Extended Abstract

Molecular Dynamics Simulations and Simulated Diffraction Spectra of Long Chain Fluorinated and Hydrogenated Substances at the Water-Air Interface

Pedro Lourenço – Instituto Superior Técnico, Lisbon, Portugal

Keywords: x-ray diffraction; fluorinated substances; molecular dynamics simulations; Langmuir monolayers; perfluoroalkylalkanes

Abstract

The dynamic behaviour and structural organization of small domains of fluorinated and hydrogenated molecules at the surface of water were studied by all-atom molecular dynamics simulations (MD) using an AA-OPLS based forcefield. The MD simulations of 1H,1H-Perfluoro-1-tetradecanol (F14OH); 1H,1H,-Perfluoro-1-octadecanol (F18OH); 1-Octadecanol (H18OH); 1-tetradecanol (H14OH) and Perfluoroeicosane (F20) at zero surface pressure and 25ºC show that both hydrogenated and fluorinated molecules spontaneously form isolated domains, with the fluorinated aggregates assembling into highly ordered domains with polygonal periphery, while the hydrogenated monolayers are less ordered and present circular domains; both results confirmed by atomic force microscopy (AFM) measurements of previous works. Furthermore, a new tool which calculates the simulated monolayers diffraction spectra was developed. By direct comparison with the experimental spectra, this tool validates or invalidates the structural organizations seen in the MD simulations. Detailed results of the F14OH, F18OH and F20 unit cells are presented and agree with the experimental ones. The diffraction spectra produced by the hydrogenated compounds is not compatible with the spectra produced from grazing incidence x-ray diffraction (GIXD) experiments. As a smaller work, the diffraction spectra of a previously simulated perfluoroalkylalkane hemimicelle was calculated which produced diffraction peaks in very good agreement with that obtained through GIXD experiments, fully validating the non-periodic structure of the hemimicelles and demonstrating that non-periodic (quasi-crystal) structures produce well defined diffraction peaks.

1. Introduction

Fluorinated surfactants find industrial applications as adjuvant components in fluoropolymer manufacture and processing, aqueous foams for fire extinction, formulations of herbicides, greases and lubricants, paints, polishes and adhesives [1][2]. However, their most exciting applications are in biomedical research and development, for instance, as emulsifiers for blood substitute formulations [3] and inverse emulsions for drug delivery in liquid ventilation context [4] or as components of the walls of microbubbles used for drug delivery and oxygen transport in blood [5]. It is of great importance to develop new models and understand if the current models can provide a good understanding of the unusual properties of these materials. Langmuir monolayers provide an excellent model for the study of molecular ordering and molecular structure in two dimensions. Amphiphilic molecules which contain a hydrophilic 'head' group and a hydrophobic 'tail' such as polyfluorinated alcohols, are insoluble in water and thus, they are known to self-assemble into Langmuir monolayers at the air-water interface[6]. Its polar head group provides the 'anchoring' to the water surface while its apolar tail is protruding into the air. Long linear perfluoroalkanes which have

no amphiphilic character have also been reported to form stable Langmuir monolayers as their bigger van der Waals forces alone are enough to stabilize the monolayer. [7] Linear fluorinated carbon chains are also known to exhibit a helical conformation. The big electrostatic repulsions between its fluorine atoms does not allow for the carbon chain to stay in an all-trans conformation [8], instead, the optimized energy configuration for each C-C-C-C dihedral is with a slight twist angle, giving the carbon chain a helical or cylindrical form, something which is not seen for their hydrogenated analogues. At very high surface pressures these molecules are known assemble into a crystalline structure, typically in a two-dimensional hexagonal arrangement, due to their intrinsic helicity. Experimentally, the crystalline structure of condensed monolayers is studied by grazing incidence x-ray diffraction, where structural information such as; crystalline inter-molecular distance, tilt of molecules and overall organization can be deduced from the measurements. Computer simulations act as a link between microscopic scales and the macroscopic world of the laboratory, showing a new atomic view of the system. The recent work put into the development of hydrogenated and fluorinated forcefields allows for molecular dynamics computer simulations of Langmuir monolayers of fluorinated surfactants and perfluoroalkanes. [9]

Here, we assess through the use of molecular dynamics computer simulations, the molecular structure and general behaviour of fluorinated films at low surface pressure and highlight the key differences between fluorinated and hydrogenated surfactants. We also try to demonstrate the tendency of the molecules to aggregate and in which phase state they aggregate in. This is complemented by developing a diffraction analysis tool for straightforward structural comparisons with the experimental film's diffraction spectra which validates the structures displayed in the simulations. As a miscellaneous work, the diffraction pattern of a previously simulated perfluoralkylalkane hemimicelle was calculated in order to validate the non-periodic quasi-crystalline structural organization.

2. Methods

All simulations were performed using the GROMACS package [10][11]. The data was analysed either through Gromacs' integrated programs or the newly developed structure factor program. The VMD software was used for the visualization of trajectories. The systems studied in this work are modelled using an all-atom force field based on the optimized potentials for liquids simulations (OPLS-AA) [12]. This force-field models each atom as an interaction site and the potential energy is written as the sum of contributions due to bond stretching, bond angle bending, dihedral angle torsion and non-bonded interactions (van der Waals plus electrostatic interactions). For non-bonded interactions of sites in the same molecule, only sites separated by three or more bonds are calculated. The interactions from intra-molecular sites separated by three bonds are multiplied by a 0.5 constant. The non-bonded interaction between sites of different atom types were computed using geometrical rules $\epsilon_{ij} = \sqrt{\epsilon_{ii}\epsilon_{jj}}$ and $\sigma_{ij} = \sqrt{\sigma_{ii}\sigma_{jj}}$. The long chain fluorinated alcohols and perfluoro-n-eicosane were modelled using the parameters for perfluoroalkanes proposed by Watkins (perfluoroalkyl moieties) and Jorgensen (alcohol moieties), [13] while the hydrogenated alcohols were modelled with the L-OPLS force field for alkanes [14], with the -CH_2OH moieties modelled by the OPLS-AA. Water was modelled with the three site spc-e rigid body model. All systems were simulated at 298.15K, using periodic boundary conditions in all directions, under NVT ensemble

conditions and using the Berendsen thermostat with a time constant of 0.5 ps. The equations of motion were solved using the leap-frog algorithm with time-steps of 2 fs. To construct the simulation systems, initial simulation boxes of 10000, 17500 and 40000 water molecules were set. The geometry of the simulation boxes (9.1x9.1x15 nm; 13x13x15 nm and 18.2x18.2x20 respectively) was chosen with a larger z dimension in order to avoid interactions with its periodic image in the z direction and generate a water slab 3.5 nm thick with two liquid-vapour interfaces. These water boxes were simulated for 3 ns in the NVT ensemble. The surfactant and F20 molecules were generated individually, and their energy minimized. Each molecule was then replicated using packmol [15] to assemble the initial starting configurations of 100, 200 or 400 residue molecules aligned in the z direction. Amphiphiles were assembled with the OH groups pointing into the water direction. The water boxes were merged with the vertically aligned molecules and the simulations were started. The very tight initial configuration was used to speed up the equilibration process of the system.

To calculate the diffraction spectra, the atomic coordinates and atom types from the simulations data were used as input for the structure factor equation:

$$I \propto \left| \sum_{Qz=Qzi}^{Qzf} \sum_{Qy=Qyi}^{Qyf} \sum_{Qx=Qxi}^{Qxf} \sum_{n}^{n_{atoms}} N(n) e^{ix_n Q_x} e^{iy_n Q_y} e^{iz_n Q_z} \right|^2$$

where Q_x, Q_y and Q_z represent the coordinates of the scattering vector. In this case, an approximation is made by assuming that all scattering electrons are at the centre of each atom. In-plane scans are produced by iterating the Q_{xy} coordinate ($Q_{xy} = \sqrt{(Q_x)^2 + (Q_x)^2}$) of the scattering vector while the rod scans are produced by iterating the Qz coordinate.

3. Results and Discussion

3.1 Molecular Dynamics Simulations

In order to get microscopic insight into the behaviour and structural organization of F18OH, F14OH, H18OH, and H14OH monolayers, MD simulations were carried out as described in the methods section. Monolayers composed of 100, 200 and 400 surfactant molecules were simulated in order to evaluate the effect of the crystal size on the stability of the monolayer. Overall, the simulations of 100 and 200 molecules presented no major differences when compared to the 400 molecules aggregates. At the start of the simulations, both hydrogenated and fluorinated surfactant molecules spontaneously aggregate into isolated domains, evidently forming a condensed phase. During the next two nanoseconds of simulation, the surfactant molecules structurally re-organize themselves until an equilibrium in the aggregate is reached. Snapshots of the final configuration of the 400 molecules aggregates of F18OH, F14OH, H18OH and H14OH are shown in figure 1. The fluorinated molecules clearly form a highly ordered structure with most molecules standing perpendicular to the surface of water. After starting the simulation, the fluorinated domains quickly take the form of a polygonal shape, with its molecules also packed in what appears to be a two-dimensional hexagonal lattice. The F14OH presents a hexagonal domain shape while the shape of the F18OH domain is more polygonal, however the rigidity and inertia of 400 F18OH molecules explains this behaviour since the simulations with 100 and 200 F18OH molecules exhibited the hexagonal domain shape (figure 2.). Periodically, a very low number of molecules on the outer edge of the domain will spontaneously lie down on the water surface along the rim of the aggregate.

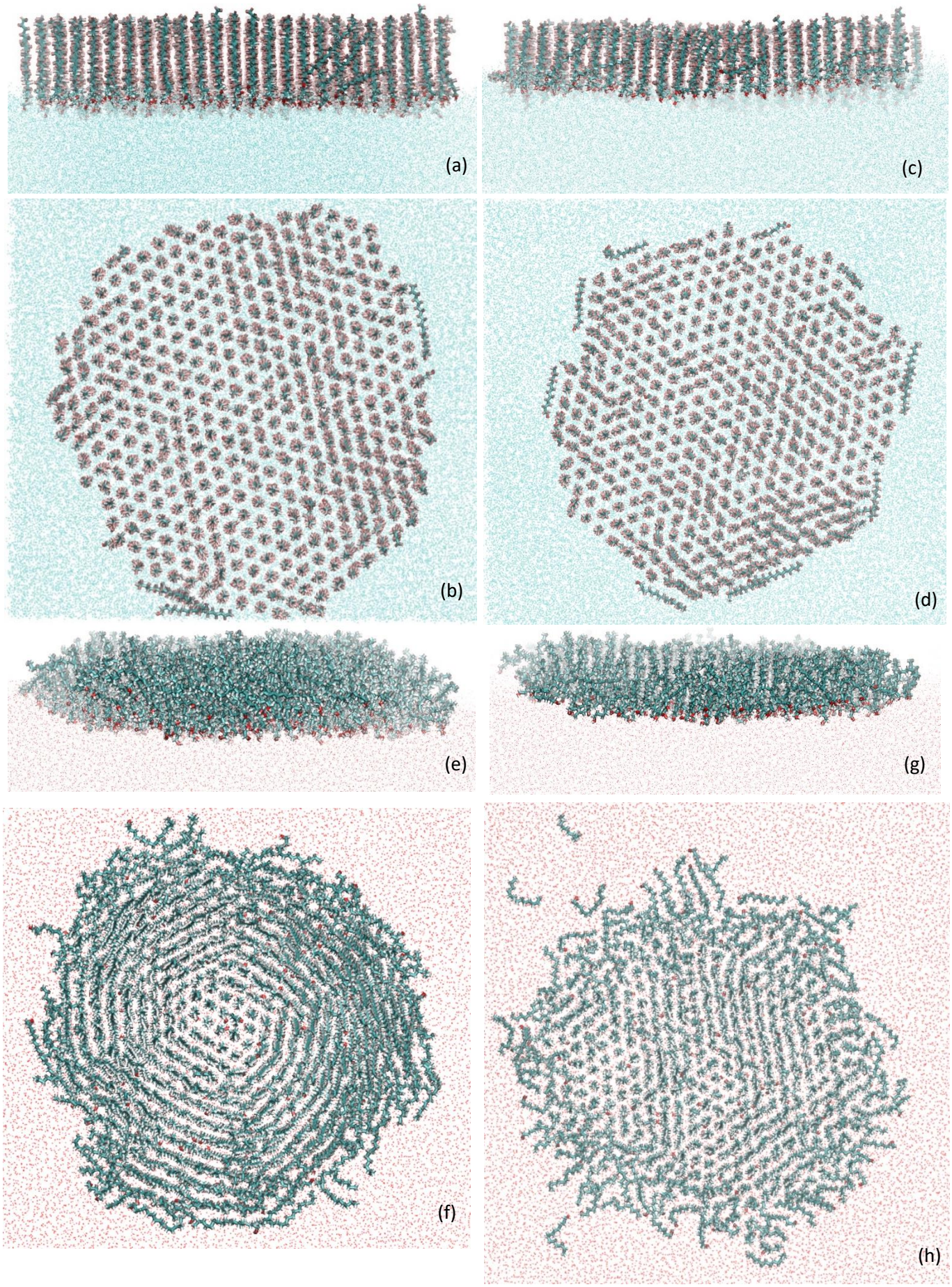

Figure 1 – (a-h) Side and top view of the final configuration of the simulated films. (a-b) F18OH; (c-d) F14OH; (e-f) H18OH; (g-h) H14OH.

This occurs more regularly for the F14OH than for the F18OH which suggests that the longer chain provides more aggregate stability and ordering. The hydrogenated surfactants on the other hand are clearly less organized and present a more amorphous structure. The molecules in the centre of the domain stand vertically and are packed more orderly, however, as one approaches the rim of the aggregate the molecules become progressively more tilted and disordered with the molecules at the periphery of the aggregate lying fully down on the water surface in various orientations giving the hydrogenated aggregates a circular and smoother shape. The H14OH monolayer, appears to be quite unstable, as the molecules on the outer layer seem to be extraordinarily disordered, with some even protruding outwards from the aggregate. Furthermore, during certain irregular and small periods of the simulation, both hydrogenated surfactants have a small number of molecules which can be seen leaving the aggregate and being isolated from the rest of the domain, in a gaseous phase, just for them to return to the aggregate later. This phenomenon occurs more regularly for the H14OH than for the H18OH, presumably due to the weaker attractive inter-molecular forces of the shorter chain alcohol producing a less stable aggregate. These simulation results further confirm the polygonal shape and well-defined and sharp height-profile of the fluorinated surfactants seen experimentally. Although these domains have a much larger scale, isolated hexagonal domains can be observed in Teixeira's AFM measurements [16] of transferred F18OH monolayers onto a silicon substrate, and in AFM measurements of Spin-coated F18OH (figure 3). The circular periphery of the hydrogenated simulations also agrees with what is seen experimentally on Teixeira's AFM measurements of mixed monolayers of F18OH and H18OH (figure 3). Simulations of F20 were also carried out in order to evaluate the effect of the lack of hydrophilic head group on the organization of the molecules. The 400 molecule F20 aggregate exhibits very similar behaviour to the fluorinated alcohols, however, for aggregates with smaller numbers of molecules, a molecular tilt angle to the water surface is present on the entire monolayer, something which is not seen for the fluorinated alcohol aggregates of smaller size. Snapshots of F20 and F18OH aggregates are shown in figure 2. It appears that the Van de Waals forces alone are enough to stabilize the perfluoroeicosane monolayer, but only after a minimum number of molecules in the aggregate has been reached. Otherwise, the minimum energy configuration for these aggregates is for the domain to have a molecular tilt, as it maximizes the interactions with the water surface. In conclusion, the simulations provide evidence of the fluorinated films to spontaneously assemble in a very ordered crystal-like aggregate while the hydrogenated films exhibit a more amorphous and disordered structure. Due to their rigidity, the fluorinated molecules visibly display two possible orientations: lying flat at the surface of water; or standing vertically parallel to the other molecules in the aggregate. As a result, the fluorinated aggregates display "clear cut" periphery due to their higher line tension. Whereas the conformational freedom and flexibility of the hydrogenated surfactants allows for a gradual orientation of the molecules at the periphery of the aggregate, which makes the domain more circular and with a less well-defined periphery. The stability, formation and size of monolayer domains has been correlated with line tension in other works [17].

For further conclusions a more quantitative analysis of the monolayers was made. An orientational order parameter was calculated by defining a unit vector for every molecule, which points from the head group of the molecule to its terminal carbon (Terminal carbon to terminal carbon for the F20). The scalar product of every unit vector pair is summed and averaged for each frame of the simulation. The order parameter value ranges from 0 to 1, with 1 representing a very ordered monolayer with all molecules pointing in the same direction. The results are shown in figure 2g. The order parameter confirms that the films formed by fluorinated chains are considerably more ordered than those formed by hydrogenated chains. For both the fluorinated and hydrogenated chains it can also be seen that the longer the chain the higher the ordering.

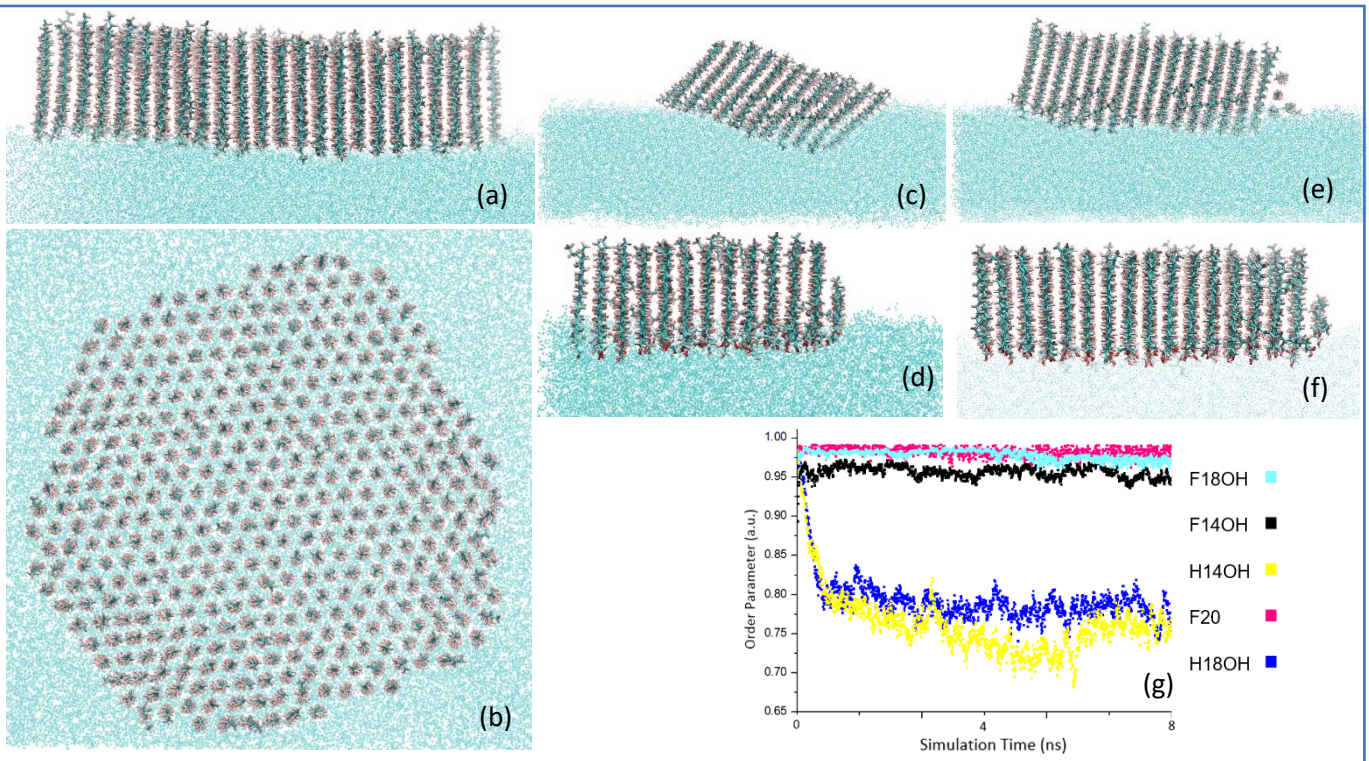

Figure 2 – Side (a) and top (b) view of the 400 molecule F20 aggregate; Side-view of 100 Molecule aggregate of (c) F20 and (d) F18OH; Side-view of 200 molecule aggregate of (e) F20 and (f) F18OH; (g) order parameter results for all the simulated films.

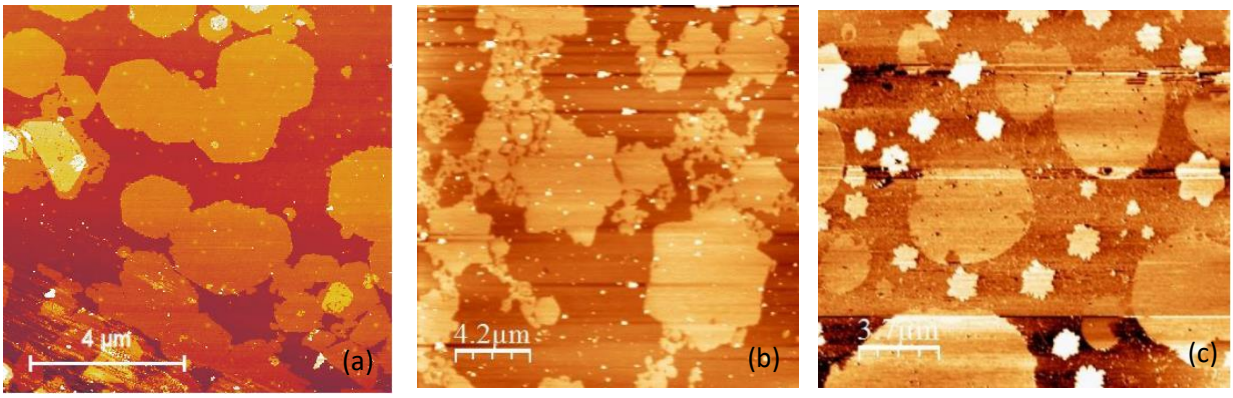

Figure 3 – AFM measurements of (a) spin-coated F18OH on Si substrate, (b) Langmuir-Blodgett film of pure F18OH and (c) Langmuir-Blodgett film of equimolar mixture of F18OH and H18OH.

3.2 Simulated Diffraction Results

For further validation of the MD results, the diffraction spectra for the simulated monolayers was calculated using the structure factor equation as explained in the methods section. Typical diffraction spectras are shown in figure 4. For the fluorinated molecules, the in-plane diffraction peaks and rod scans corresponding to the miller indexes (10) and (11) were calculated and greatly agree with the experimental ones further confirming the hexagonal lattice of the fluorinated domains. The simulation unit cell parameters are presented in table 1, along with the experimental unit cell taken from the measured diffraction spectra of previous works.[18][7] The simulated unit cell area is in very good agreement with the experimental and it's γ angle is very close to the 60º of a perfect hexagonal lattice (-1.6% less than 60º). Even if visually the films might appear to have a very slight tilt, it is not seen in the diffraction spectrum, as the out-of-plane scans show maxima at Qz=0 which agrees with the experimental spectra. The internal structure of the hydrogenated aggregates on the other hand appears to disagree with what is experimentally seen from GIXD (double peak at xc= 15 nm and xc= 16.24 nm instead of a single peak). This peak splitting for the hydrogenated alcohols disagrees with the experiments as the Qxy splitting of the peaks is observed only for the H18OH at lower temperatures and higher pressures [20] [21]. This result might suggest that some special reparameterization of the forcefields might be needed for thin-film simulations, as the molecular interactions in Langmuir monolayers are known to significantly differ from the molecular interactions in the bulk [22], however, for a more definite conclusion boxes with a higher number of H18OH molecules should be simulated in the future. The average crystalline coherence length of the simulations was also extracted from the width of the simulated peaks and compared to an approximate measurement of the diameter of the aggregates which is shown in figure 4. The fluorinated films exhibit molecular ordering on the entire dimension of the aggregate while the diffracted coherence length is systematically smaller than the diameter of the aggregate for both the H18OH and the H14OH, thus the hydrogenated films do not exhibit ordering on the entire dimension of the aggregate providing yet another evidence that the hydrogenated surfactant aggregates are not completely crystalline.

Table 1 – Experimental and Simulated Unit Cells for the fluorinated aggregates.

	SIMULATED UNIT CELL			**EXPERIMENTAL UNIT CELL**		
	F18OH (25ºC)	F14OH (25ºC)	F20 (25ºC)	F18OH (18ºC)	F14OH (22ºC)	F20
a (nm)	0.577	0.578	0.576	0.574	0.576	0.567
b (nm)	0.577	0.578	0.576	0.574	0.576	0.567
γ(degrees)	58.9	59.12	59.01	60	60	60 (hip.)
azimuth (degrees)	0	0	0	0	0	0 (hip.)
tilt (degrees)	0	0	0	0	0	0 (hip.)
unit cell area (nm^2)	0.285	0.286	0.284	0.285	0.287	0.278

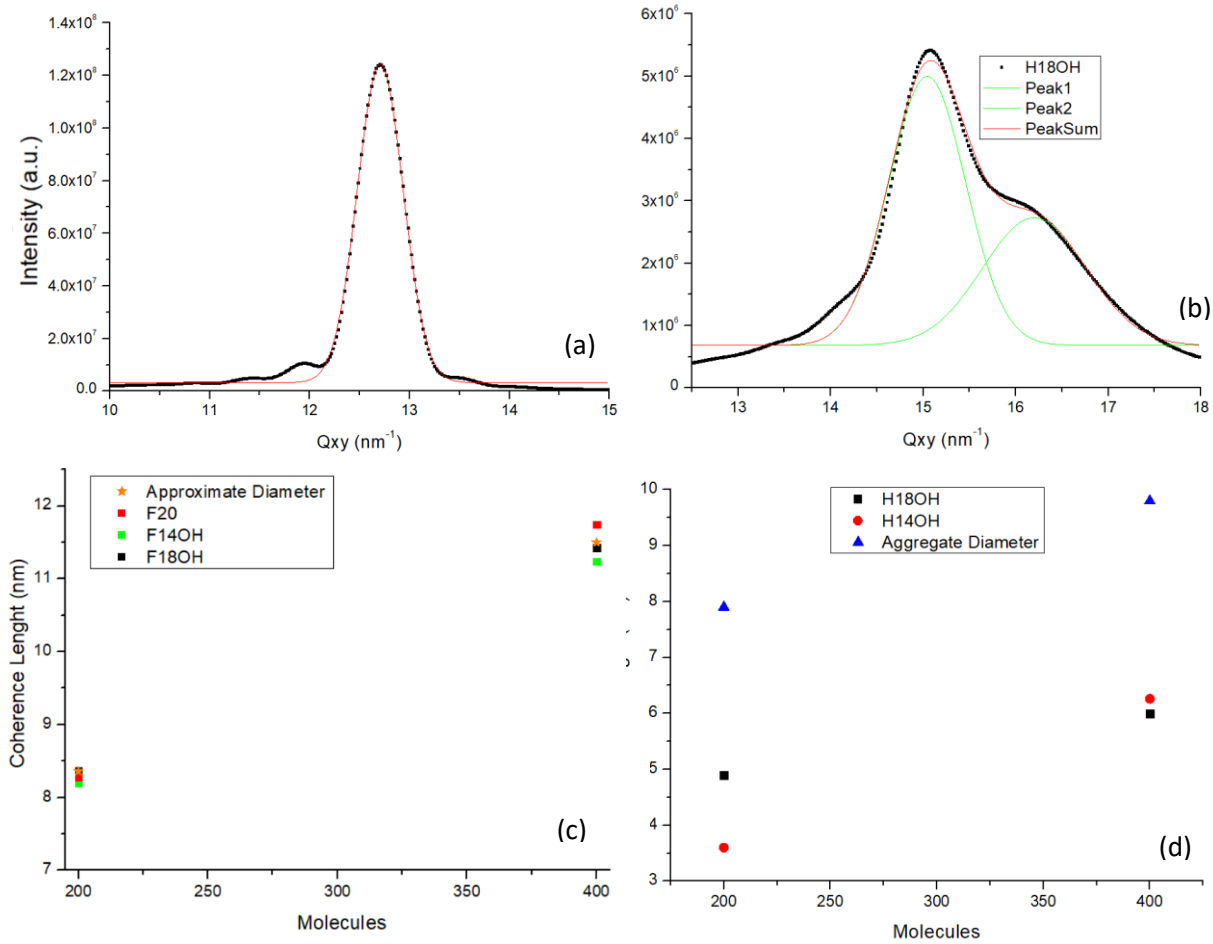

Figure 2 – Typical simulated diffraction peak for the (a) fluorinated and (b) hydrogenated aggregates fitted with gaussian curves; Coherence length and aggregate diameter as a function of number of molecules for the (c) fluorinated and (d) hydrogenated aggregates.

3.3 Diffraction Results - Perfluoroalkylalkane

When unexpected molecular structures arise from MD simulations, there is a debate on whether such complex, non-periodic structures could produce a diffraction spectrum compatible with the experimental one. Such is the case for the perfluoroalkylalkane monolayers, where experimentally they were thought to be formed by upright molecules in the centre being slightly more tilted towards the rim of the aggregate as shown in figure 5. However, recently in our group, the F8H16 simulations showed that the hemi-micelles have in fact an almost 90º degree tilt at the rim of the aggregate and that the hydrogenated chains are partially submerged giving the hemi-micelles a non-periodic structure. [23] A definite validation of these simulation results was obtained by comparing the experimental GIXD spectrum of the system with that calculated from the simulated trajectories. The results are presented in figure 5. In the spectrum obtained from the simulated system one can clearly observe an in-plane peak at Qxy = 12.63 nm-1, which corresponds to the stacking of the fluorinated segments and a second

one at Qxy = 14.77 nm-1 associated with the diffraction of the hydrogenated blocks. This is in very good agreement with the experimental diffraction spectra presented which shows a peak at Qxy = 12.45 nm-1 and a second one at Qxy = 14.44 nm-1. And thus, the complex and non-periodic molecular organization proposed by the MD simulations for the internal structure of the hemimicelles is fully confirmed by the diffraction results.

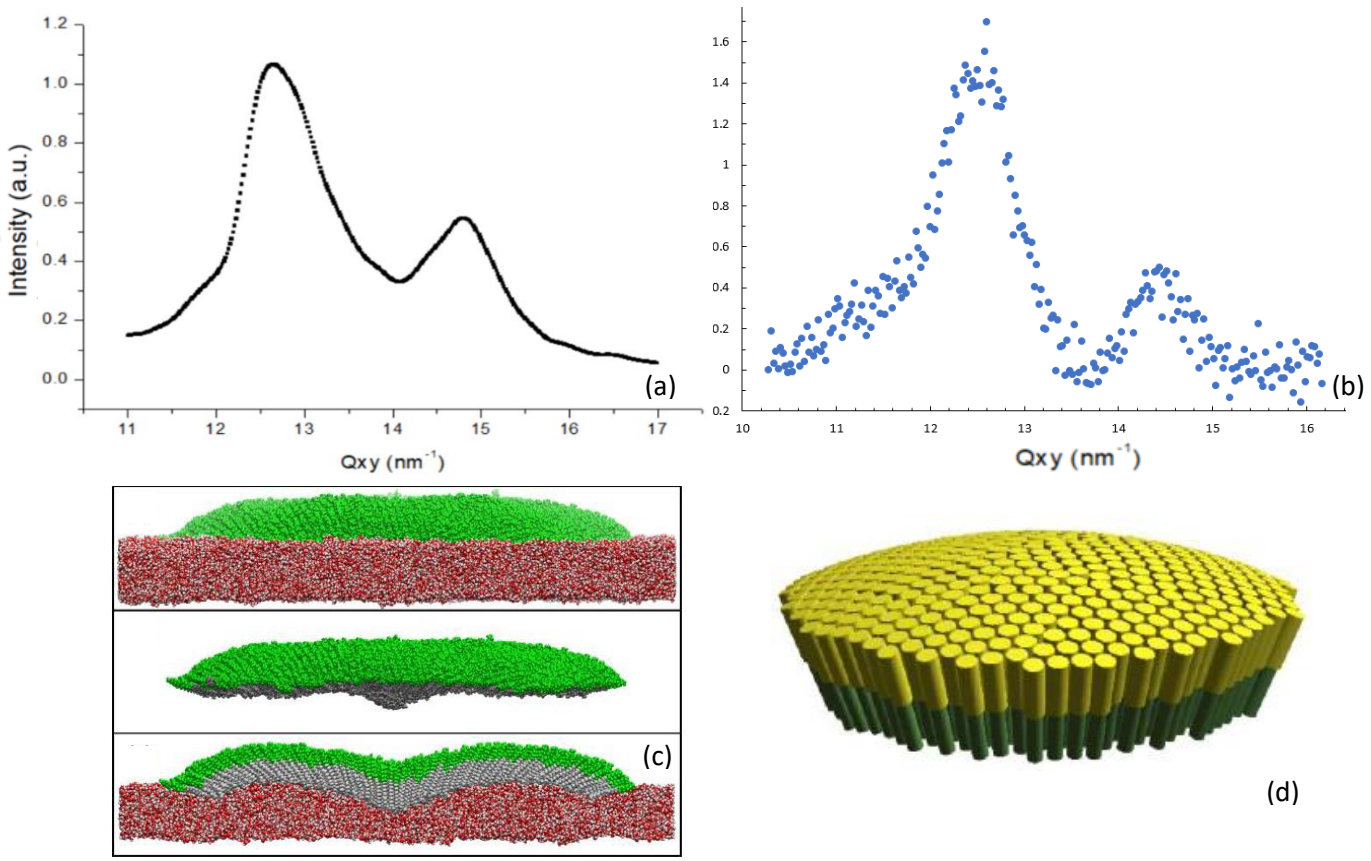

Figure 3 – Diffraction spectra of the (a) simulated hemi-micelle and (b) experimental; (c) New MD results of the hemi-micelle and (d) old model of the hemi-micelle.

4. Conclusions

In this work, the atomistic MD simulations performed were able to highlight some key differences between perfluorinated chains and hydrogenated chains. Due to their rigidity, the perfluorinated chains evidently tend to assemble into very ordered polygonal aggregates independently of the molecule's head group (including the inexistence of a head-group, like the F20), while the hydrogenated chains, due to their higher flexibility, formed less ordered aggregates with a circular-like profile. These results are in agreement with the morphologies observed by AFM measurements of the respective Langmuir-Blodgett films from previous works. Furthermore, the structure factor program developed was crucial to validate (or invalidate) the MD simulation results. The structural organization of the fluorinated aggregates obtained from MD simulations agrees with that experimentally found from GIXD experiments as the experimental and simulated diffraction peaks coincide. The simulated H18OH on the other hand exhibits a type of unit cell in disagreement with the tilted hexagonal lattice from the experiments,

suggesting that some future reparameterization of the force fields might be needed. The molecular organization of the simulated F8H16 hemi-micelle was found to produce a diffraction spectrum compatible with the experimental one, fully confirming the simulated structure. The F8H16 micelle diffraction results also demonstrated that non-periodic and amorphous structures without a translational unit cell (quasi-crystals), produce clear diffraction peaks similar to those which are considered crystals with well-defined unit cells. Traditionally, the parameterization and development of forcefields for computer simulations is done by fitting the simulation results of the pure condensed in-bulk compounds with its corresponding experimental data. However, the interactions of molecules in Langmuir monolayers significantly differ from the interactions of the same molecules in the bulk. As it was demonstrated in this work, calculating the diffraction spectra from MD monolayers produces good quantitative data for comparison with the monolayer experiments, which could be used for fitting and parametrization of new forcefields.

5. References

[1] R.C. Buck, J. Franklin, U. Berger, J.M. Conder, I.T. Cousins, P. de Voogt, A.A. Jensen, K. Kannan, S.A. Mabury, S. van Leeuwen, Perfluoroalkyl and polyfluoroalkyl substances in the environment: terminology, classification, and origins, Integr. Environ. Assess. Manage. 7 (2011) 513–541.

[2] A. Drame', E.T. Givenchy, S.Y. Dieng, S. Amigoni, M. Oumar, A. Diouf, T. Darmanin, F. Guittard, Perfluoroalkyl and polyfluoroalkyl substances in the environment: terminology, classification and origins, Langmuir 29 (2013) 14815–14822.

[3] J.G. Riess, Oxygen carriers (blood substitutes)—Raison d'Etre, chemistry, and some physiology, Chem. Rev. 101 (2001) 2797–2919.

[4] H.M. Courrier, T.F. Vandamme, M.P. Krafft, Reverse water-in-fluorocarbon emulsions and microemulsions obtained with a fluorinated surfactant, Colloids Surf. A: Physicochem. Eng. Aspects 244 (2004) 141–148.

[5] S. Rossi, C. Szíjjártó, F. Gerber, G. Waton, M.P. Krafft, Fluorous materials in microbubble engineering science and technology—design and development of new bubble preparation and sizing technologies, J. Fluor. Chem. 132 (2011) 1102–1109.

[6] M. P. Krafft, M. Goldmann, Monolayers made from fluorinated amphiphiles, Current opinion in Colloid & Interface Science 8 (2003) 243-250

[7] M. Li, A. A. Acero, Z. Huang, S. A. Rice, Formation of an ordered Langmuir monolayer by a non-polar chain molecule, Nature 367 (1994) 151-153

[8] S. S. Jang, M. Blanco, W. A. Goddard III, G. Caldwell, R. B. Ross, The source of helicity in perfluorinated N-alkanes Macromolecules 36 (2003) 5531-5341

[9] W. L. Jorgensen, J. Tirado-Rives, The OPLS Potential Functions for Proteins. Energy Minimizations for Crystals of Cyclic Peptides and Crambin. J. of American Chem. Soc. 6, 110 (1988)

[10] Van Der Spoel, D.; Lindahl, E.; Hess, B.; Groenhof, G.; Mark, A. E.; Berendsen, H. J. C. GROMACS: Fast, Flexible and Free. J. Comput. Chem. 26, (2005), 1701−1718.

[11] Pronk, S.; Páll, S.; Schulz, R.; Larsson, P.; Bjelkmar, P.; Apostolov, R.; Shirts, M. R.; Smith, J. C.; Kasson, P. M.; van der Spoel, D.; Hess, B.; Lindahl, E. GROMACS 4.5: a High-Throughput and Highly Parallel Open Source Molecular Simulation Toolkit. Bioinformatics, 29, (2013) 845−854.

[12] Jorgensen, W. L.; Maxwell, D. S.; Tirado-Rives, J. Development and Testing of the OPLS All-Atom Force Field on Conformational Energetics and Properties of Organic Liquids. J. Am. Chem. Soc. 118, (1996) 11225−11236.

[13] E. K. Watkins, W. L. Jorgensen, Perfluoroalkanes: Conformational Analysis and Liquid-State Properties from ab Initio and Monte Carlo Calculations, *J. Phys. Chem. A, 105 (*2001) 4118-4125

[14] K. Pluhackova, H. MOrhenn, L. Lautner, W. Lohstroh, K. S. Nemkovski, T. Unruh, R. A. Bockmann, Extension of the LOPLS-AA Force Field for Alcohols, Ester and Monoolein Bilayers and its Validation by Neutron Scattering Experiments, *J. Phys. Chem. B (*2015) 119, 49, 15287-15299

[15] Martínez, L.; Andrade, R.; Birgin, E. G.; Martínez, J. M. Packmol: A Package for Building Initial Configurations for Molecular Dynamics Simulations. *J. Comput. Chem.* 2009, *30*, 2157–2164.

[16] M. Teixeira, Complex Interfacial Behaviour of Mixtures of Fluorinated and Hydrogenated Alcohols (2014)

[17] A. J. García-Sáez, S. Chlantla, P. Schwille, Effect of line tension of the lateral organization of lipid membranes, The Journal Of Bio. Chem. 282, 46 (2007) 33537–33544

[18] A. C. M. Pedrosa, Nanostructure fluorinated molecular films (2017)

[19] C. Lautz, Th. M. Fischer, M. Weygand, M. Losche, P.B. Howes, K. Kjaer, Determination of alkyl chain tilt angles in Langmuir monolayers: A comparison of

[20] Brewster angle autocorrelation spectroscopy and x-ray diffraction The Journal of Chemical Physics 108, (1998) 4640.

[21] G. Brezesinski, V. M. Kaganer, H. MOhwalkd, P. B. Howes Structure of octadecanol monolayers: An x-ray diffraction study The Journal of Chemical Physics 109, 2006 (1998);

[22] D. Murakami, U. Langer, Z. Khattari, Th. M. Fischer, Fluorinated Langmir Monolayers Are More Viscous than Non-Fluorinated Monolayers *J. Phys. Chem. B (*2010), *114,* 5376–5379

[23] G. M. C. Silva, P. Mogado, P. Lourenço, M. Goldmann, E. J. M. Filipe, Self-assembled hemimicelles of perfluoroalkylalkane "primitive" surfactants: Spontaneous formation and structure by molecular dynamics simulations (2018)