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Role of molecular self-assembling in Langmuir-Blodgett film growth

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The elusive role of molecular reorganization in the growth of ordered organic multilayers using the Langmuir-Blodgett technique has been investigated with x-ray and neutron reflectivity, and atomic force microscopy. Use of deuterated tails as markers directly shows that molecules get attached to the substrate in asymmetric configuration but, apart from the first layer, reorient themselves to a symmetric configuration. An exchange of molecules between first and second layers could also be detected. Thickness remains unchanged between second and third monolayer deposition but density is doubled.

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Ultrathin metal-organic films formed by the Langmuir-Blodgett (LB) technique[1–3] can be extremely useful to explore physics and chemistry in confined geometries and in designing of model biological membranes due to possibility of having well-defined molecular orientation and ordering in these films.[2–5] In a typical LB film deposition process a fatty acid is spread on an aqueous solution of a metal salt and a compressed mono-molecular layer[3] is formed at a fixed pH and temperature. Multilayer LB films of fatty-acid-salt molecules are then deposited[1,2] simply by a series of up–down strokes (dipping) of a substrate through this compressed fatty acid monolayer. Although complicated molecular films[2,3] can be formed by this technique, growth and molecular orientation of even simple fatty-acid-salt films on a substrate are not well understood.

It is known[1,2] that for depositing a LB film of a divalent fatty-acid-salt like Cadmium stearate (CdSt) or Cadmium arachidate (CdA) on a hydrophilic substrate, one needs to have water-to-air up stroke first for attaching hydrophilic $\mathrm{Cd(COO)_2}$ (head) group to the substrate with hydrocarbon chains (tails) pointing normal to the substrate. Then a series of air-to-water-to-air stroke cycles are repeated to form a well-ordered multilayered LB film. It is also known through measurement of contact angle between dipping substrate and Langmuir monolayer[1] that in water-to-air and air-to-water strokes, transfer of molecules normally take place through head–head and tail–tail attachments, respectively. Consequently it was assumed[1,2] that head–head bonding exists in LB film, and as a result both the tails of the molecules of these divalent salt remain on one side of the head group. However, x-ray scattering measurements indicate[4] that in all the layers, apart from the first layer, the molecular configuration is symmetric with the tails remaining on both sides of the head group as observed in crystals of these materials.[6] To resolve this contradiction between the above models, we have performed neutron reflectivity studies of trilayer LB films of CdSt having alternate deuterated (D) and hydrogenated (H) tails, and x-ray scattering measurements on CdA LB films obtained through one, two, and three monolayer transfers.

In Fig. 1 we have summarized the results obtained from these studies. In first panel we have shown the first water-to-air stroke through a compressed fatty acid monolayer on water containing Cd-ions along with the observed meniscus of the water during this stroke. The configurations of the fatty acid molecules and the ions in the Langmuir monolayer are known from x-ray scattering studies.[7] The formation of the cadmium salt and the molecular configuration normal to the substrate, as depicted, were clearly evident in the electron density profile obtained from x-ray reflectivity measurement, shown in Fig. 2(a). In the second panel the air-to-water stroke is shown along with meniscus indicating hydrophobic tail–tail transfer of molecules from Langmuir monolayer to LB film. If this film is taken out through null water surface (water not covered by the precursor fatty acid monolayer), salt molecules self-assemble by flipping the tails in opposite direction giving rise to a film having three monolayer thickness as observed in x-ray measurement [Fig. 2(b)]. Consequently this upper layer has about 50% coverage with large height fluctuations as seen in Atomic Force Microscopy (AFM) measurements (Fig. 3). The meniscus in the third panel indicates head–head transfer in the third stroke confirming the molecular configuration (under water) shown in the second panel. However, the x-ray reflectivity data [Fig. 2(c)] cannot clearly distinguish between the molecular configurations shown in third and fourth panels. Neutron reflectivity measurements with deuterated tails as markers in H-D-H and D-H-D LB films were carried out to resolve this problem. The two types of tails are indicated as black and white blocks in Fig. 1. The extracted scattering density profiles (Fig. 4) indicate symmetrical distribution of H and D about the upper head group layer as shown in fourth panel. The deuterated tails as markers also served to depict the exchange of molecules between layers deposited in the first and second strokes.

We have used[5] an alternating trough for depositing H-D-H and D-H-D LB films by spreading H-stearic and D-stearic acid on each side of the trough with common subphase of water containing 6×10^{-4} molar $\mathrm{CdCl_2}$ at pH 6.5 and temperature 14.5 °C. For one, two, and three layer deposition of CdA films, we used arachidic acid on one side of the trough and null water on the other side and the subphase was maintained as above. All the depositions were done with dipping speed of 3 mm/min at 30 mN/m surface pressure. The iso-

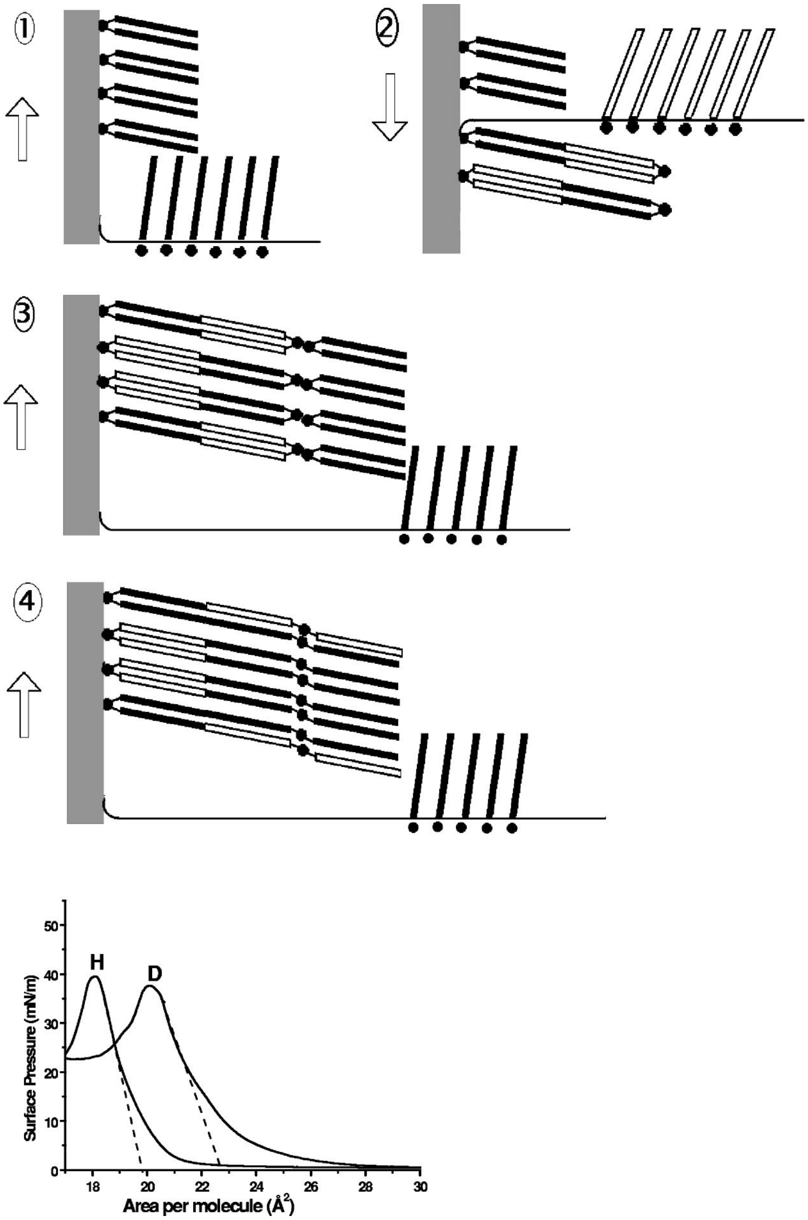

FIG. 1. (Panels 1–4) First three strokes in LB deposition of fatty acid salts of a divalent metal on a hydrophilic substrate. Schematic view summarizing the results of neutron and x-ray reflectivity and AFM studies, with normal (hydrogenated) hydrocarbon chains as black and deuterated chains as white blocks. Refer text for details. Pressure-area isotherms of hydrogenated (H) and deuterated (D) CdSt Langmuir monolayers is shown in the bottom. Tangents (dashed lines) are used to calculate area per molecule at deposition pressure. Isotherms include collapse of the monolayers.

therms of H- and D-stearic acids on the subphase described above are also shown in the Fig. 1. It is to be noted here that these densities are the same for CdSt and CdA and the in-plane area of each molecule in symmetric configuration is known to be about 20 Å^2.[3,4,8] This specific molecular area was also obtained here for the compressed Langmuir monolayer of the hydrogenated fatty acids used in the LB film deposition. However, for deuterated fatty acids we obtained specific area of about 23 Å^2 in most compressed phase and this was used for the LB deposition. This indicates a tilt of about 22° as against 8° tilt in hydrogenated molecules.[7] It may be noted that this higher tilt angle for deuterated molecules was also observed in optical measurement of monolayer LB films.[9]

X-ray scattering data were collected on a triple axis goniometer using Cu$K\alpha 1$ radiation from a rotating anode generator followed by Si(111) monochromator. AFM images were collected in contact mode with a silicon nitride cantilever and integrated tip using a 100 μm piezo scanner. All the instrumental details have been published earlier.[5] The neutron reflectivity measurement was performed in the CRISP reflectometer[10] at the ISIS pulsed neutron source, using the white beam time of flight method. Measurements were made in the q range 0.008 to ~0.35 Å^{-1} using a wavelength band of 1.0 to 7.0 Å^{-1} and three different glancing angles of incidence of 0.25°, 0.65°, and 1.5°.

The in-plane averaged scattering length density, as a function of depth, $\rho(z)$ was used to calculate[11] the reflectivity corresponding to the films after dividing a film into a series of layers having "head" and "tail" blocks of the LB films. The $\rho(z)$ for each layer can be expressed as

$$\rho(z)=\sum_i N_i(z)S_i(z), \tag{1}$$

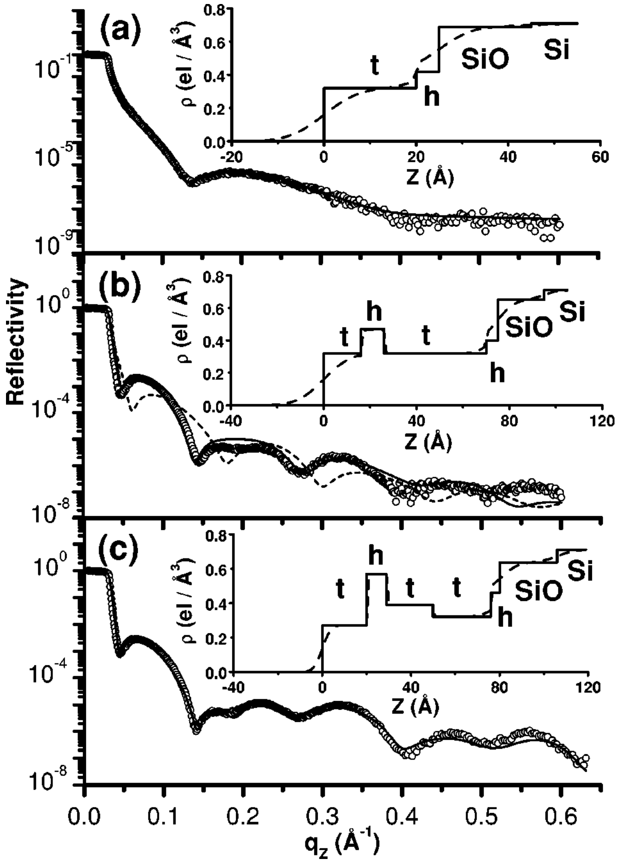

FIG. 2. Experimental (symbols) and calculated (solid line) x-ray reflectivity profiles for (a) 1 ML, (b) 2 ML, and (c) 3 ML films on Si(001). The respective electron density profiles with (dashed line) and without (solid line) roughness are shown in insets (t– tail; h–head). The dashed line in the middle panel shows the calculated profile of 2 ML film based on the configuration shown in Fig. 1, panel 2 (under water).

where $N_i(z)$ is the number density of the element i and $S_i(z)$ is the scattering length of that element. For x-rays this scattering length is $r_0 Z_i$ (where Z_i is the atomic number of element i and r_0 is the classical electron radius) and for the neutron it is b_i (scattering length of that element). Analysis of neutron and x-ray data was done using a simple model having two sublayers representing the head and tail of the first layer and three sublayers for the head and two tails of the upper layer. We also included silicon oxide layer near the substrate and roughness for each interface. The obtained electron density profiles for the films are shown in Fig. 2 along with the x-ray data and fits. The obtained scattering density profiles for H-D-H and D-H-D films along with neutron data and fits are shown in Fig. 3. Better fits to the x-ray and neutron data could be obtained with more elaborate models but basic features of the density profiles remain unchanged. These elaborate models will not be presented here.

The correctness of the molecular configuration model in the first deposited layer (Fig. 1, first panel) is evident from the close matching [Fig. 2(a)] of the experimental and calculated reflectivity profile for 1 ML film. The obtained electron density, 0.42 electron Å^{-3}, yields 42 electrons in the head group, confirming asymmetric molecular configuration of cadmium salt. In this configuration we get only one head group within the area occupied by two tails.

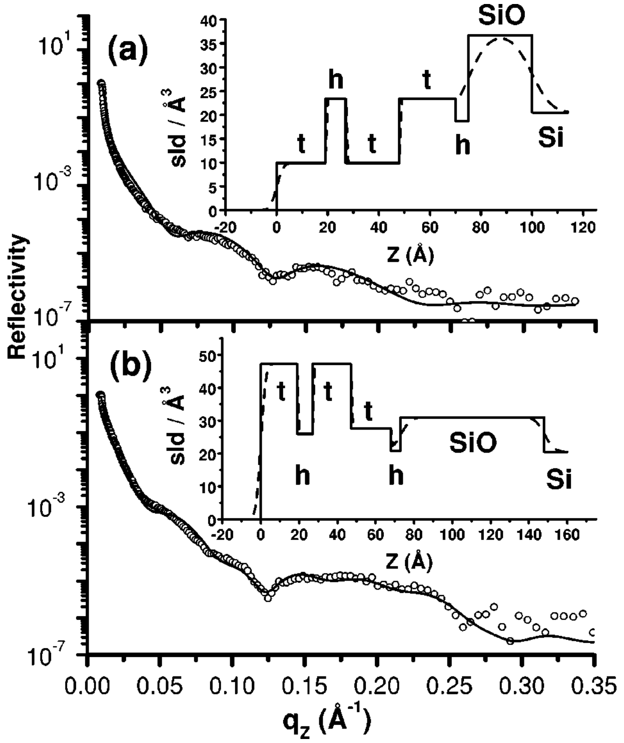

FIG. 3. Experimental (symbols) and calculated (solid line) neutron reflectivity profiles for (a) H-D-H and (b) D-H-D films on Si(001). The respective scattering length density ($\times 10^{-7}$) profiles with (dashed line) and without (solid line) roughness are shown in insets (t–tail; h–head).

The positions of the peaks and the dips in the reflectivity profiles of 2 ML and 3 ML films (Fig. 2) clearly show that thicknesses of these two films are identical. The calculated reflectivity profile for 2 ML film from the asymmetric configuration under water, as shown in second panel of Fig. 1, does not match with the reflectivity data [Fig. 2(b)] at all. As the film comes out of water, it is expected to get terminated hydrophobically resulting in the symmetric configuration.

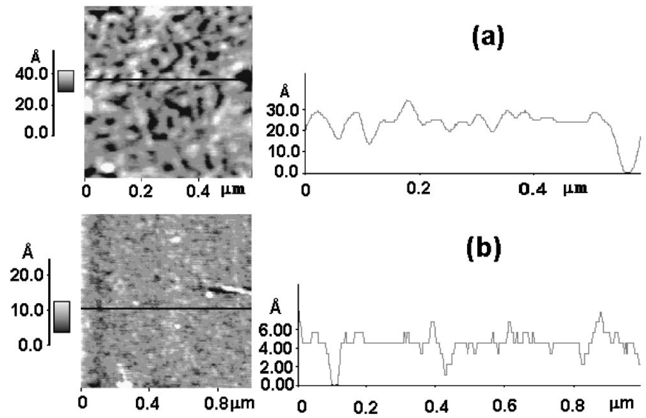

FIG. 4. AFM images of (a) 2 ML and (b) 3 ML films on Si(001) along with typical line profiles drawn through each image.

This molecular rearrangement in the film, as it is taken out from null water, will leave 50% surface-area uncovered. From the calculated profile [Fig. 2(b)] we get about 76 electrons in the head group indicating that this area may be occupied by water. Figure 4(a) shows the AFM image along with the line profile for 2 ML film. The large height fluctuations in 2 ML film as compared to the 3 ML film [Fig. 4(b)] indicate clustering of the molecules leading to formation of patches in the former.

The calculated reflectivity profile for the 3 ML film [Fig. 2(c)] yields the electron density of 0.57 electron $Å^{-3}$ in the upper head group layer corresponding to 95 electrons which indicates symmetric arrangement of the tails about this layer (Fig. 1, fourth panel). In this configuration we get only one head group within the area occupied by one tail. The configuration of the lower layer remains unchanged for both 2 ML and 3 ML films. To understand the role of lower layer in the 3 ML film and to investigate the molecular configuration of the upper layer, we performed neutron reflectivity studies of D-H-D and H-D-H films. The obtained scattering length densities of the head groups for both the films show the doubling of head-to-tail ratio in the top layer as compared to that in the layer near substrate, confirming the x-ray result.

The scattering length densities for three tail-sublayers of the D-H-D film come out to be 47.2, 47.2, and 27.6, counting from top downward. For the H-D-H film these numbers are 11.0, 11.0, and 26.0 (refer to Fig. 4 insets). Assuming 23 $Å^2$ and 20 $Å^2$ as specific molecular areas for D and H, respectively, we can infer number ratios between these species in the three sublayers for both films. For the D-H-D film the D-to-H ratio in each top tail sublayer is 66:34 and that in the layer near substrate is 41:59. The corresponding ratios for the H-D-H film are 20:80 and 39:61. The same D-to-H ratios in the top two tail sublayers in both the films confirm symmetric configuration about the upper head group. The almost equal proportion of D and H in the layer near substrate indicates exchange of molecules after the second stroke in both D-H and H-D transfer sequences. It is also interesting to note that the overall D-to-H ratio for the D-H-D and H-D-H films are 1.7:1.3 and 0.8:2.2, respectively, consistent with the expected number ratio. These results indicate that there is very little loss of transferred molecules from the LB film to the Langmuir monolayer in subsequent strokes.

For the H-D-H film deposition, after the second transfer 50% of the newly transferred deuterated tails exchange their position with the hydrogenated tails transferred in the first stroke (refer first and second panel of Fig. 1 and assume that white blocks are deuterated tails) and as a result we observe equal mixture of D and H in the first layer. After the arrival of the hydrogenated tails in the third water-to-air stroke in a hydrophilic transfer, the molecules of the top layer flip in the symmetric configuration resulting in the H-to-D ratios mentioned above. An almost exactly same growth process is applicable in the case of D-H-D film. It is also to be noted here that a large difference in D-to-H ratio is maintained between the layer near substrate and the upper composite layer for both films.

Neutron and x-ray scattering results and AFM measurements presented here constitute a direct experimental evidence of the role of molecular self-assembly in LB film growth. We have shown, for the first time, that the first deposited layer has an asymmetric configuration with two hydrocarbon chains on one side of the head group and that these molecules undergo an exchange with those deposited in the second stroke. We have established a connection between the head-to-head and tail-to-tail transfer process[1,2] and the equilibrium crystal structure[4,6] of the salt molecules through the flipping of the molecules from asymmetric to symmetric configuration. Our results preclude the formation of X and Z type structures,[1] important for optoelectronic applications, in LB films of amphiphiles with two hydrocarbon chains.

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