

Air-water interface-induced smectic bilayer

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We show, using surface pressure versus molecular area isotherms measurements and x-ray reflectivity, that the long diblock semifluorinated *n*-hexaeicosane molecules, $F(CF_2)_8-(CH_2)_{18}H$, form a stable smectic bilayer phase, noted M_1 , with a total thickness of 3.3 nm, at an apparent molecular area about 0.3 nm^2 , though in the bulk the used molecules do not form smectic phases at any temperature. We discuss different molecular packing models according to our experimental data and deduce that molecules are antiparallel with fluorinated chains outwards and interleaved hydrocarbon chains inwards.

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It is well established that amphiphilic character is a major factor, not only for the formation at the air-water interface of Langmuir films [1], but also for building the layered smectic phases. It has been shown that smectogenic molecules such as the 4'-*n*-octyl-4-cyanobiphenyl series (8CB) can spread also as Langmuir films at the air-water interface molecules [2].

It is also well established that the phase behavior of condensed matter, and more particularly liquid crystals, can be strongly influenced by the presence of interfaces. For example, Ocko *et al.* [3] have shown that a smectic ordering can be induced at the surface of a nematic phase, which may extend into the bulk. It has also been shown that a smectic phase can be induced from Langmuir monolayers by the air-water interface at temperatures where the used compound exhibits a crystalline phase in the bulk [2,4]. Such behavior can be understood respectively in terms of *surface freezing* [5] and *surface melting* [6].

During the last decade, many authors have shown that semifluorinated *n*-alkanes, $F(CF_2)_n(CH_2)_mH$ (denoted F_nH_m) can exhibit stable smectic phases in large domains of temperatures depending on *n* and *m* values [7–10]. Moreover, despite the missing of a hydrophilic head group in these molecules, F_8H_{12} , $F_{10}H_{12}$, and $F_{12}H_{18}$ have been initially shown by Gaines [11] to form Langmuir films at the air-water interface. Nevertheless, the long term stability of the two first monolayers has been contested by Huang *et al.* [12], who focused their work on the structural characterization of the stable $F_{12}H_{18}$ monolayer. Obtaining such films at the air-water implies the following interesting question: Since the two parts of the molecules are both hydrophobic chains, which one will go through the contact of the water subphase?

In this Rapid Communication, we show that the shorter F_8H_{18} semifluorinated *n*-hexaeicosane molecules undergo, at ambient temperature, the formation of a stable bilayer of staggered molecules where fluorinated chains form the external envelope and hydrocarbon chains form the inner part. More interesting is that, despite the missing of any liquid crystalline mesophase of the F_8H_{18} compound in the bulk, the obtained bilayer possesses similarities with the corresponding smectic layers observed with shorter semifluorinated *n*-alkanes, i.e., having lower values of *m*.

Our results may contribute also to the understanding of molecular packing of this class of compounds versus intermolecular distances. Indeed, despite their simple chemical structure, an accurate determination of their molecular packing is actually still under debate [13,14], mainly because: (i) there is a large difference between the cross sections of fluorinated and hydrogenated blocks, respectively 0.285 and 0.185 nm^2 , and (ii) fluorocarbon and hydrocarbon chains are practically nonmiscible.

The used $F(CF_2)_8-(CH_2)_{18}H$ compound was synthesized and purified (>98%) by one of us (M.S.). Its preparation was carried out according to a well-known procedure [7]. At ambient temperature, it exhibits a crystalline phase which melts to an isotropic liquid at a temperature equal to 66°C . The length, $L(F_8H_{18})$, of a fully extended F_nH_m molecule may be calculated using classical numerical methods or deduced directly from the literature [15],

$$L(F_8H_{18}) \approx l_F + l_H = 1.21 \text{ nm} + 2.44 \text{ nm}. \quad (1)$$

Its volume, $V(F_8H_{18})$, defined as the envelope of interpenetrating van der Waals spheres, may be calculated by the Kitaigorodsky method [16,17],

$$V(F_8H_{18}) \approx V_F + V_H = 0.178 \text{ nm}^3 + 0.314 \text{ nm}^3. \quad (2)$$

The π -A isotherm diagrams were obtained with a Teflon-made Langmuir trough (Riegler & Kirsten). The experiments were performed at $T = 24^\circ\text{C}$. The surface pressure was measured continuously using a Wilhelmy plate with an accuracy of about 0.1 mN/m .

The setup used for measurements of x-ray specular reflectivity of liquid surfaces is described elsewhere [18]. The wavelength of the x-ray beam is 0.154 nm ; its intensity is

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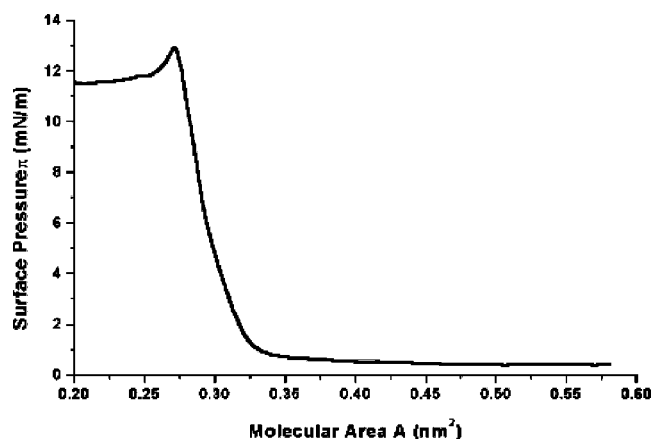


FIG. 1. Surface pressure (π) vs molecular area (A) isotherm diagram obtained on compressing of the F_8H_{18} spread at the air-water interface, at $T=24^\circ\text{C}$. The compression speed was about $0.04\text{ nm}^2/\text{molecule}/\text{min}$.

about 2×10^6 photons per second; the horizontal beam width is 8 mm and its height is $50\ \mu\text{m}$. A Langmuir trough is inserted in the center of the goniometer. The experimental curves were fit using a one-, two-, or three-slab model. Electron densities in each slab are calculated from the number of electrons in the part of the molecule that forms the considered slab and the product of the molecular area A by the slab thickness. The roughness σ of the interface induced by thermal fluctuations is also taken into account in the model [19]. The area per molecule A is determined by the Langmuir trough, so the free parameters of the model are the thicknesses of the slabs and the roughness σ . A normalized standard quadratic error χ^2 is computed for each fit. A value of χ^2 about 1 means that the fit is good, whereas a value well above 2 implies a bad fit and that the model has to be rejected.

Figure 1 shows the π - A isotherm obtained during a cycle of compression and decompression of F_8H_{18} Langmuir film. The obtaining of such reproducible π - A isotherm diagram is a direct evidence that F_8H_{18} molecules spread as a Langmuir film at the air-water interface, despite the missing of any hydrophilic part in the molecules.

For molecular areas greater than 0.35 nm^2 , the surface pressure π is practically constant and equal to 0 mN/m. For molecular areas about 0.30 nm^2 , the surface pressure increases abruptly and regularly up to 12 mN/m, at which the film collapses. However, the film becomes unstable already when compressed to surface pressures higher than 6 mN/m, which was found to be equal to the surface equilibrium pressure π_e . It is rather surprising that such monolayer reduces the surface tension of about 6 mN/m only, before collapse occurs. Comparatively, condensed monolayers of long hydrocarbon chains of fatty acids, lead usually to a surface pressure up to 35 mN/m. Even the fully perfluorinated n -eicosane $F(\text{CF}_2)_{20}\text{F}$ molecules, which contain no hydrophilic head group also, have been shown to form stable monolayers at the air-water interface, which could be compressed to surface pressure up to 20 mN/m [20].

We would like to point out that we checked the long term stability of the F_8H_{18} Langmuir film at surface pressures lower or equal to 6 mN/m as follows: the molecular area A

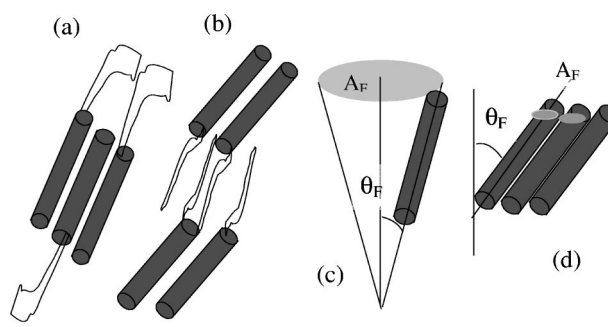


FIG. 2. Two bilayer molecular packing models: HF_2H (a) and FH_2F (b); representation of the occupied area A_F by fluorinated chains in the FH_2F model: assumed to be fully disordered (c) or ordered (d).

was observed to not decrease when the surface pressure was servo-controlled at 6 mN/m, nor was the 6 mN/m surface pressure value observed to decrease at a fixed molecular area of 0.28 nm^2 . For the sake of simplicity, we label the observed phase as M_1 . We discuss in the following its molecular packing according to x-ray reflectivity experiments and considering both monolayer and bilayer models.

One may assume in a first step that the M_1 phase is a monolayer where molecules are oriented normally to the interface. The first monolayer model, labeled FH, is where the fluorinated chains extend up towards the air and hydrocarbon chains towards the water subphase. The second monolayer model, labeled HF, is where the fluorinated chains are in contact with the water subphase. Basically, recent molecular dynamics calculations, carried by Kim and Shin [21] on $F_{12}H_{18}$ monolayers, showed that the FH and HF models are thermodynamically equivalent. The third monolayer model, we label HF-FH, is where molecules orient themselves anti-parallel by regards to each other.

Also, because of the natural tendency of semifluorinated molecules to form layered structures, interleaved bilayer molecular packing models should also be considered. Two types of bilayers can be suggested: HF_2H and FH_2F (see Fig. 2). The first packing model consists of the superposition of three slabs, where the central slab contains (interleaved) fluorocarbon chains and the two outer slabs contains hydrocarbon chains. For the second bilayer packing model, the central slab contains (interleaved) hydrocarbon chains and the two outer slabs contain fluorocarbon chains.

Experimentally, we observed also that oil (a small drop of hexadecane deposited on the top of the film at the air-water interface) does not wet the F_8H_{18} film in its M_1 phase. More precisely, we observed that the drop of hexadecane does not spread over the film and does not alter the M_1 phase x-ray reflectivity.

Figure 3 shows experimental x-ray reflectivity data obtained from F_8H_{18} film compressed to a surface pressure of $\pi=4\text{ mN/m}$ and a molecular area of 0.30 nm^2 . The experimental curve has been fit using all the possible monolayer and bilayer packing models: FH, HF, FH-HF, HF_2H , and FH_2F . All fit parameters values are reported in Table I, except for the FH-HF model, for which no acceptable χ^2 values were obtained ($\gg 5$).

For the FH and HF monolayer packing models, the given thickness values of the fluorinated slab is about 1.8 nm and

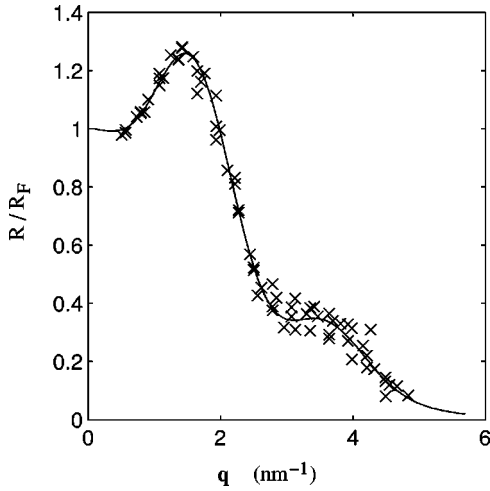


FIG. 3. Experimental reflectivity curve (\times) obtained from the F_8H_{18} film spread at the air-water interface compressed to a surface pressure $\pi=4$ mN/m. The solid curve corresponds to the best fit of the experimental curve using the FH₂F model. Results of fits with other models are presented in Table I.

exceeds the length of a fully extended fluorinated chain (2.0 nm). Thus, these two models should be rejected. Consequently, all the three monolayer packing models have to be rejected.

Using the first bilayer packing model, HF₂H, the thickness of the fluorinated slab was found equal to 1.9 nm as reported in Table I. This value indicates that fluorinated chains of two adjacent molecules should be almost fully staggered by regards to each other. This result should not be accepted because the drop of hexadecane would have wet the film but this is not the case.

For the second bilayer packing model, FH₂F, the thickness values of the fluorinated and the hydrocarbon slabs can be accepted but needs some further discussion from the space filling model point of view: The two hydrocarbon chains are allowed to occupy an area A of 2×0.30 nm² and a volume V_H of $2 \times 0.30 \times 1.35$ nm³ (≈ 0.82 nm³). As we can notice, V_H value may be accepted since it is greater than the minimum volume of 2×18 -CH₂-units, i.e., 2×0.314

TABLE I. Fits parameters values of the experimental x-ray reflectivity curve, recorded at a surface pressure π equal to 4 mN/m, obtained using different packing models: FH, HF, HF₂H, and FH₂F. h_1 , h_2 , h_3 , and d represent respectively the thickness of the upper, medium, lower slab, and the overall film. The value found for the roughness σ of the film is typical at air-water interface at low surface pressures.

Model	Monolayer packing models		Bilayer packing models	
	FH	HF	HF ₂ H	FH ₂ F
h_1 (nm)	1.81 (F)	1.04 (H)	0.45 (H)	0.87 (F)
h_2 (nm)			1.90 (F)	1.35 (H)
h_3 (nm)	1.50 (H)	2.08 (F)	0.81 (H)	1.07 (F)
d (nm)	3.31	3.12	3.16	3.29
σ (nm)	0.33	0.50	0.43	0.35
χ^2	2.4	5.7	0.6	0.7

nm³ (≈ 0.63 nm³), given in Eq. (2). Because of the large area (0.30 nm²) they are allowed to occupy, hydrocarbon chains should be in a liquid state (L_1 phase).

Now, let us consider first lower fluorinated chains (we label as F_3). Each chain is allowed to occupy a volume, V_{F_3} , of $2 \times 0.30 \times 1.07$ nm³ (≈ 0.64 nm³), which is much greater than the minimum volume of eight-CF₂-units, i.e., 0.18 nm³, given in Eq. (2). In order to have a better view of the fluorinated chain orientation, we may compare their experimental area value ($A_{F_3} = 2 \times 0.30$ nm²) to the area that fluorinated chains would occupy respectively in a disordered state and in an ordered state,

$$A_{\text{dis}} = \pi(l_F)^2 \sin^2 \theta_F, \quad (3)$$

$$A_{\text{ord}} = A_p / \cos \theta_F. \quad (4)$$

The angle θ_F represents the mean tilt angle of the fluorinated chains, defined with regards to the normal to the air-water interface. In Eq. (4), A_p and l_F represent respectively the cross section and the length of the fluorinated chain, assumed as a rigid rod. Their tilt angle may be measured according to

$$\theta_{F_3} = \arccos(h_3/l_F), \quad (5)$$

where h_3 represents the thickness of the considered fluorinated slab.

Note that because of the probable existence of many gauche-gauche defects in the hydrocarbon chains, it is not possible to calculate with Eq. (5) a mean tilt angle for hydrocarbon chains. Nevertheless, one could give its maximum value: $(\theta_H)_{\text{max}} \approx 55^\circ$.

Replacing l_F by 1.2 nm and h_3 by 1.07 nm, one finds $\theta_{F_3} \approx 28^\circ$, $A_{F_3,\text{dis}} \approx 1.00$ nm², and $A_{F_3,\text{ord}} \approx 0.32$ nm² for the lower fluorinated chains. In a similar manner, one finds for the upper fluorinated chains: $\theta_{F_1} \approx 41^\circ$, $A_{F_1,\text{dis}} \approx 1.95$ nm², and $A_{F_1,\text{ord}} \approx 0.38$ nm². As we can notice, $A_{F,\text{ord}} < A_{F,\text{dis}}$: Fluctuations of the fluorinated chains are likely to be restricted by neighbor chains.

Let us now compare our results with those obtained by Gaines [11] and Huang *et al.* [12]. On the basis of the low surface tension of the fluorinated chains and their large cross section, Gaines suggested in his work that the fluorinated chains should point upwards with regards to the air-water interface, i.e., FH monolayer packing model. The statement of Gaines was corroborated later by Huang *et al.*, at least for the $F_{12}H_{18}$ monolayer by means of x-ray diffraction and reflectivity analysis. However, the FH packing should not be taken as a general behavior of F_nH_m molecules at the air-water interface. Indeed, since the film stability is mainly governed, at a short range, by van der Waals interactions between fluorocarbon-fluorocarbon and hydrocarbon-hydrocarbon chains, then the resulting molecular packing within the film should depend on the competition between these two types of interactions and also on steric effects. For example, at a fixed hydrocarbon chain length, e.g., H_{18} , one should expect the occurring of the FH packing for long fluorocarbon blocks as found by Huang *et al.*, and the occurring of a FH₂F bilayer packing with shorter fluorocarbon chains as reported in our study for the F_8H_{18} film.

Let us now compare our results with those found in the literature for the bulk state of semifluorinated alkanes. For example Mita *et al.* [10] showed that $F_{10}H_m$ molecules exhibit a smectic phase depending on temperature and also on the m value ($6 < m < 12$). In this case, the interlayer spacing was observed to be approximately equal to the length of the fully extended $F_{10}H_m$ molecules. More detailed results have been reported by Russel *et al.* [13] for the $F_{12}H_m$ series. In this case, the smectic phase was observed to occur versus temperature for $2 \leq m \leq 14$. The interlayer distance was found to be also close to the length of a fully stretched $F_{12}H_m$ molecule, whereas in the solid phase ($m > 14$) the interlayer spacing was observed to be slightly lower than twice the molecular length. It is interesting to note that, in our study, the thickness value d of the observed bilayer is also close to the length L of a fully stretched F_8H_{18} molecule: $d/L \approx 0.91$.

Finally, we would like to add an interesting recent report, made by Gang *et al.* [22], on the surface structure of three semifluorinated alkanes which corroborate the smectic fea-

ture of our own F_8H_{18} bilayer. These authors showed by means of x-ray reflectivity and surface tension measurements that a surface layer forms at the free surface of the bulk of $F_{12}H_8$, $F_{12}H_{14}$, and $F_{12}H_{19}$ compounds. For low values of m (8 and 14) the structure of the surface layer is fully crystalline, whereas for the longer molecule ($m = 19$), the surface layer is disordered and exhibits only short range order. In this case, the thickness of the surface layer was also found to be about the length of the fully extended molecules. The authors suggest that the surface layer is a monolayer but do not reject a bilayer packing of staggered molecules.

As we can conclude, upon compression of the F_8H_{18} molecules, a smectic bilayer is obtained at a molecular area of about 0.3 nm^2 and a surface pressure range between 0 and 6 mN/m. In this phase, the molecular organization consists of an antiparallel bilayer molecular packing where the external slabs consist of fluorinated chains and the internal slab contains fully interleaved hydrocarbon chains.

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