	23.3	16.7
141. quinoline	298.15	42.59	44.2	33.7
142. (1-methylethyl)benzene	298.15	27.69	29.4	21.4
143. 1,2,4-trimethylbenzene	298.15	29.19	31.8	24.0
144. 2,6-dimethylheptan-4-one	298.15	25.80	27.9	20.2
145. 1-chloronaphtalene	298.15	39.23	39.9	28.4

^aThe results are compared with experimental and simulation data reported by Caleman et al.⁴ Blue font indicates that the calculated value differs more than 10% from the experimental ones; a red font indicates that it differs by more than 25%. The index numbers and the names of molecular systems are the same as those used by Caleman et al.⁴ The temperature units are Kelvins. The simulation error is estimated to be less than 1 mN m^{-1} .

agreement between the liquid density from slab simulations and from bulk NPT calculations gives us confidence that the results reported in this work are correct. The dielectric constant is not affected by truncation of dispersion interactions. More work is needed to improve the performance of OPLS/AA for several systems at the liquid–vapor interface, but the results reported in this work show that it is possible to have a nonpolarizable model that describes liquid and interfacial properties at the same time.

AUTHOR INFORMATION

Corresponding Author

*E-mail: jra@xanum.uam.mx.

Notes

The authors declare no competing financial interest.

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