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Structural and thermodynamic behavior of alkane chains at the liquid/vapor interface

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Computer simulations for several alkane fluids were carried out to study thermodynamics and structural behavior of the molecules at the liquid-vapor interface. Three different models were used to simulate the fluids, one of them was proposed in this work and we obtained a slightly better agreement than the other models with experimental data. The fluid structure at the interface was analyzed at temperatures close to the melting point using the new model and it was found that molecules at the free surface present more order than those at the bulk liquid phase. By calculating the order of the hydrocarbon chains a strong structure of molecules was observed at the interface than those in bulk, moreover, some of those molecules at the interface were aligned perpendicular to the interface. Previous simulations report stronger structures at the interface by the formation of a monolayer of alkane chains, however, those simulations started at very low temperatures and they did not reproduce thermodynamic properties such as the interfacial tension correctly. The model proposed in the present work not only presents good agreement with surface tension data but also shows evidence that the fluid structured as experiments indicated at temperatures close to the melting temperature.
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I. INTRODUCTION

Studies of fluids at interfaces have been investigated for a long time not only for their scientific interest but also for their many industrial applications. For instance, the knowledge of interfacial properties of simple and complex fluids will help us to better understand areas such as lubrication, wetting, adsorption, coating, etc.

Although people have studied fluids at different interfaces, special attention has been dedicated to the liquid-vapor interface where several experiments,[1,2] theory,[3–5] and computational works have been carried out.[6,7] Moreover, many of those studies have been conducted on hydrocarbon fluids.

In particular, alkane systems are important in many practical applications of chemical and oil industry and nowadays it is possible to find a large number of articles dedicated to study their structural, physical, and chemical properties.[8,9] In particular liquid-vapor phase diagrams of alkanes have been constructed and, also, thermodynamic and structural properties have been studied.[10,11] The frozen layer found in experiments at the liquid-vapor interface at temperatures some degrees above the melting point[2,12–14] from some of those studies is found to be interesting.

On the other hand, from a theoretical point of view, people have used equations of states, such as the statistical associating fluid theory (SAFT), to investigate the behavior of those fluids where good results have been found when they are compared with experiments.[15–17]

However, for the last years an alternative tool, computer simulations, to study such complex systems at interfaces has been used with good results. In particular, this technique can help us to obtain more information from a molecular point of view which sometimes might be difficult to obtain from actual experiments. Although different simulation methods have been used, probably the most popular technique to investigate interfacial properties has been Molecular Dynamics (MD). For instance, using MD, not only have the phase diagrams of alkanes of different chain lengths been constructed[18] but also thermodynamic properties such as surface tension. Here, two main routes have been used to calculate the surface tension: the thermodynamic[7,19,20] and the mechanical approaches.[8,10,21]

It is worthy to mention that the agreement between the computer simulations and the experiments strongly depends on the force field employed in the simulations, i.e., the potentials and the parameters used for the intra and the inter molecular interactions. Therefore, several force fields have been proposed in the literature.[18,22–26]

As stated before, some experiments for long alkane molecules (from 14 to 50 CH_n groups)[2] have observed the presence of a frozen layer of alkane molecules at the liquid-vapor interface at few degrees above the melting temperature. Therefore, in order to observe the formation of that layer from a molecular scale some computer simulations have been carried out. For instance, several years ago Yamomoto *et al*. carried out simulations for an alkane model and they were able to observe a layer formed at the interface.[27,28] On the other hand, Smith *et al*. conducted simulations of the heptadecane system and they observed a monolayer developed at the liquid-vapor interface with a crystalline structure.[29] However, those

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TABLE I. Parameters of the force fields used in this work.

Nonbonded interactions $V_{ij}(r_{ij}) = 4\varepsilon_{ij}\left(\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{6}\right)$			
Pseudo-atom type		σ (nm)	ε (kJmol^{-1})
This work	CH_3	Same as Trappe	
	CH_2		
Trappe[a]	CH_3	0.375	0.81481728
	CH_2	0.395	0.38246525
NERD[b]	CH_3	0.391	0.86470406
	CH_2	0.393	0.38080236
Smith *et al.*[29,c]	CH_3	0.390	0.732
	CH_2	0.390	0.493
Combination rules		$\sigma_{ij} = \frac{\sigma_i+\sigma_j}{2}$	$\varepsilon_{ij} = \sqrt{\varepsilon_i \varepsilon_j}$

Angle bending parameters $V_{angle}(\theta_{ijk}) = \frac{1}{2}k^{\theta}_{ijk}\left(\theta_{ijk} - \theta^0_{ijk}\right)$			
angle		k_0 (kJ mol^{-1}rad^{-2})	θ^0 (deg)
This work	$CH_3CH_2CH_2$	400	111.0
	$CH_2CH_2CH_2$	400	112.0
NERD, Trappe	$CH_xCH_2CH_2$[d]	519.6543	114.0
Smith *et al.*[29]	$CH_xCH_2CH_2$[d]	527	114.0

Torsional parameters $V_{dihedral}(\phi_{ijkl}) = \sum_{n=0}^{5} C_n (\cos(\phi))^n$							
	Dihedral angle	(kJ/mol) C_0	C_1	C_2	C_3	C_4	C_5
Trappe	$CH_xCH_2CH_2CH_2$	8.39736	−16.78632	1.13393	26.31760	0.00000	0.00000
NERD	$CH_xCH_2CH_2CH_2$	7.64906	−14.54141	1.13393	23.32439	0.00000	0.00000
Smith *et al.*[29]	$CH_xCH_2CH_2CH_2$	10.6695	−16.7945	−1.1340	26.3300	0.00000	0.00000

Torsional parameters $V_{dihedral}(\phi_{ijkl}) = k_\phi(1 + \cos(n\phi - \phi_s))$			
Dihedral this work	k_ϕ(kJ mol^{-1})	ϕ_s(deg)	n
All dihedrals	5.000	0–360	3

[a]From Ref. 22.
[b]From Ref. 18.
[c]From Ref. 29.
[d]x denotes both functional groups CH_x, $x = 3, 2$.

simulations started at very low temperatures, below the melting temperature, and none of those studies calculated thermodynamic properties. In fact, we conducted simulations of different alkanes using the same force fields proposed in those works and we found that those models did not reproduce the interfacial tension given by the experiments correctly.

In this paper we present computer simulations of the liquid-vapor interface of alkane molecules of different chains. Although studies for long chains were conducted to compare the structure with previous works, we were interested in smaller alkanes to investigate if similar structural trends about the freezing surface were observed. Moreover, we studied not only structural properties but also the interfacial tension of those systems. Three different force fields were used, two of them already reported in the literature and the other was proposed by our group where we found that it presented good agreement with the experiments.

II. COMPUTATIONAL METHOD AND MODEL

Simulations of different alkanes at the liquid-vapor interface were conducted at different thermodynamic conditions. For alkanes we used three united atom (UA) force fields: NERD, originally reported by de Pablo *et al.*,[18] Trappe by Martin and Siepmann,[22] and a third one proposed in this work constructed with the same Lennard-Jones parameters of the Trappe model but with a different angular and torsional potential (see Table I). We call this model TrM.

The new force field was proposed in order to have a model that better reproduced the structures observed in the experiments, i.e., that molecules close to the melting temperature ordered perpendicular to the surface. Then, the angle potential was chosen to have less rigidity than the Trappe force field, which allowed the molecule to be more extended whereas the torsional potential was chosen to have more trans configuration of the molecules. The form of the torsional potential has been also used in systems of amino acids with good results.[30,31]

The selection of the parameters for the TrM force field was considered after many molecular dynamics calculations on different alkane systems (from butane to decane). Since the model was based on the Trappe model we started these simulations with the equilibrium parameters of the Trappe force field. Then, by changing those values MD simulations were conducted and the results were fitted with liquid-vapour data. Therefore, the potential constants were assigned by the best fitting of our parameters with the experiments. Then, surface tension values were used to refine the final parameters. By this way we obtained agreement between previous models and with experiments, moreover, the proposed model reproduced

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similar, and in some cases better, thermodynamic values than other force fields already reported in the literature. The simulations for some systems are given in Secs. III A and III B and others are reported in the supplementary material.[36] All systems started with 972 molecules in a parallelepiped box using the NPT ensemble at temperatures around the melting point and pressure of P = 1 bar. Since the initial configuration of the molecules started with an ordered structure we ran simulations for 500 ps to melt the systems. Then, the last configurations of those systems were used for the NVT simulations in a rectangular box with two free surfaces at the ends of the box (in the Z direction) to have liquid-vapor interfaces. Therefore, the box cell in the NVT ensemble was different for each alkane simulated, for hexane the simulation box was X = Y = 5.07 nm and Z = 20.27 nm, for octane X = Y = 5.581 nm and Z = 22.325 n, for decane X = Y = 6.01 nm and Z = 24.03 nm, and for heptadecane X = Y = 6.15 nm and Z = 36.92 nm.

Surface tensions were calculated using the mechanical approximation[8,10,32] by calculating the components of the pressure tensor,

$$\gamma = \frac{1}{2}\int_{-\infty}^{\infty}[P_N(z) - P_T(z)]dz = \frac{L}{2}[\langle P_N\rangle - \langle P_T\rangle],$$
$$= \frac{1}{2A}\left\langle \sum_i \sum_{j>i}\left(\frac{x_{ij}^2 + y_{ij}^2}{2r_{ij}} - \frac{z_{ij}^2}{r_{ij}}\right)\frac{du_{ij}}{dr_{ij}}\right\rangle, \quad (1)$$

where $P_N(z)$ and $P_T(z)$ are the normal and tangential components of the pressure tensor, respectively, A is the surface area, L the box length, u_{ij} is the potential of interaction, and the factor of 1/2 comes from the two surfaces. The brackets represent a configurational average.

All molecular dynamics were carried out using GROMACS 4.5.4. simulation package[33] using Berendsen thermostat with a time step of dt = 0.005 ps and with the usual periodic boundary conditions in all three directions. Bond lengths were constrained by a Linear Constraint Solver (LINCS) algorithm and we used a cutoff of 2 nm for the short-range interactions. The cutoff length was almost the maximum value allowed in our simulation box.

Then, simulations for alkanes were carried out for 2 ns for equilibration followed by 4 ns, where the last 2 ns were used for data analysis.

III. RESULTS

A. Phase diagrams and surface tensions

In order to validate and compare our model with previous models reported in the literature we first calculated properties such as liquid-vapor coexistences and surface tensions.

Density profiles were determined by calculating local densities in slabs along the z-axis (slabs parallel to the surface). The slab thickness was obtained by the division of the box length in 200 equal layers,

$$\rho(z) = \frac{N(z)}{Adz}, \quad (2)$$

where A is the superficial area and $N(z)$ is the number of particles in each slab with thickness dz. In each system the thickness was about 1 Å. In order to have mass density Eq. (2) is multiplied by an appropriate factor which includes the Avogadro number and the molecular mass of the specie.

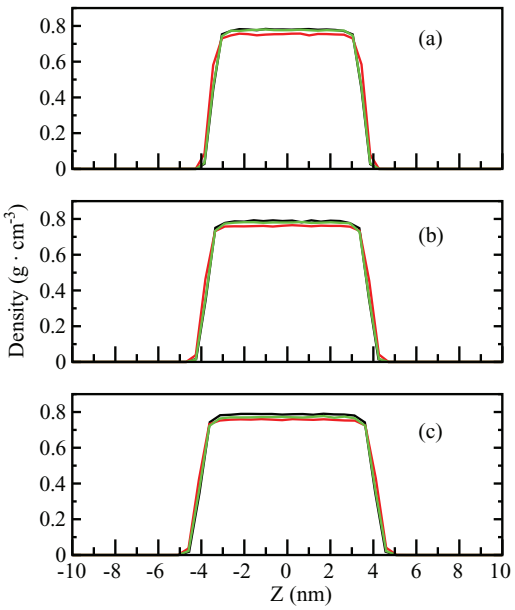

FIG. 1. Atomic density profiles of (a) hexane at T = 180 K, (b) octane at T = 220 K, and (c) decane at T = 260 K. The black lines refer to TrM, the red lines to NERD, and the green lines to Trappe force fields, respectively.

In Figure 1 density profiles for different alkanes at temperatures close to the melting temperature are shown. There, it is possible to observe a well defined liquid and vapor phase along the simulation box. The plots were calculated using an atomistic representation, however, it is also possible to calculate density profiles from the center of mass of the molecules as shown in Figure 2.

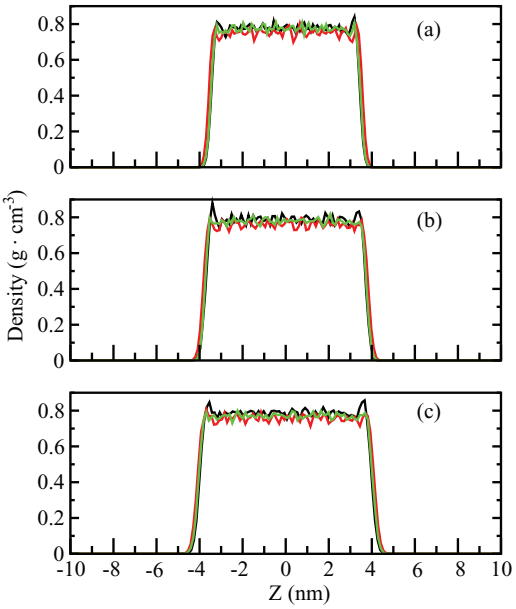

FIG. 2. Density profiles calculated from the center of mass of the molecules. (a) Hexane at T = 180 K, (b) octane at T = 220 K, and (c) decane at T = 260 K. The black lines refer to TrM, the red lines to NERD, and the green lines to Trappe force fields respectively.

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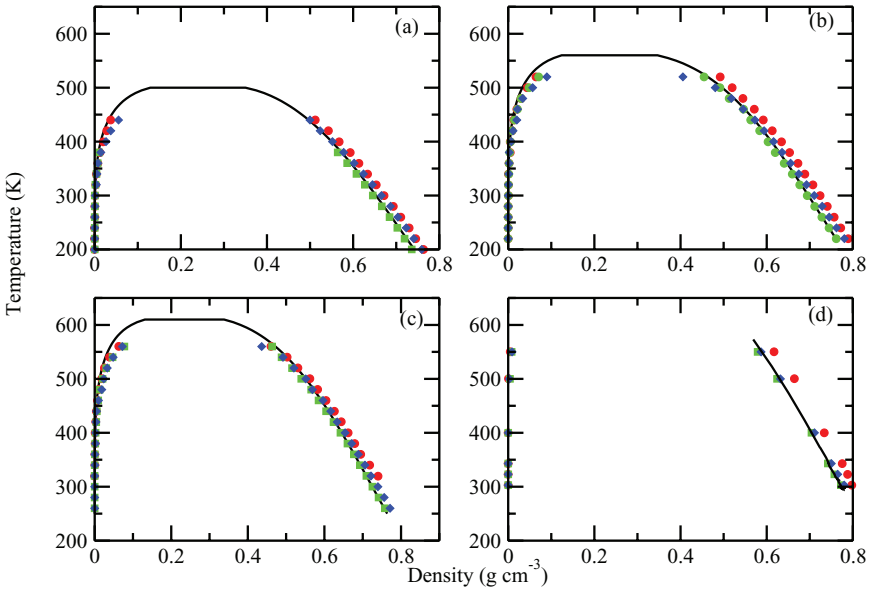

FIG. 3. Liquid-vapor coexistence lines for (a) hexane, (b) octane, (c) decane, and (d) heptadecane. Red circles are for the TrM, green squares are for NERD, and blue diamonds for Trappe force fields, respectively. The black solid line corresponds to the experiments given by the NIST.[34]

In both profiles the bulk vapor and liquid densities were similar to each other, however, interesting from the center of mass profiles were the two small peaks located at the liquid-vapor interface at low temperatures. Somehow, those peaks indicated that the chains were structured in a different way than the chains in the middle of the bulk liquid phase. When the temperature was raised much above the melting point the profiles became smooth and those peaks disappeared. We will discuss more about this issue in Sec. III B.

From the plots of Figure 1 it was possible to construct the liquid-vapor phase diagrams for the different alkanes (hexane, octane, and decane). Therefore, the liquid-vapor coexistences are shown in Figure 3 where we observed similar results to those obtained in previous works[8–11] and with the results given by the NIST.[34] We also calculated few points for the liquid-vapor coexistence of a long alkane such as heptadecane. In this case we observed that the Trappe and the Nerd data agreed slightly better with the experiments given by the NIST.[34]

The melting temperature for hexane, octane, decane, and heptadecane obtained from the NIST are 178 K, 216 K, 243 K, and 295 K, respectively.[34] However, to the best of our knowledge, melting temperatures reported by simulations are not given for all the systems studied in this work. We found data for octane and decane; for octane the melting temperature was found between the interval of 200 K and 210 K whereas for decane between 210 K and 220 K.[35] It is noted that the simulation melting temperatures were lower than those reported by the NIST.

Although all the models gave good values when they were compared with experiments the NERD model presented better agreement for hexane, octane, and decane alkanes. In particular, it was observed that for the octane system (Figure 3(b)) the TrM and Trappe results departed slightly more from the actual liquid line than those of the NERD model. We also did simulations for other alkane systems, from butane to decane, to have the liquid-vapor coexistences. The rest of the alkanes are presented in the supplementary material.[36]

Vapor pressures were also calculated for the different alkanes and in Figure 4 we show the data for hexane, octane, and decane systems where we observed agreement with experimental data given by the NIST. For better visualization the plot is given in a log scale for pressure and an inverse scale for temperature.

Surface tensions were also calculated for the alkane fluids using the three different models, NERD, Trappe, and

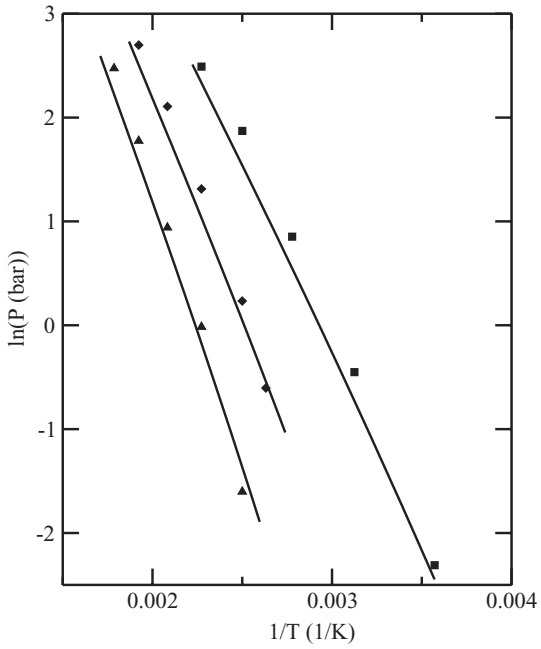

FIG. 4. Vapor pressures for hexane (squares), octane (diamonds), and decane (triangles). The black solid lines correspond to the experiments given by the NIST.[34]

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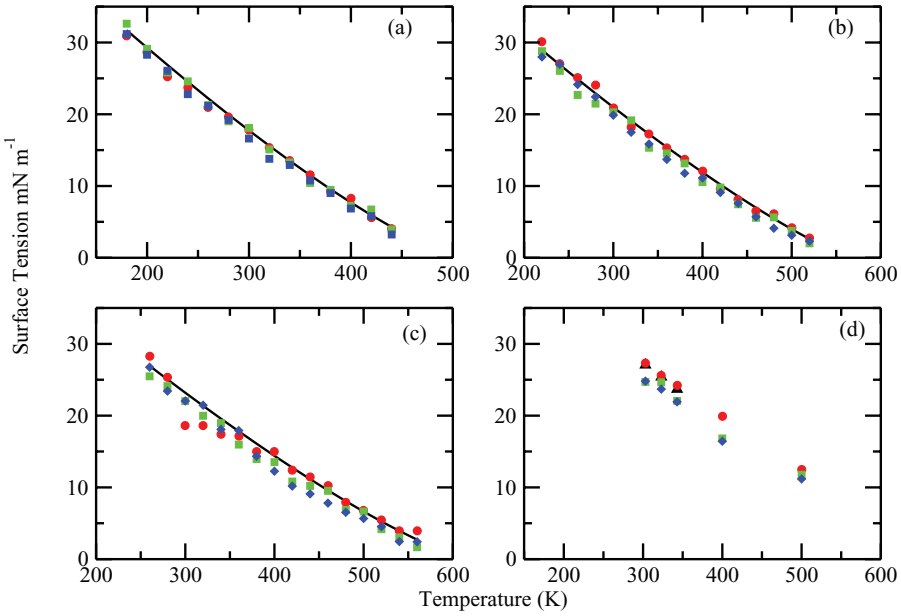

FIG. 5. Surface tension for (a) hexane, (b) octane, (c) decane, and (d) heptadecane. Red circles are for the TrM, green squares are for NERD, and blue diamonds for Trappe force fields, respectively. The black solid line corresponds to the experiments given by the NIST.[34] In (d) the experimental data in black squares (overlapped by the red circles) were taken from Ref. 40.

TrM. The results are given in Figure 5 as a function of the temperature. As a general feature we observed the same tendencies in all cases, however, it was depicted that TrM data presented slightly better agreement with the experimental results (except for few points of decane at low temperatures).

Since the calculations of surface tensions could be sensitive to the cutoff radius,[37–39] in all simulations a large cutoff was used (as indicated in Sec. II). Moreover, long range corrections were included. Therefore, since we had mainly Lennard-Jones interactions it was expected that the surface tension should be essentially independent of the cutoff radius.[8,11,37–39]

In Sec. III B, we show that the model not only gives us correct thermodynamics but also it can help us to better understand the structure of the molecules at the interface.

B. Structure of the molecules

As it was indicated previously the density profiles of Figure 2 present two peaks at the liquid-vapor interface. In fact, the peaks were more evident at low temperatures. Although those peaks were observed in all the models, in particular the peaks were higher for the TrM model than for the NERD and Trappe models. Since those profiles were constructed using the center of mass of the molecules the results suggested that more molecules were distributed near the interface than in the bulk liquid phase. As the temperature increased those peaks decreased until they vanished at high temperatures (not shown here).

In order to have more information about the the structure of those molecules at the interface we analyzed them in terms of an order parameter relative to the z-axis. Since in the simulations we used united atoms, the order parameter was calculated using the formula

$$S_{zz} = \frac{1}{2}\langle 3\cos^2\theta - 1\rangle, \tag{3}$$

where θ is the angle between the vector normal to the interface and the vectors which joined nearest neighbour atoms along the chain.[29] Therefore, the parameter S_{zz} gave us more information about complete order parallel to the interface ($S_{zz} = -0.5$) or complete order normal to the interface ($S_{zz} = 1.0$).

As stated before few experiments on long alkane chains, such as heptadecane, have shown a frozen layer at the surface at temperatures close to the melting point. Therefore, some people have conducted computer simulations to study the phenomenon. For instance, previous simulations of Smith *et al.*, for a longer alkane chain (heptadecane) observed a strong positive peak, close to unity, in the order parameter.[29] Those simulations indicated that there was a well developed layer of alkane molecules at the liquid-vapor interface. Moreover, those molecules were located perpendicular to the interface, mostly in all trans conformation, with a hexagonal structure. However, those simulations were conducted at temperatures well below the melting temperature (about 20 K lower than the melting point).

We carried out our own simulations with the same force field used by Smith *et al.*[29] for the same system, heptadecane, at temperatures above the melting point and we did not observe any formation of a molecular layer until the temperature was dropped below the melting temperature. Then, we observed that the S_{zz} order parameter took a value close to unity (Figure 6). We also noted the hexagonal structure in the monolayer with the alkane molecules located perpendicular to the interface as experiments and previous simulations observed (bottom of Figure 7). The hexagonal array was determined by calculating the two dimensional pair correlation

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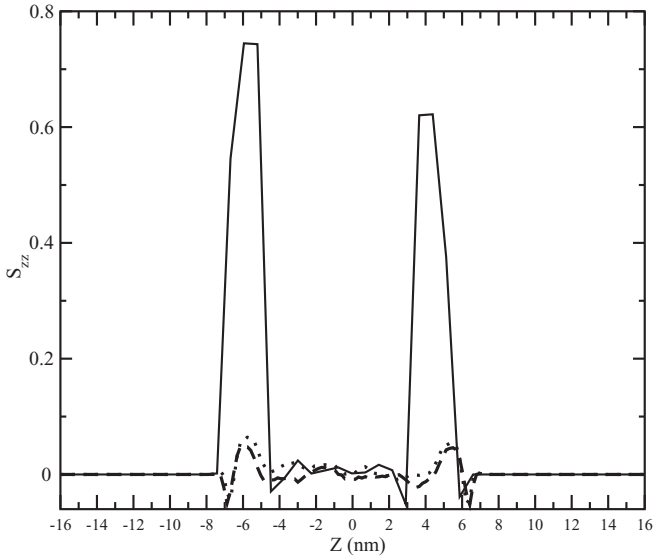

FIG. 6. S_{zz} order parameter for heptadecane with the force field used by Smith *et al.*[29] Solid line for the system at T = 255 K, dotted line at T = 290 K, and dashed line at T = 300 K. The melting temperature for the system is T = 295 K given by the NIST.

function (g(r)) of the center of mass of the molecules at the interface (not shown here). In addition we calculated the surface tension using the Smith *et al.*[29] force field and we found that this model gave numbers above, up to 25% or more, of the experimental values (see Table II), i.e., the agreement with the experiments was not good. Therefore, this model failed to reproduce the surface tension correctly although it

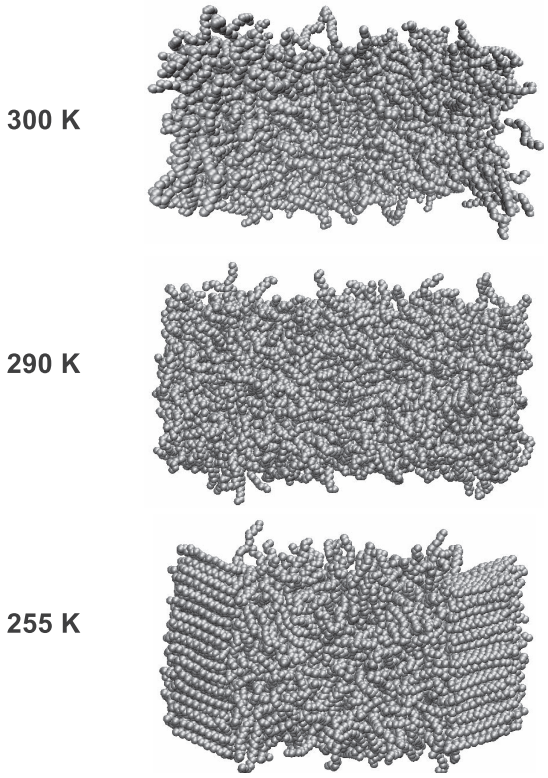

FIG. 7. Snapshots for heptadecane fluid at different temperatures with the force field used by Smith *et al.*[29]

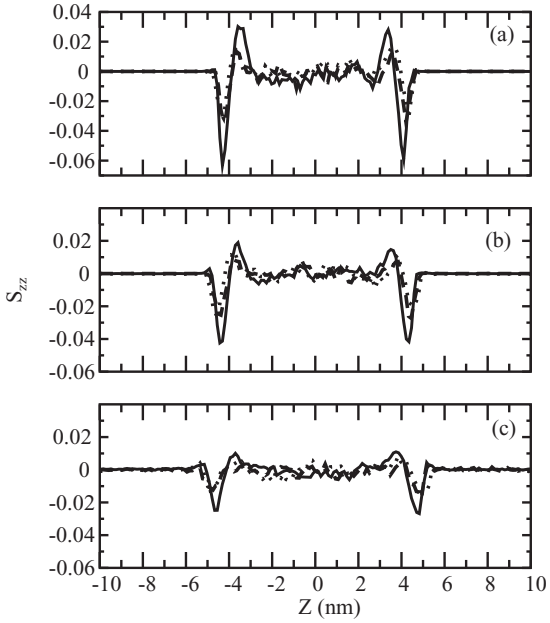

FIG. 8. S_{zz} order parameter for decane at (a) T = 260 K, (b) 300 K, and (c) T = 360 K. The solid lines refer to TrM, the dotted lines to NERD, and the dashed lines to Trappe force fields, respectively.

produced a stronger structure at the interface than the other models.

We also did simulations for a shorter chain (decane) with the same Smith *et al.*[29] force field, however, we did not observe any monolayer of molecules even at low temperatures. These results suggested that only for long chains the formation of strong structures was obtained with this force field.

Then, we conducted simulations with the force field proposed in this work. For a long chain, heptadecane, similar features were observed as in Figure 7, however, we dropped the temperature at T = 200 K to observe the formation of layers at the interface. On the other hand, for short chains (hexane, octane, and decane) different features were depicted. Since similar tendencies were observed for the short alkanes we present only explicit results for the decane system as the representative fluid. In Figure 8 the order parameter S_{zz} of the decane system for the three different models and for different temperatures is shown. As a first interesting issue we observed two peaks at the liquid-vapor interface of the order parameter. Although those peaks had small values they were evident at low temperatures. As the temperature increased those peaks became smaller (Figure 8(c)), until, at high temperatures, they vanished. In the bulk liquid phase, the order parameter ($S_{zz} \approx 0.0$) indicated that the molecules were uniformly distributed, as we expected.

By observing in more detail the order parameter S_{zz}, in Figure 8 we depicted negative and positive peaks close to the liquid-vapor interface. Those peaks were observed in all the models, however, the peaks for the Trappe and the NERD force fields were similar to each other whereas for the TrM the peaks were higher.

The presence of those peaks suggested that molecules at the interface were more ordered than those molecules in the centre of the liquid phase. The negative peak seemed to

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TABLE II. Comparison for surface tension values (mN/m) for hexane, decane, and heptadecane of this work and those reported in literature.[10]

T(K)	TrM[a]	Trappe[a]	NERD[a]	Trappe[b]	NERD[b]	Smith *et al.*[29,a]	Exp.[c]
				Hexane			
300	17.8	16.6	18.1	18.9	19.8		17.8
320	15.3	13.7	15.1	17.0	17.9		15.6
340	13.5	12.9	13.3	15.0	15.8		13.5
360	11.5	10.8	10.4	12.8	13.6		11.5
380	9.2	9.1	9.4	10.7	11.4		9.6
400	8.2	6.8	7.2	8.5	9.2		7.7
420	5.6	5.8	6.7	6.4	7.0		5.9
				Decane			
260	27.0	26.7	25.4			33.3	26.9
280	24.8	23.4	24.1			31.2	25.0
300	24.5	22.0	22.0			29.7	23.2
320	21.4	21.4	20.0			27.1	21.3
380	15.0	14.3	13.9	17.9	18.3		16.1
400	14.8	12.2	13.5	16.3	16.5		14.4
420	12.4	10.2	10.8	14.7	14.7		12.8
440	11.4	9.1	10.2	13.0	12.8		11.2
460	10.2	7.8	9.5	11.2	10.9		9.6
480	7.9	6.5	6.8	9.4	9.0		8.1
500	6.7	5.6	6.6	7.4	7.0		6.6
				Heptadecane			
303	27.31	24.80	24.70				27.06[40]
323	25.58	23.69	24.65				25.38
343	24.24	21.92	22.05				23.68

[a]From this work.
[b]From Ref. 10.
[c]From Ref. 34.

be produced by the molecules in the gas phase at the interface where some CH_n groups of the molecules preferred to be parallel to the surface. However, since there are just few molecules in the gas phase this peak might not be representative to give us good information about the surface structure. On the other hand, the next positive peak indicated that there were CH_n sites which preferred to be perpendicular to the interface. In fact, the positive peak was located in the same position where the peaks of the center of mass density profile were observed, i.e., in the inner liquid phase (see Figure 9). These

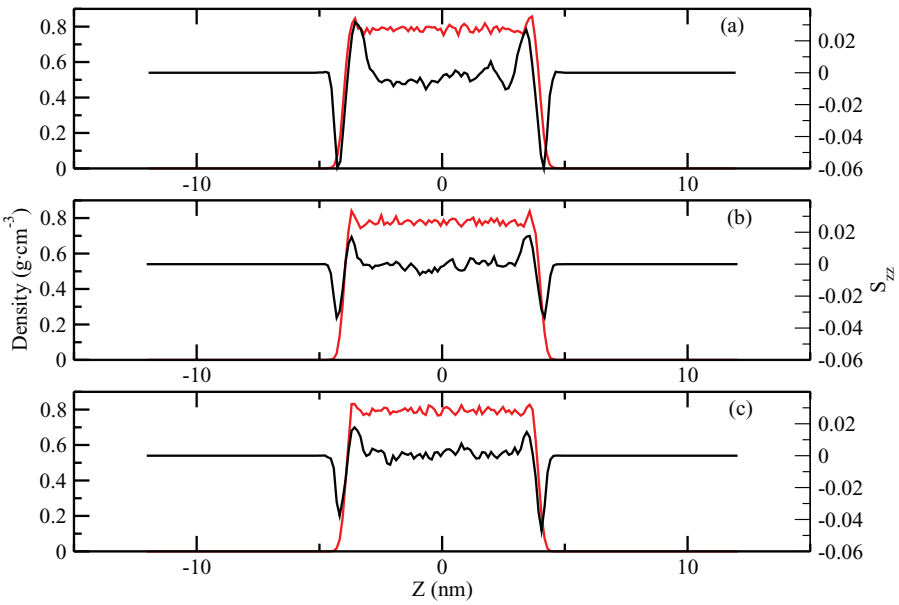

FIG. 9. S_{zz} Density profile (red lines) calculated from the center of mass of the decane molecules (left scale) and S_{zz} order parameter (right scale) for the decane system at temperature (a) T = 260 K with TrM force field, (b) T = 233 K with NERD force field, and (c) T = 233 K with Trappe force field (black lines).

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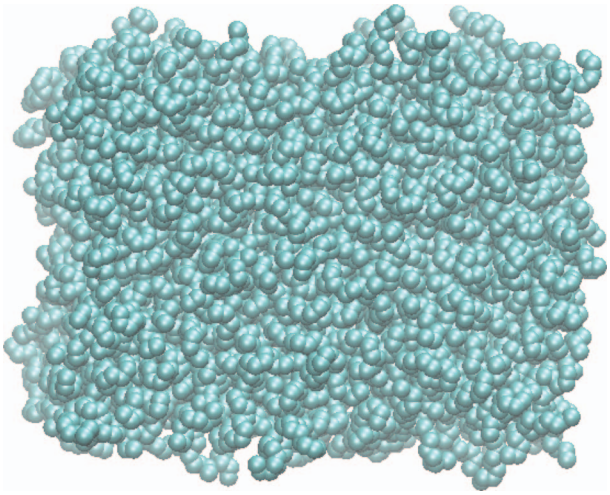

FIG. 10. Snapshot for decane at T = 238 K.

results could explain the experimental observations that the molecules presented an order perpendicular to the surface at temperatures close to the melting point.

Despite all the simulations we did not depict the same features to those found with Smith *et al.*[29] force field for any of the short alkane chains studied in this work. Although we observed slightly more ordered molecules close to the interface than those in the middle (in the liquid phase) they did not present much high order. We even did simulations at very low temperatures, however, the results in the order parameter did not change significantly by using NERD, Trappe, and TrM force fields and we did not observe any formation of a monolayer at the interface (Figure 10). Moreover, we simulated the system up to 20 ns to see if the layer was formed at long times, however, the results remained the same, i.e., we still observed similar order to that shown in Figure 8.

IV. CONCLUSIONS

In the present paper we carried out computer simulations of alkane chains to study the structure of those fluids at the liquid-vapor interface.

Nowadays, there are well established computational models of alkane molecules such as NERD and Trappe which were constructed to reproduce thermodynamic data (e.g., liquid-vapor densities and surface tensions) with experiments correctly. However, it was not clear if those models would have given us more information about the structure or array of alkanes at interfaces. Therefore, in order to better investigate the structure of those molecules at the liquid-vapor interface without spoiling the thermodynamics we proposed a model that we call TrM which was constructed from the Trappe force field by modification of the angular and the torsional potentials. Although it was not the main purpose to construct the TrM model to improve thermodynamics we observed that we obtained a slightly better agreement in the surface tension with experiments than the NERD and Trappe force fields. In the case of liquid-vapor densities the results were similar among all the models.

In general all the models present more order at the interface as indicated by the peaks of the S_{zz} order parameter (Figure 8), however, with the NERD and Trappe models the order was less pronounced than with the TrM force field. Moreover, we observed that alkane molecules were more structured at the interface than in the bulk region.

It was observed a slightly more concentration of chains close to the interface, as the density profiles of the center of mass (Figure 2) shown, than at the bulk phase. Moreover, those molecules present more order, as the S_{zz} order parameter indicated, at temperatures close to the melting temperature. In fact, in our simulations the order parameter showed that molecules in the interface arrayed with some CH_n groups perpendicular to that interface.

The order parameter, for short chains, was not as high as shown by previous authors in long chains, where they observed that the molecules aligned in all trans conformation and with a hexagonal array at the interface.[27–29] However, those computational models basically captured the monolayer for a long chain and at temperatures quite below the melting temperature whereas the experiments report that structure for temperatures few degrees above the melting temperature.

The TrM model proposed showed more structure at the interface and more order of the molecules at the liquid-vapor interface at temperatures close to the melting point. For a long chain the TrM model formed a strong layer at the interface at temperatures quite below the melting point as the Smith *et al.*[29] model. Moreover, the TrM model reproduced the surface tensions correctly whereas the Smith *et al.*[29] model did not. In the Trappe and NERD models that structure was not observed. For short alkanes even when the order was weak it indicated that molecules ordered perpendicular to the surface next to the liquid phase. As the temperature increased, above the melting temperature, the structure disappeared. Moreover, the model also captured thermodynamics properties such as the surface tension for those short chains quite well.

Since surface freezing is a very low process, it is possible that we did not observe the strong structure as previous works because the time was not long enough, however, in our case the systems were simulated for several nanoseconds and for that time the results did not change significantly. We also increased the cutoff, however, we still observed the same trends (the thermodynamics properties only changed less than 2%). On the other hand, we recalled that the simulation models used in the present paper were adjusted by fitting liquid-vapor data, therefore it was not expected that they work properly at low temperatures or even below the melting point and it might be also the reason that we did not observe crystallization of the systems. However, it was observed that as the temperature reduced the molecules reduced their movements as it was indicated by the mean square root displacement calculations (not shown here).

Finally, we believe that the proposed model in this work helped us to have more insight about the structure of the alkane systems at the liquid-vapor interface and at the same time it kept good agreement with the thermodynamic data.

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