

Structure of perfluoroalkane fluids at the liquid-vapor interface: a molecular dynamics study

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Structure of perfluoroalkane fluids at the liquid-vapor interface was studied by molecular dynamics simulations at different temperatures. It was observed that fluids formed a freezing layer at the liquid-vapor interface with a strong structure which it was more pronounced at low temperatures, close to the melting point. Whereas molecules did not have any preference orientation in the bulk fluid they developed a monolayer of molecules aligned perpendicular at the interface. Similar results have been observed for alkanes fluids in the same interface, however, the structure of those molecules is weaker than that reported for perfluoroalkanes. As the temperature increased the layer melted until it vanished. Finally, thermodynamic studies were also conducted in terms of surface tensions and good agreement with experimental data was found.

Keywords: Structure; freezing layer; surface tension; computer simulation.

Se estudia la estructura de los fluidos perfluoroalcanos en la interfase líquido-vapor mediante simulaciones por computadora. Se observó que los fluidos forman una monocapa congelada en la interfase a temperature bajas, cercanas al punto de congelamiento. Las moléculas que se encuentran en la interface se orientan perpendicularmente a la superficie mientras que las moléculas en el centro no lo hacen. Este fenómeno se ha observado en fluidos tipo alcanos, sin embargo, el orden que tienen esas moléculas es menor a la que presentan los perfluoroalcanos. Cuando la temperatura se aumenta la estructura de la capa desaparece. Finalmente, se realizan calculos de propiedades termodinámicas, como la tensión superficial obteniéndose un buen acuerdo con datos experimentales.

Descriptores: Estructura; capa congelada; tensión superficial; simulaciones por computadora.

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1. Introduction

Fluids at interfaces have been study for long time not only for their importance in scientific areas, such as lubrication, adsorption, coating, etc., but also for their several industrial applications. In particular, among the different interfaces, special attention has been considered for the liquid-vapor interface where extensive experiments [1, 2], theory [3–5] and computer simulations [6–8] have been carried out. Of special attention has been the study of the structure that fluids have at the liquid-vapor interface. For instance, some works on alkane fluids have found that hydrocarbon chains present a well ordered freezing layer at the interface close to the melting temperature. The phenomenon has been observed not only in actual experiments [2] but also in computer simulations [8–11], although the freezing layer in the simulations is observed at lower temperatures than those reported in the experiments.

Besides alkanes, other molecules with long chains, such as perfluoroalkanes, have been also matter of several studies since those molecules have a lot technological applications in areas of chemistry, physics, medicine and pharmacy [12–14]. However, to the best of our knowledge a freezing layer, at the liquid-vapor interface, has not been reported or study in perfluoroalkane systems. Therefore, in the present paper we are interested to investigate in more detail the structure of these systems.

Then, we conducted molecular dynamics simulations for different perfluoroalkane molecules at the liquid-vapor interface to study the structure of the molecules. As in a previous paper the structure was characterized with density profiles along the interface and by calculating an order parameter of the molecules [8].

Finally, thermodynamic properties for the fluids were also calculated and surface tension data were obtained and reported in the present paper.

2. Computational method and model

Simulations for several perfluoroalkane systems at the liquid-vapor interface were conducted at different temperatures. The molecules were simulated with an united atom model using the force field given by Escobedo and Chen [15] for the short interactions and for the angle potentials whereas the dihedrals in the molecule were handle with the Ryckaert - Bellemans potential parametrized by Lee et al. [16]. The model consists of rigid bonds and it also considers bond bending potentials for the intramolecular interactions. In fact this model is slightly different of that of alkanes used in a previous work where it uses a bond stretching potential.

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 configuration of those systems were used for the NVT simulations in a rectangular geometry with two free surfaces at the ends of the box (in the z-direction) to have two liquid-vapor interfaces.

All molecular dynamics were carried out using GRO-MACS 4.5.4. simulation package [17] with a time step of $dt = 0.005$ ps. Temperature was controlled with Berendsen thermostat and usual periodic boundary conditions in all three directions were imposed. Bond lengths were constrained by a LINCS algorithm and we used a large cutoff of 2 nm for the short-range interactions. Then, 2 ns of simulations were carried out for equilibration followed by 4 ns and the last 2 ns were used for data analysis.

3. Results

3.1. Structure of the molecules

The first analysis to study the structure of the molecules was carried out in term of density profiles. A typical system is shown in Fig. 1, for the perfluorodecane fluid at $T = 288$ K where the density profile was calculated using the center of mass of the molecules. From Fig. 1 it is possible to observe two peaks located at the liquid-vapor interface. In fact, those peaks indicated that the chains were structured in a different way that in the middle, *i.e.* in the bulk liquid. At low temperatures those peaks became stronger and it was possible to depict the formation of a structured layer of molecules at the interface. Moreover, the molecules in the layer were located perpendicular to the interface, mostly in all trans conformation, as it can be noted in Fig. 2. Figure 2 is a snapshot for the system a temperature of $T = 240$ K. The experimental melting temperature for this system is reported at $T = 399$ [18] however, it was not found any simulation data for the melting temperature of this system.

The structure of the perfluoroalkanes molecules was also characterized by measuring an order parameter relative to the z-axis. For the united atom model the order parameter was calculated with the following formula,

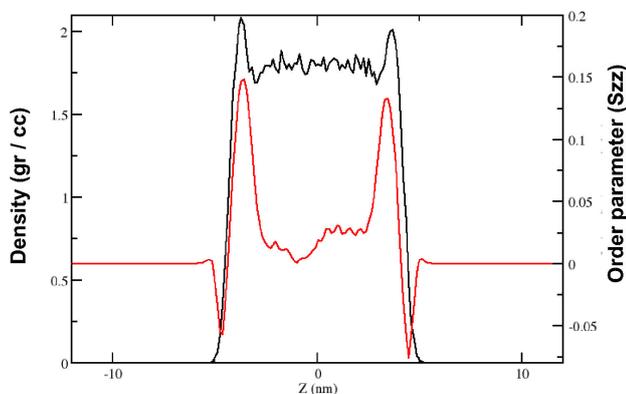


FIGURE 1. Density profile (left scale, black line) and order parameter (right scale, red line) for perfluorodecane at $T = 288$ K.

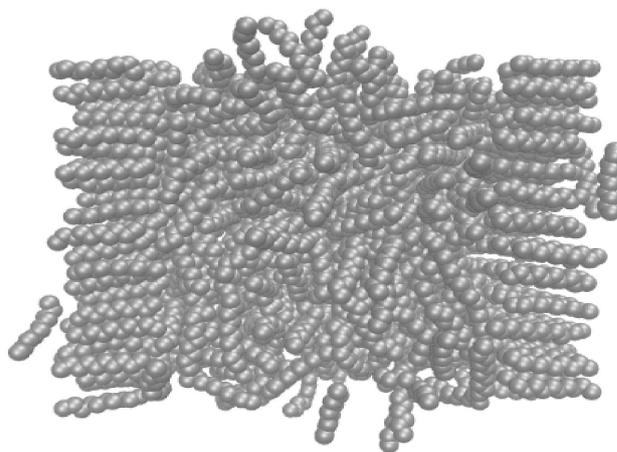


FIGURE 2. Snapshot of the last configuration of the perfluorodecane system at $T = 240$ K.

$$S_{zz} = \frac{1}{2} \langle 3 \cos^2 \theta - 1 \rangle \quad (1)$$

where θ is the angle between the vector normal to the interface and the vectors which joint nearest neighbor atoms along the chain [11]. For $S_{zz} = -0.5$ the molecules present a complete order parallel to the interface and for $S_{zz} = 1.0$ the order is normal to the interface.

The order parameter for the perfluorodecane is also shown in Fig. 1 where it is possible to observe two peaks at the liquid-vapor interface. At low temperature those peaks were stronger and at high temperatures they became smaller. In the middle of the system, in the bulk liquid, the order parameter was $S_{zz} \approx 0.0$ indicating that molecules were uniformly distributed. Similar peaks have been observed previously in alkanes systems, however, the peaks are smaller than those in this work, suggesting that perfluoroalkanes form a stronger structure at the interface [8, 11]. By observing in more detail the order parameter, S_{zz} in Fig. 1, we depicted a negative and a positive peaks close to the liquid-vapor inter-

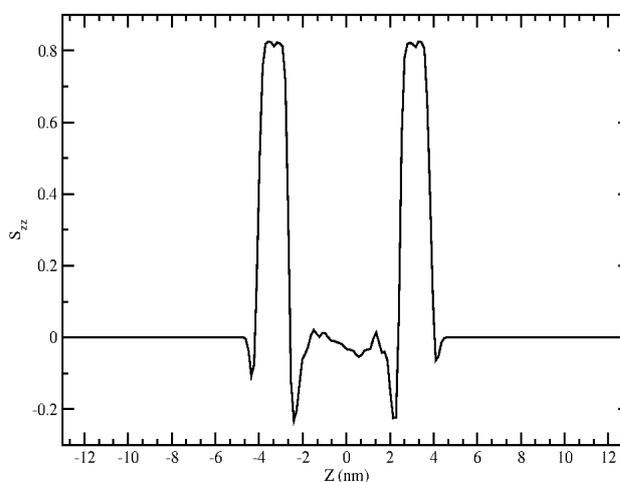


FIGURE 3. Order parameter, S_{zz} , at $T = 240$ K for the perfluorodecane system.

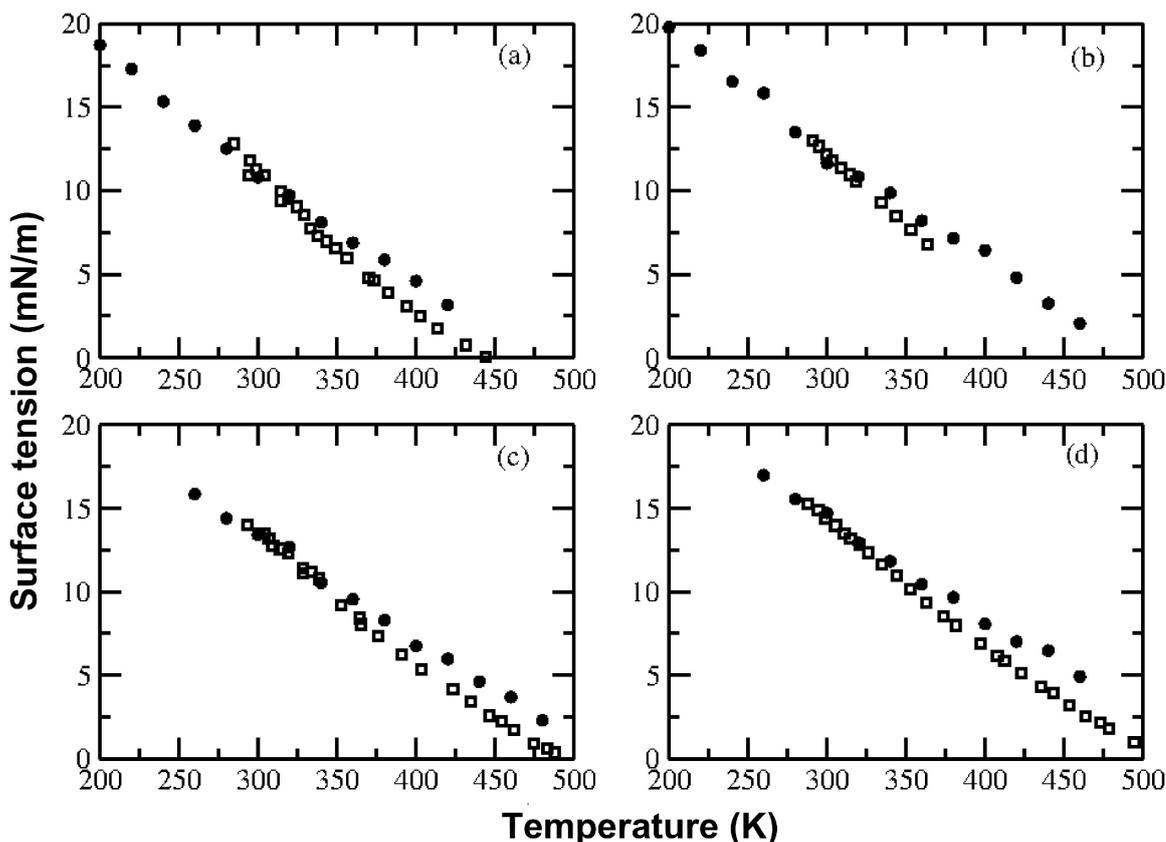


FIGURE 4. Surface tension as a function of the temperature for several perfluoroalkanes. a) perfluorohexane, b) perfluoroheptane, c) perfluorooctane and d) perfluorononane. Solid symbols are simulations of the present work and open symbols are experiments of reference [18].

face as it was observed in alkanes systems [8], however, in this case the peaks were higher than those for alkanes. The negative peaks were formed by the molecules in the gas phase at the interface indicating that some CF_n groups in the chains preferred to be parallel to the surface. On the other hand, the positive peaks indicated that there were CF_n sites which preferred to be perpendicular to the interface. Moreover, the positive peaks were 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 Fig. 1). As the temperature decreased the peaks in the order parameter became more pronounced. In Fig. 3 the S_{zz} order parameter is shown for the perfluorodecane system at low temperature where the peaks reached nearly a value of unity indicating that molecules were almost totally perpendicular at the interface as it can be depicted in Fig. 2. In that figure it was possible to observe the well order of the molecules perpendicular to the interface. It is also possible to depict some molecules in the vapor phase which are parallel to the interface.

Simulations with different perfluoroalkane molecules were conducted with different chain lengths and similar results were obtained in all cases, *i.e.* a monolayer with some CF_n groups perpendicular to the interface. At low temperatures the order perpendicular to the interface is high and at high temperatures the order decreases. However, it was not

observed any particular tendency of the order of the structure with the chain lengths.

3.2. Surface tensions

Studies of surface tensions of these systems were also analyzed. Several simulations were conducted for different perfluoroalkanes and in Fig. 4 we show some representative plots.

Surface tensions were calculated using the mechanical approximation, *i.e.* by calculating the components of the pressure tensor [19–21]

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

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.

In Fig. 4 the surface tension for several perfluoroalkanes are shown at different temperatures. Since surface ten-

sion might be sensitive to the cutoff used in the simulations, calculations were conducted for a large cutoff as indicated in the methodology. As a first issue we observed that in general the surface tensions for perfluoroalkanes were lower than those for alkane fluids [8]. However, as it can be observed the surface tensions had good agreement with the experiments reported by other authors [18]. In fact the surface tension showed nearly a linear dependence with temperature. As a general feature we observed in all the fluids that at low temperatures (lower than 350 K) the agreement with the experiments was good whereas at high temperatures the data slightly deviated from the experiments.

The present results were also compared with other simulations and it was found a difference of about 2% [20,22,23].

4. Conclusions

In the present work we conducted analysis of perfluoroalkane fluids to investigate the structure of the molecules at the liquid-vapor interface. It was observed that molecules formed a monolayer at the interface where some of CF_n groups arrayed perpendicular to the interface. The issue was characterized by two peaks in the order parameter, S_{zz} , and in the density profiles along the axis perpendicular to the interface. The perpendicular array of the chains was strong at low temperatures and when the temperature was increased those peaks disappeared indicating that the monolayer vanished. Since similar behavior have been also observed for alkane molecules the present results suggest that molecules with long chains, somehow, form a freezing layer at the interface. However in the case of pefluoroalkane molecules they present higher perpendicular order at the interface than the alkanes. It is also observed more molecules at the liquid/vapor interfaces of these systems than those observed for alkane systems [8], as the density profiles show. On the other hand, the layer is composed of molecules where most of them array perpendicular to the interface, although there are few molecules in the vapor phase that array parallel. The perpen-

dicular alignment of the molecules can be explained on one hand by the inhomogeneity of the system, since molecules on the surfaces present mainly interactions from the molecules in the bulk. On the other hand, due to the rigidity of the molecules their average length is nearly the same as their trans configuration and they present more freedom to have rotational movements at the surface. At low temperatures the configuration energy is higher and they keep their perpendicular structure, however, at high temperatures the kinetic energy might break the structure on the surface and the perpendicular order in small.

Finally, the force field used in the simulations was also tested to calculate thermodynamic properties, such the surface tension and it was found that data agree good with experiments at low temperatures whereas at high temperatures the agreement was not very good. The deviation at high temperatures might be produced due to the vicinity of the critical point since the large fluctuations that simulations present close to that point due to the finite size of the systems, however, it is also possible that the deviation comes from the electronegativity of the fluorine at high temperatures which is not considered in the force field. On the other hand, it was observed that in general the surface tensions for these systems are lower than those for alkane molecules, however, this issue can be explained by considering that the van der Waals interactions between highly fluorinated molecules are very small compared with the corresponding non-fluorinated molecules. Therefore, the difference between the free energy of fluorinated molecules at the surface and in the bulk should be small making low surface tensions of these molecules compared with the corresponding alkanes.

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