Liquid-vapor equilibria and interfacial properties of n-alkanes and perfluoroalkanes by molecular simulation

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ABSTRACT

A molecular-dynamics study is presented to assess the performance of a united-atom model in the prediction of liquid-vapor interfacial properties for short-chain perfluoroalkanes and their alkane counterparts. In particular, the ability of this model to discriminate between the surface-energy values of these two types of compounds was investigated over a wide temperature range corresponding to the liquid-vapor region. Comparisons with available experimental data and surface-tension predictions given by other force-field parameterizations, including those based on the more computationally demanding all-atom method, were performed to gauge the viability of this model. It was found that the model used in this study captures qualitatively the expected behavior of surface energy between alkanes and perfluoroalkanes and yields values that are in excellent agreement with experimental data, especially in the high-temperature limit as the critical temperature is approached.
INTRODUCTION

Surface tension is a thermodynamic property that plays an important role in a variety of scientifically interesting and technologically relevant areas, including oil and water repellency, wetting, adhesion, and contact-angle (CA) hysteresis. It reflects the underlying chemical character of a given compound and its affinity to interact with other materials—including itself—in a variety of states. A full understanding of the factors that impact surface tension can in principle be obtained through rigorous molecular simulation, using methods based on force fields that describe the interaction energies of all atomic degrees of freedom accurately. However, simulation strategies at this level of detail pose severe computational challenges because of the inherently large length scales involved and the number of particles necessary to capture the key aspects of surface-related phenomena. Therefore, availability of accurate, validated, coarse-grained strategies is paramount.

Liquid-vapor (L-V) surface tension, $\gamma_{LV}$, is of particular interest because it can be determined through both experimental and molecular-simulation techniques. Availability of experimental data for surface tension provides a basis by which to evaluate the performance of force-field parameterizations. In turn, these validated models can be used to gain insight into the factors that affect repellency, wetting, and other relevant surface-tension-mediated phenomena. Typically, one of two approaches can be employed during molecular simulation to obtain $\gamma_{LV}$. In the thermodynamic route, the free energy of the system is computed as the interfacial surface area is varied while the number of molecules, volume, and temperature are kept constant, i.e., in the canonical, or NVT, ensemble; in the mechanical route, the surface tension is computed from the pressure
tensor, also within the canonical ensemble. Inaccuracies in determining $\gamma_{LV}$ by molecular simulation arise from several sources: (i) force fields that do not faithfully describe the molecular interactions characteristic of the particular system over a very broad range of states, namely, liquid and vapor; (ii) lack of proper accounting for the long-range corrections to thermodynamic properties in heterogeneous systems that arise from the inevitable truncation in the evaluation of the potential energy function; and (iii) poor equilibration of L-V interfaces at temperatures approaching the critical point, i.e., $T \to T_c$.

Each of these points is elaborated further here. First, the study of surface-related phenomena requires large system sizes to minimize the effects of the interfacial region over the bulk and has triggered the development of coarse-grained strategies. These approximate approaches aim at striking a balance between computational efficiency, i.e., coarse graining, and atomic resolution. However, the coarse-graining process can introduce fundamental limitations in the ability of a model to preserve and capture the key physics of the phenomena of interest. Second, while the implementation of long-range corrections to thermodynamic properties of interest is straightforward for bulk homogeneous systems, its implementation in heterogeneous systems is a more challenging task. Difficulties arise because of the drastic changes in density across the interface dividing the liquid and vapor phases. Last, equilibrating coexisting liquid and vapor phases at high temperature represents a challenge because of the characteristic increase in the fluctuations near the critical point, which can then translate into non-equilibrium states as a result of the finite sizes of the simulation cells.

Here, we report the study of L-V equilibria and interfacial properties of n-alkanes ranging from six to twelve carbons in length, and the corresponding perfluoroalkanes. The
objective is to evaluate a simple and computationally economical UA force-field parameterization for the accurate prediction of L-V interfacial properties and to compare these to values obtained using more computationally demanding methods. Perfluorinated compounds are of particular interest for studies related to interfacial phenomena due to their remarkably low surface tension and dielectric constant, chemical and thermal stability, and biocompatibility; their technological importance is well established. The alkanes serve as a base case for this work, as they are well studied and ample data are available for validation; they are also of interest as model fluids for the eventual study of oil repellency. The focus of this work is on predicting surface-tension data at orthobaric conditions while addressing three central questions. First, can a simple UA model discriminate between the surface tension, \( \gamma \), of perfluoroalkanes with respect to their corresponding alkane counterparts over a wide temperature range in the L-V region? Second, how do the predicted surface-tension values compare against available experimental data for these compounds? Third, how does the performance offered by the UA model used in this work compare with that of other existing models? The second question aims at providing a sound comparison between the temperature-dependent properties predicted and those obtained by experiments, by taking into account both the absolute values at given temperature points as well as the overall behavior, including the limiting case near the critical temperature, \( T_c \). The third question is driven by computational economy and aims at gauging the performance of such an inherently simple coarse-grained model in predicting L-V properties with respect to the performance offered by more sophisticated and computationally demanding models.

SIMULATION DETAILS
We use a united-atom (UA) force field originally reported by Escobedo and Chen.\textsuperscript{1} This force-field parameterization is one of the few that have been explicitly designed to treat both fluoroalkanes and alkanes. It is one of three developed by the authors, based on the earlier works of Cui et al\textsuperscript{2} and Nath et al\textsuperscript{3}, for the purpose of studying the temperature-induced order-disorder transition of a partially fluorinated diblock copolymer. The parameterization chosen for this work is their “M2 model”; the parameters of this model are summarized in Table I of their work. The main differences between the M2 model in Escobedo and Chen\textsuperscript{1} and its prior versions\textsuperscript{2,3} lie in the functions describing the bending interactions for both types of compounds and the torsion interaction for the case of alkanes. Escobedo and Chen\textsuperscript{1} found the prediction of liquid density by model M3 to be in closer agreement with experimental data than that given by model M2 for compounds C\textsubscript{10}F\textsubscript{22} and F(CF\textsubscript{2})\textsubscript{6}—H(CH\textsubscript{2})\textsubscript{6} at temperature values between 300 K and 360 K. However, as shown in Fig. 2 of that work,\textsuperscript{1} the differences in liquid-density predictions between these two models decrease with temperature. Another difference is their introduction of a binary interaction parameter for CH\textsubscript{n}—CF\textsubscript{n} interactions; this binary interaction parameter was chosen to reproduce the azeotrope observed to form in mixtures of n-hexane and perfluorohexane.\textsuperscript{5} This binary interaction parameter is not important for the compounds studied here, but may become significant for subsequent studies of compounds with only partial fluorination. We have modified the bonded atom interaction, from the original, rigid, 0.154 nm bond between united atoms, to a flexible, harmonic function with a spring constant, $K_{\text{bond}}$, equal to 96,500 K/Å\textsuperscript{2} for both alkanes and perfluoroalkanes. With this function, an equilibrium bond-
length of 0.153 nm yielded the best liquid-density values and was used throughout this work.

Bulk molten systems were prepared for simulation by molecular dynamics using the Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) software. Each simulation cell was prepared with 6000 to 6400 UA groups, arranged in molecules from C6 to C12. The dimensions of the supercells along the x-, y-, and z-directions were assigned such that \( L_x = L_y \) and \( L_z = 3L_x \). These systems were first annealed at high temperature \( (T > T_b) \) and constant density for 500 ps, followed by NPT simulation for 1 ns at a constant pressure of 1 atm and a target temperature between the melting point, \( T_m \), and the normal boiling point, \( T_b \), for each compound. The pressure and temperature of the system were kept constant using a Hoover\(^7\) barostat and a Berendsen\(^8\) thermostat, respectively. The equilibrated molecular coordinates were then unfolded along the z-direction, and new periodic boundaries were created such that \( L_z = 9L_x \), thereby creating two liquid-vacuum interfaces and increasing the total volume of the system by about a factor of three. The geometry of the system was such that the free surfaces were oriented along the \( xy \)-plane with normal vectors parallel to the \( z \)-direction. This procedure was repeated for each perfluoroalkane at the lowest-temperature value assigned to each compound; alkane systems were prepared by switching the chemical identity of each molecule of the equilibrated perfluorinated systems and re-equilibrating. Generating alkane systems using this approach ensured a direct correspondence in the interfacial area for each pair of compounds. Initial mismatches in the liquid density of the newly generated systems were quickly healed and did not pose any implementation difficulties.
Table 1 summarizes the system dimensions and number of molecules used for each chain length.

Table 1: Cell dimensions and number of molecules.

|   | $L_x$ (Å) | N no. of molecules |
|---|-----------|--------------------|
| C6 | 45.80     | 1000               |
| C7 | 49.43     | 900                |
| C8 | 49.49     | 800                |
| C9 | 49.07     | 700                |
| C10| 48.16     | 600                |
| C12| 47.97     | 500                |

Systems corresponding to higher temperatures were prepared by applying a heating schedule that raised the temperature from its lowest value to the target temperature at increments of 10 K every 100 ps, followed by a final equilibration period of 200 ps at the target temperature, to relax further any remaining thermo-mechanical stresses imposed by the heating schedule and to minimize chemical-potential gradients brought about by both the volume expansion and the action of the heating schedule. The equations of motion were integrated in the canonical ensemble (NVT) using the Nose-Hoover Chains algorithm\textsuperscript{9} with a time step of 1 fs. The non-bonded interactions were made to vanish smoothly and continuously through the use of cubic splines in the region between $r_s = 1.2$ nm and the cut-off distance, $r_c = 1.49$ nm. While the use of such a smooth cut-off alters the potential interaction slightly at long distances, i.e., $r_s \leq r \leq r_c$, it eliminates spurious impulses associated with the discontinuity that would result from abrupt truncation at a
finite distance. The z-component of the center of mass (c.o.m.) for the slab was fixed at each time step by shifting the coordinates of all molecules. The c.o.m. was calculated by taking into account the bulk-phase region of the liquid only, which in turn was determined by monitoring the number of neighbors within interaction range for each molecule. The Verlet neighbor list was used to facilitate the computation of the distances between non-bonded particles.

For purposes of computing the surface tension, the volume of the system, $V_{\text{tot}}$, was divided into $N$ sub-volumes along the z-direction. Each subdivision corresponded to a bin with dimensions along the x-, y-, and z-directions equal to $L_x$, $L_y$, and $\delta z$, respectively. A value of 0.3 nm was chosen for $\delta z$, and the bins were distributed in such a way that the center of the supercell and the central bin along the z-direction coincided. The $z$-dependence of the pressure tensor was obtained by computing the virial pressure equation\textsuperscript{10} in each of the sub-volumes, including both bonded and non-bonded contributions.

The surface tension was calculated following the mechanical method of Kirkwood and Buff\textsuperscript{11} by integration of the difference between the normal, $p_n(z) = p_{zz}(z)$, and tangential pressure tensor components, $p_t(z) = (p_{xx}(z) + p_{yy}(z))/2$, along the z-direction

$$\gamma = \frac{1}{2} \int_{-z}^{z} \left( p_n(z) - p_t(z) \right) dz$$ \hspace{1cm} (1).

The factor of one-half in eqn (1) accounts for the two interfaces arising from the symmetry of the simulation box. When dealing with a heterogeneous system with two coexisting phases, an additional correction to the surface tension is required. This
correction was estimated using the method outlined in Refs. 12 and 13, which involves fitting the resulting profile, \( \rho(z) \), of the system to a hyperbolic-tangent profile given by

\[
\rho(z) = \frac{1}{2} \left[ (\rho_L + \rho_V) - (\rho_L - \rho_V) \tanh \left( \frac{\text{sgn}(z) z - \text{sgn}(z) \xi}{2 \xi} \right) \right]
\]  

(2).

Here, \( \rho_L \) and \( \rho_V \) are the bulk liquid and bulk vapor densities, respectively, \( z_\xi \) is the position of the Gibbs dividing surface, and \( \xi \) is a parameter that relates to the thickness of the interface. The tail correction for the surface tension, \( \gamma_{\text{tail}} \), is given by

\[
\gamma_{\text{tail}} = \frac{\pi}{4} (\rho_L - \rho_V)^2 \int_0^\infty ds \int_{r_c}^\infty dr \frac{d U_{\text{nb}}(r)}{dr} r^4 g(r) (3 s^3 - s) \coth \left( \frac{sr}{2 \xi} \right)
\]  

(3).

Typically, approximations to the solution of this integral include (i) the assumption that the radial distribution function approaches a value of unity at the cut-off distance and beyond, i.e., \( g(r \geq r_c) = 1 \), and (ii) the omission of the repulsive part of the non-bonded potential-energy function, \( U_{\text{nb}}(r) \). Equation (3) applies strictly to the case of an abrupt truncation of the unmodified non-bonded potential-energy function. However, since a potential-energy function was modified with cubic splines in the region \( r_s \leq r \leq r_c \), a slightly modified form of this tail correction was introduced to avoid double-counting. The modified tail correction is described in more detail in the Supplemental Material.\(^{14}\)

The data collection involved assigning the position of all the particles in the simulation to their corresponding \( z \)-discretized bins at each time step, thereby creating snapshots of the system configuration while computing the properties of interest, e.g., density, energy, and pressure. The averages of the corresponding data sets were computed by blocking over 5-ps intervals, which were then accumulated over the entire 20 ns of simulation time.
RESULTS AND DISCUSSION

Liquid-vapor equilibria and surface-tension calculations for both alkanes and perfluoroalkanes were conducted at temperatures between 300 K and 520 K, in 20 K increments. The lowest temperature assigned to n-alkanes, \( \text{C}_n\text{H}_{2n+2} \), and perfluoroalkanes, \( \text{C}_n\text{F}_{2n+2} \), with carbon number, \( n \), equal to 6, 7, 8, 9, 10 and 12, were set to values of 300 K, 320 K, 340 K, 360 K, 380 K, and 400 K, respectively. In all cases, the low-temperature values were higher than the corresponding melting temperature, \( T_m \), for that compound. The conditions for equilibrium, which are necessary to ensure a state of coexistence between the liquid and vapor phases, were each confirmed individually. Diffusional equilibrium was inferred by analyzing density profiles, \( \rho(z) \). Representative density profiles for perfluorohexane (\( \text{C}_6\text{F}_{14} \)) are shown in Figure 1. Each profile is symmetric about the center of the simulation cell \( (z = 0) \). A region of high density (liquid phase) is joined to a region of low density (vapor phase) by two interfaces, where \( d\rho(z)/dz \) is nonzero (periodic boundary conditions apply in all three directions).
Figure 1: Density profiles corresponding to C6F14 illustrating the typical temperature dependence of the L-V density at orthobaric conditions. The six profiles cover a temperature range between 300 K (blue) and 400 K (red). The liquid density is highest at the lowest temperature and decreases with temperature. Conversely, the vapor density is lowest at the lowest temperature value and increases with temperature. The dotted arrows indicate the direction in which the density changes with increasing temperature.
The standard deviation of residuals for the fitted data was less than 0.005 g/cc at all temperatures.

Figure 2: Time-dependence profiles corresponding to (a) the position of the Gibbs dividing surface, $|z_\xi|$, (b) the interfacial-width parameter, $\xi$, and (c) the liquid and vapor densities. For purposes of clarity in (a), the curves are displaced by 10 Å for every 20 K
increment above 360 K. Solid lines were used to identify the temperatures at which the three properties fully equilibrated. Dashed lines corresponded to either non-equilibrated system or systems with pronounced fluctuations. Systems corresponding to dashed lines were not included in the calculation of any L-V property. The vertical arrows indicate the trend with increasing temperature.

The time evolution of the liquid phase density, $\rho_L$, vapor phase density, $\rho_V$, interface position, $|z_\xi|$, and interfacial width, $\xi$, was determined by fitting eqn 2 to density profiles obtained for each 5 ps interval of simulation time; $|z_\xi|$ and $\xi$ were averaged over both interfaces. The typical behavior of these profiles is shown in Figure 2 for perfluorononane ($C_9F_{20}$) at temperatures from 360 to 480 K, in 20 K increments. In Fig 2(a), the time evolution of the position of the Gibbs interface is typical of these time-evolution profiles. It exhibits an initial non-equilibrium period during which the position of the interface changes, which in some cases persists for longer than 5 ns. This is usually followed by a constant steady-state value characteristic of equilibrium coexistence. The equilibrated profiles correspond to temperatures from 360 K to 440 K. At 460 K, the interface position appears to equilibrate eventually, but shows significant fluctuations in the values of $z_\xi$ for periods longer than 10 ns; at 480 K the interface position does not equilibrate during the 20-ns of simulation time. A similar assessment can be made from Fig 2(b) and (c). At all temperatures, the liquid-density profiles attained constant values. However, at 480 K, the vapor density continues to increase, indicative of a non-equilibrated interface; this was attributed to the diffusion of liquid molecules into the vapor phase, thereby revealing the presence of a finite chemical-
potential gradient. The observed increase of the vapor density at the highest temperature and the constant value of the bulk liquid densities are consistent with a moving interface and therefore do not correspond to a state of coexistence. Mechanical equilibrium was inferred by examining the pressure profiles. Figure 3 shows representative profiles corresponding to perfluorohexane ($C_6F_{14}$) at temperatures from 300 K to 400 K.

Figure 3: Pressure profiles corresponding to $C_6F_{14}$ in a temperature range from 300 to 400 K, in increments of 20 K. The vapor pressure increases with increasing temperature, as indicated by the dashed vertical arrow, while the excursion in pressure within the interfacial regions decreases.
These profiles are characterized by two regions of constant and equal pressure—the coexisting liquid and vapor phases—separated by two regions where the pressure is strongly varying—the interfacial regions. As shown in Figure 3, equality of pressure in the liquid and vapor phases signifies mechanical equilibrium.

Figure 4: (a) Plots of temperature versus the scaled difference in liquid and vapor densities, used to determine the critical temperature, $T_c$, of the perfluoroalkanes according
to eqn 5 with a $\beta$-exponent value of 0.325; (b) plots showing the L-V phase coexistence envelopes for the perfluoroalkanes.

The coexistence pressure increases with temperature, as expected. The conditions of thermal equilibrium were facilitated by the action of the thermostat (not shown). These equilibrium criteria were applied to all compounds in this study and were used to determine the highest temperature at which coexistence between the two phases was reliably established. The alkanes included a total of seven temperature points separated by 20 K increments, i.e., 120 K above the minimum temperature set for each compound, whereas the perfluoroalkanes included only five, i.e., 80 K. The upper-temperature bound for the perfluoroalkanes is lower than that for the alkanes because of the lower critical temperatures, $T_c$, of these compounds and the increase in fluctuations when in closer proximity to the critical point.

The equilibrium bulk liquid and bulk vapor densities from the fits of eqn 2 were used to determine the critical temperatures and to construct the L-V phase coexistence envelopes. The critical temperature, $T_c$, was determined from the $y$-intercept corresponding to the linear fit of the following Ising-type scaling relation,

$$T - T_c \propto (\rho_L - \rho_V)^{1/\beta}$$

(5),

where $\beta$ is a well-known exponent equal to 0.325.\textsuperscript{15} The resulting critical-temperature values were then used, along with the law of rectilinear diameters,\textsuperscript{16,17} to determine the critical density, $\rho_c$, of each compound. Representative plots of eqn 5 for the perfluoroalkanes are shown in Fig 4(a), while the corresponding L-V phase envelopes are shown in Fig 4(b). Similar plots were obtained for the alkanes also but are not shown.
here. Saturation curves were constructed from linear fits to the bulk vapor phase regions corresponding to the pressure profiles at each temperature point such as those shown in Figure 3.

The accuracy of the UA model in describing L-V equilibria was assessed by comparing the liquid densities, $\rho_L$, critical temperatures, $T_c$, critical densities, $\rho_c$, and normal boiling temperatures, $T_b$, against available experimental data;\textsuperscript{18-21} these comparisons are tabulated in Tables S1 and S2 of the Supplemental Materials\textsuperscript{14}; the overall agreement is excellent, with deviations from experiment smaller than 3%. A comparison with similar level of detail could not be made for the perfluoroalkanes due to the limited publicly available experimental data for these compounds. Nonetheless, the observed agreement was comparable to that seen for the alkanes. The predicted values for critical temperatures, densities, and boiling temperatures for the two types of compounds were found to be in excellent agreement with experimental data: the values of the alkanes were between 0.3% and 2.1%, and those of the perfluoroalkanes ranged between 0.3% and 3.3%. Also, a slight overprediction of all properties was observed in all cases, with the exception of $\rho_c$ and $T_c$ of alkanes. Again, a full comparison for all perfluorinated compounds was hampered by the lack of available experimental data for these compounds. The agreement in the predictions of L-V properties of this work and the experimental data available for these two types of compounds is consistent with previous results obtained with the UA models by Cui et al\textsuperscript{2} and by Nath et al\textsuperscript{3}, upon which the modified version of the M2-model\textsuperscript{1} used here was based.
The surface-tension values of perfluoroalkanes and the corresponding alkanes were computed as described in Section II.

Figure 5: Pressure-tensor difference profiles corresponding to C6F14 at temperatures between 300 K and 360 K. The tallest profile corresponds to the lowest temperature and the dotted arrow points in the direction of increasing temperature. The height of the peaks decreases with temperature and is expected to vanish at the critical temperature, $T_c$.

A representative set of profiles corresponding to the pressure-tensor anisotropy, that is, the difference between the normal and tangential components of the pressure tensor, is shown in Figure 5. These profiles correspond to C6F14 at temperatures from 300 to 380 K. The features of these profiles are similar to those shown in Fig 3. In particular, the pressure-tensor anisotropy is constant and equal to zero in both liquid and vapor phases,
and nonzero only within the interfacial regions. Integration of these profiles according to eqn 1 yields the surface tension, which can then be plotted as a function of temperature as shown in Figure 6. In addition, knowledge that the surface tension goes to zero at the critical temperature can be used to extend these curves to \( \gamma = 0 \). The entire surface-tension data set, including the point at \( T_c \), for all compounds was fitted to a smooth function to provide missing data points in the high-temperature region. The Cahn-Hilliard (CH) power law\(^{16,17,22} \) provided a theoretically sound choice of function form for data fitting and avoids errors in the predicted surface-tension values that can arise from the use of mathematically suitable but otherwise arbitrary functions. The CH power law is given by

\[
\gamma = \gamma_0 \left(1 - \frac{T}{T_c}\right)^\mu
\]

(6),

where \( \gamma_0 \) is a surface-tension amplitude parameter, and \( \mu \) is the critical exponent. The experimentally observed critical exponent of 1.26 was used in all fits: values of \( \gamma_0 \) for both sets of compounds are shown in Table 4, and the C-H fits are shown in Figure 6 as solid profiles.

Table 2: surface-tension amplitudes obtained from the C-H fits.

| n  | \( \gamma_0 \) (mN/m) | \( \text{C}_n\text{F}_{2n+2} \) | \( \text{C}_n\text{H}_{2n+2} \) |
|----|----------------------|-------------------|-------------------|
| 6  | 41.50                | 62.54             |
| 7  | 42.64                | 61.13             |
| 8  | 41.78                | 61.27             |
| 9  | 41.65                | 61.07             |
| 10 | 42.13                | 60.98             |
| 12 | 42.79                | 59.80             |
The figure shows results specific to compounds C_{12}H_{26} and C_{12}F_{26}; however, the trends illustrated here were observed in the rest of the compounds as well (e.g., see figures S2, through S4 of the Supplemental Materials, Ref. [14]) and are summarized here as follows. First, the UA-model overestimates the surface-tension values of C_{n}H_{2n+2} at low temperatures by between 9% and 24% of the experimental values;\(^{18}\) however, the C-H fits show that better agreement is obtained with increasing temperature and predict values that approach the experimental values in the region near the critical temperature. Second, the model captures qualitatively the differences expected for these two types of compounds; i.e., the surface-tension values of alkanes are higher than that of their perfluoroalkane counterparts at any temperature value within the L-V region. This finding is significant, in that it sheds light on an apparent misconception regarding the limitations of the UA method. Hariharan and Harris\(^{23}\) presented a UA-based study in which their model could not capture surface-tension differences between decane and perfluorodecane. References\(^{24-26}\) to that work\(^{23}\) seem to suggest that this is caused by an inherent limitation of the UA method. However, the results in this work demonstrate that this is not the case; rather, the issue is with the specific UA model used and its parameterization. Third, agreement with surface tension at low temperature for C_{n}F_{2n+2} was found to be superior to that of the alkane compounds, with differences ranging between 0.2% and 10%. Although comparisons at high temperatures could not be made for these compounds, good agreement is expected based on the accurate prediction of T_{c} as given by the model and the corresponding C-H fits and are left as predictions of the UA model to be scrutinized when this data becomes available.
Figure 6: Representative temperature dependence of surface tension of perfluoroalkanes (open symbols) and corresponding alkanes (filled symbols); solid lines are the CH fits to the calculated data. The surface tension decays with temperature and vanishes at the critical point predicted by the UA model. At temperatures below the critical point of the perfluorinated compounds, the surface-tension values of alkanes are always higher than the perfluorinated ones, in agreement with experimental observations.\textsuperscript{18,23,27,28}

The performance of the UA model was further assessed using literature results based on other force-field parameterizations. The comparisons for the alkanes include two
compounds, \( C_6H_{14} \) and \( C_{10}H_{22} \), and four different force-field parameterizations: two based on the UA method—NERD\(^3\) and TraPPE,\(^{29}\) as given by the work of Mendoza et al\(^{30}\)—and two based on the AA method—OPLS\(^{31}\) and Smith,\(^{32}\) as given by the work of Ismail et al.\(^{33}\) These models use Ewald sums to treat the dispersion interactions in all cases as well as the Coulombic interactions in the case of the OPLS model. Therefore, the computational toll required by the UA model in this work is considerably lower than either the NERD or the TraPPE UA models in Ref. 30, and much less costly than the AA-based models, i.e., OPLS or Smith in Ref. 33. The tabulated comparisons are shown in Table 5 where results for each model is represented by sets of two columns: one containing the surface-tension values at different temperatures, and one with the corresponding percent differences from the experimental values. The values in Table 5 corresponding to the AA models were read from parts (a) and (b) of Figure 3 in Ref. 33, whereas the values for the NERD and TraPPE models were interpolated from the entries in Table 3 of Ref. 30.

The differences between the surface-tension values predicted by this work and those given by the NERD model are quite similar. This finding is not surprising if one takes into account the fact that the M2 parameterization for alkanes as given by Escobedo and Chen\(^1\) was based on the NERD model. Nonetheless, the results demonstrate that a simple UA-model with a smoothly vanishing dispersion can generate results that are as good as those obtained with Ewald sums. The TraPPE model yields better agreement for the \( C_6H_{14} \) compound, but not for \( C_{10}H_{22} \). The results corresponding to the OPLS model show better agreement at low temperatures, i.e., \( 300 \text{ K} \leq T \leq 340 \text{ K} \), for \( C_6H_{14} \) but systematically deteriorate with increasing temperature. The Smith model gives the best
predictions for compound C$_6$H$_{14}$, but the results corresponding to C$_{10}$H$_{22}$ are limited to two temperature values, which are in similar agreement to the ones given in this work. Comparisons at temperatures higher than 400 K are not shown because of the limited high-temperature data included in Ref. 33.

Table 3: Tabulation of surface-tension values for compounds C$_6$H$_{14}$ and C$_{10}$H$_{22}$ as given by the UA model in this work and those given by the NERD,$^3$ TraPPE,$^{29}$ OPLS,$^{31}$ and Smith$^{32}$ models from Refs. 30 and 33. The columns titled “% diff.” refer to the differences between model predictions and experimental data.$^{18}$

A similar assessment for the performance of the UA model of this work in predicting surface tension of perfluoroalkanes is also included.
| T (K) | OPLS-F | % diff. | EXP6 | % diff. | This work | % diff. | Exp. |
|------|--------|---------|------|---------|-----------|---------|-----|
| 300  | 11.07  | -0.6    | 11.52| 3.4     | 11.29     | 1.4     | 11.14|
| 320  | 9.24   | na      | 9.91 | na      | 9.50      | na      | na  |
| 340  | 7.17   | na      | 8.23 | na      | 7.32      | na      | na  |
| 360  | na     | na      | na   | na      | 6.43      | na      | na  |
| 380  | na     | na      | na   | na      | 4.66      | na      | na  |
| 300  | 12.29  | -0.2    | 12.67| 2.9     | 12.35     | 0.2     | 12.32|
| 320  | 10.52  | na      | 10.94| na      | 11.32     | na      | na  |
| 340  | 8.86   | na      | 9.37 | na      | 9.53      | na      | na  |
| 360  | na     | na      | na   | na      | 8.24      | na      | na  |
| 380  | na     | na      | na   | na      | 6.43      | na      | na  |
| 400  | na     | na      | na   | na      | 5.10      | na      | na  |
| 300  | 13.58  | 1.8     | 14.09| 5.6     | 13.63     | 2.2     | 13.34|
| 320  | 11.68  | 5.3     | 12.32| 11.0    | 12.21     | 10.0    | 11.10|
| 340  | 10.26  | na      | 10.47| na      | 10.47     | na      | na  |
| 360  | na     | na      | na   | na      | 9.44      | na      | na  |
| 380  | na     | na      | na   | na      | 7.57      | na      | na  |
| 400  | na     | na      | na   | na      | 6.14      | na      | na  |
| 420  | na     | na      | na   | na      | 4.97      | na      | na  |
| 300  | 14.32  | 2.7     | 14.53| 4.3     | 14.49     | 4.0     | 13.94|
| 320  | 12.54  | 2.5     | 12.93| 5.7     | 13.17     | 7.7     | 12.23|
| 340  | 10.81  | na      | 10.47| na      | 10.47     | na      | na  |
| 360  | na     | na      | na   | na      | 9.95      | na      | na  |
| 380  | na     | na      | na   | na      | 8.56      | na      | na  |
| 400  | na     | na      | na   | na      | 7.29      | na      | na  |
| 420  | na     | na      | na   | na      | 6.03      | na      | na  |
| 440  | na     | na      | na   | na      | 5.04      | na      | na  |
| 300  | 16.40  | na      | 16.52| na      | 14.89     | na      | na  |
| 320  | 14.52  | na      | 14.74| na      | 13.95     | na      | na  |
| 340  | 12.21  | na      | 12.58| na      | 12.58     | na      | na  |
| 360  | na     | na      | na   | na      | 10.64     | na      | na  |
| 380  | na     | na      | na   | na      | 9.54      | na      | na  |
| 400  | na     | na      | na   | na      | 8.41      | 6.5     | 7.90 |
| 420  | na     | na      | na   | na      | 7.07      | na      | na  |
| 440  | na     | na      | na   | na      | 5.88      | na      | na  |
| 460  | na     | na      | na   | na      | 4.43      | na      | na  |
| 480  | na     | na      | na   | na      | 3.85      | na      | na  |
| 500  | na     | na      | na   | na      | 3.28      | na      | na  |
Table 4: Predicted surface-tension values for C_{n}F_{2n+2} as given by this work and by the OPLS-F\textsuperscript{34} and EXP6\textsuperscript{35,36} models in Ref. 37 along with the corresponding \% differences from the limited experimental data points.\textsuperscript{23-28}

The comparisons are based on the work of Tsige et al,\textsuperscript{37} where results generated with two AA models, i.e., OPLS\textsuperscript{34} and EXP6,\textsuperscript{35-36} are given. The OPLS model used by Tsige et al will be referred to as the OPLS-F from here on to avoid confusion with the OPLS parameterization of Ref. 31. The key findings are shown in Table 6 using the same conventions as in Table 5 but including all C_{n}F_{2n+2} compounds in this study, i.e., carbon numbers, n, between 6 and 12. In order to make direct comparisons with the data given by Tsige et al for compounds with carbon number between 7 and 10, additional surface-tension values were generated between 300 K and the minimum temperature values for each compound as given in the L-V equilibrium calculations. The experimental data points for compounds with carbon number between 6 and 9 given in that work\textsuperscript{37} were from Ref. 27; the single data point of C_{10}F_{22} was taken from Ref. 23; and the data for C_{12}F_{26} was taken from Ref. 28. The data points from Refs. 27 and 28 were interpolated to obtain values at the temperature increments chosen for this work. The overall agreement with the available experimental data is remarkably good, with errors ranging between 0.2\% and 10\%. Furthermore, the overall performance of the UA model is better than the EXP6 AA models and quite similar to that of the OPLS-F model. Again, this is a remarkable result given the superior computational appeal offered by the simple UA model presented in this work over either of the AA models in Ref. 37. It is worth noting that the most pronounced discrepancy between the predicted surface-tension values in the
three models was found for perfluorodecane (C_{10}F_{22}) at 300 K. However, according to some references, the data point at 300 K falls below the experimental melting temperature of this compound, which may account for the discrepancy.

CONCLUSIONS

A rigorous molecular dynamics study was presented to assess the performance of a UA model in the prediction of liquid-vapor interfacial properties for short-chain n-alkanes and perfluoroalkanes, i.e., compounds with carbon numbers between 6 and 12, at orthobaric conditions. The decision to include L-V data was made to produce a set of self-contained data covering a wide temperature range all the way up to the critical temperature, $T_c$, where the predictions of the model could be checked at this limiting case. The model reproduced properties for L-V equilibrium in excellent agreement with experimental data and was able to describe properly the temperature dependence of the L-V surface tension for both types of compounds. In particular, it was found that the predicted surface-tension values for alkanes in the low-temperature region were slightly overestimated, but improved with increasing temperature and approached the experimental values at temperatures near the critical point, $T_c$. A similar comparison for the perfluorinated compounds was found to be in excellent agreement with experimental data in the low-temperature region, where experimental data is available; based on the better performance for n-alkanes with increasing temperature, we infer that the simulation results for perfluoroalkanes are at least as good at higher temperatures, where the experimental data is lacking. The high-temperature predictions of surface tension of both
compounds were facilitated by C-H fits, which avoids errors in the predicted surface-tension values that could arise from the use of other mathematically suitable but otherwise arbitrary functions.

Furthermore, the surface-tension predictions for compounds C₆H₁₄ and C₁₀H₂₂ given by the UA model of this work were found to be similar or better than those obtained using AA and other UA models, both of which relied on the computationally demanding Ewald sums. In addition, comparisons for the surface-tension predictions of perfluoroalkanes against two AA models were surprisingly close and, in general, were more accurate than those observed with the alkanes; unfortunately, these comparisons were hindered by the current dearth of experimental data.

Overall, it was demonstrated that the simple UA model of Escobedo and Chen performs remarkably well in describing the surface-tension behavior of short chain perfluoroalkanes and their alkane counterparts with respect to experimental data and with respect to other models, including the ones based on the AA method. Given the computational economy and inherent simplicity of the UA model, this is a significant result and demonstrates the versatility and viability of the UA method to predict L-V properties.
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14. Supplemental Material can be found at [web address] for a more detailed description of (i) the procedure used to calculate the tail corrections to the surface
tension; (ii) two tables with the liquid densities, $\rho_L$, critical temperatures, $T_c$, critical densities, $\rho_c$, and normal boiling temperatures, $T_b$, of alkanes and perfluoroalkanes and their corresponding comparisons against available experimental data; and (iii) a set of three figures illustrating trends in the L-V surface-tension behavior of the entire set of compounds addressed in this work, i.e., $n$-C$_n$H$_{2n+2}$ and C$_n$F$_{2n+2}$ with n between 6 and 12.

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