Langmuir-Blodgett Films: From micron to angstrom

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Combining optical microscopy and atomic force microscopy, a complete characterization of Langmuir-Blodgett bilayers made of arachidic acid has been performed. At macroscopic scales, both techniques can be used to control the homogeneity of the transferred films. By atomic force microscopy, roughness and thickness of the bilayers could be determined. These are compatible with a normal orientation of the fully extended aliphatic chains with respect to the substrate. Molecular-resolution images give the first direct experimental evidence for the presence of pairs of dislocations in those systems.

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Langmuir-Blodgett (LB) films [1] have attracted much attention in the past because of their numerous potential applications in various areas of surface sciences; besides their potential use in molecular electronics [2], one may also take advantage of their striking nonlinear properties in the field of integrated optics [3] or use them as biological sensors [4]. Furthermore, LB films can be considered as model systems for the study of some typical phenomena of physics in two dimensions.

For those reasons, many experiments have been recently performed on such systems in order to fully characterize their physical properties (electrical, tribological), as well as their structure. In this regard, much progress has been achieved using x-ray [5] or electron [6] diffraction, spectroscopic (infrared or Raman) experiments [7], and x-ray [8] or neutron [9] reflectivity. It must be emphasized, however, that these techniques only give access to spatially averaged information. In particular, the structural defects within the films that can be evidenced this way are only macroscopic.

However, in the last years scanning probe microscopies, mainly scanning tunneling [10] and atomic force [11-13] microscopies (STM and AFM), have been shown to be promising techniques for the elucidation of the structure of LB films at the molecular level. In particular, their use allows one to visualize LB films in the direct space, which should reveal the presence of intrinsic topological defects of two-dimensional solids; this is probably the most important advantage of these local probe microscopies over diffraction techniques. In this regard, STM pictures obtained on bilayers transferred on highly oriented pyrolitic graphite are still the object of controversy, since no precise mechanism for electron tunneling through a 50-Å-thick organic layer has been clearly identified. Thus one may think that atomic force microscopy is probably, right now, best suited for the investigation of the organization of LB films at the molecular level.

Though much is known about the structure of LB films, we shall show in this Letter that the combination of optical microscopy and AFM allows us to fully describe those systems at any scale (from macroscopic down to molecular scales). In particular, we present experimental data obtained with AFM from which we deduce bilayer height and give evidence for the presence of defects at the molecular level.

All the experiments described below were performed in a clean, temperature-controlled (20 ± 0.2°C) room. For our study we used arachidic acid first deposited from hexane solution on the surface of water at $p\mathrm{H}=6$ in the presence of $\mathrm{BaCl_2}$ at 10^{-4} mol/L. Substrates used for monolayer deposition were hydrophobic silanated silicon wafers [14]. X-ray surface diffraction has shown that those substrates only exhibit short-range positional order (within a few molecular spacings) [15]. Isotherms, performed with a temperature-controlled (20 ± 0.05 °C) Lauda Langmuir trough, confirmed the existence of a solid-condensed-liquid transition at a surface pressure of 24 mN/m. Bilayers were obtained by vertical dipping and raising of the substrate through the monolayer surface in this solid phase, at a pressure of $P=30$ mN/m. Transferred areas were equal within less than 10% to the geometrical area of the substrate.

Optical microscopy images were obtained with a Reichert Polyvar metallographic microscope working in reflection with the "ellipsometric contrast" mode, in which observations are performed between crossed polarizers at almost full numerical aperture [16]. This method has already been shown to be able to detect organic layers a few tens of angstroms thick on silicon wafers. It is worth mentioning that Blodgett already showed, in 1935, that the presence of monolayers on a solid substrate could be evidenced by the use of polarized light microscopy [17], though this has been forgotten since that time.

AFM experiments were performed with a Nanoscope II microscope from Digital Instruments. Two types of scan heads were used: one for large scan (80×80 $\mu\mathrm{m}^2$ scan range) and another one for molecular-resolution images (1×1 $\mu\mathrm{m}^2$ scan range). Calibrations were performed with rulings, for lateral distances, and ball bearings, for vertical distances, in the case of the big scan head; in the case of the small scan head, we used mica

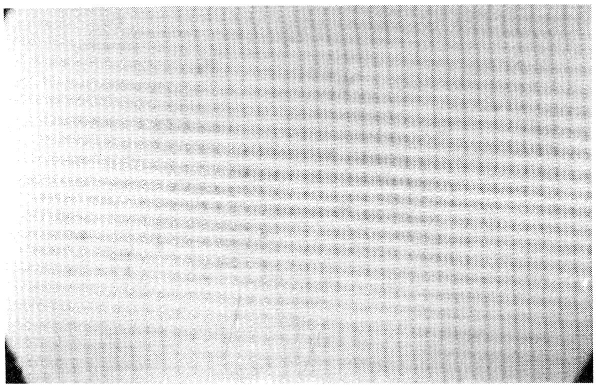


FIG. 1. Observation in optical microscopy (ellipsocontrast) of an arachidic acid bilayer transferred on a silanated silicon wafer. The dark regions are indicative of the presence of defects within the bilayer. Horizontal size of this picture is 250 μm.

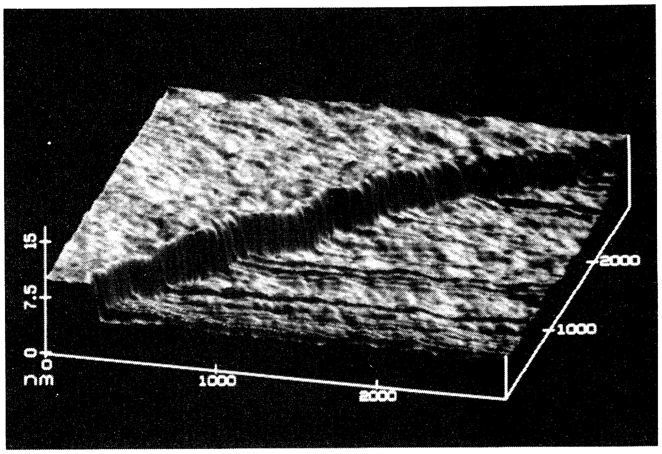


FIG. 2. AFM image of the edge of a hole in a transferred bilayer. The height of the step is 54 Å.

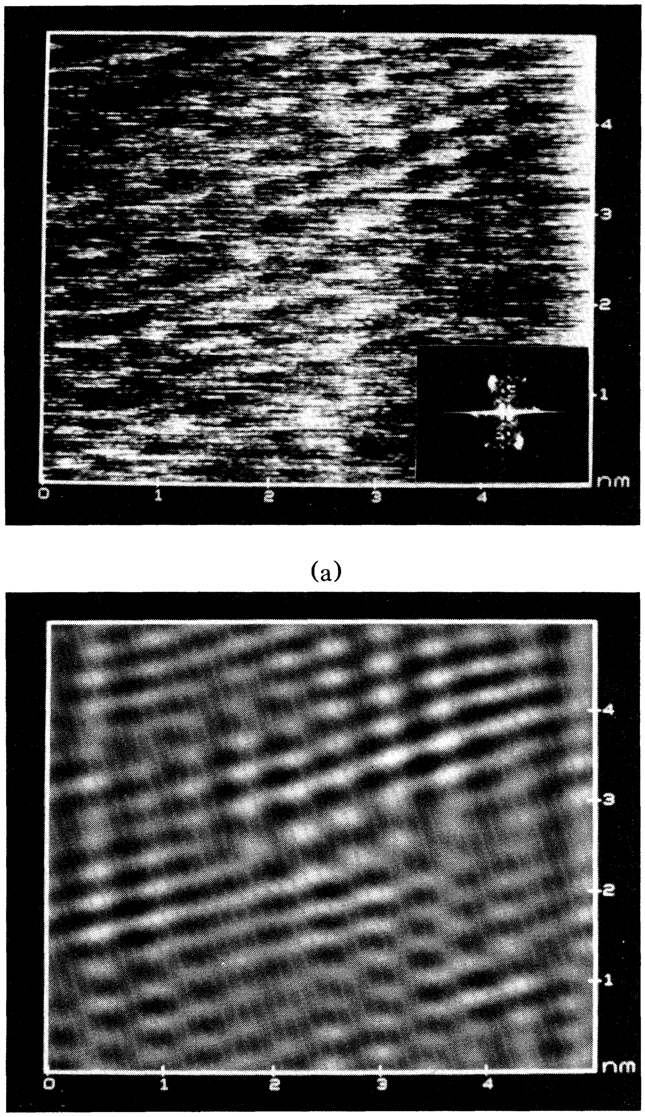
sheets for both calibrations. All images presented here were obtained with a cantilever of spring constant $k=0.58$ N/m. Pictures were taken indifferently in constant-force or constant-height modes. Typical values of forces used in these experiments were in the range 1×10^{-8} to 2×10^{-8} N; for higher forces, we observed surface degradation at large scales or molecular-detail disappearance at small scales, as already reported [11].

Figure 1 shows an optical microphotograph of the bilayer-covered substrate. Obviously this method of observation allows a quick and easy characterization of LB films. Within the bilayer, defects, whose lateral extension is of a few microns, can be detected this way. From this visual inspection one may expect that these defects are about one bilayer deep. Otherwise the transferred bilayer was found to be homogeneous on the whole substrate.

We first performed AFM experiments on bare and silanated wafers in order to measure the rms roughnesses of the substrates, which were found to be 5 Å for bare wafers and 3.5 Å for silanated ones, at the 1-μm scale, in agreement with x-ray reflectivity data [18]. This result confirms the smoothing effect of the silane layer. At the same scale, the rms roughness of the bilayer surface was found to be equal to that of the silane layer, i.e., 3.5 Å. Furthermore, we have observed that the bilayer closely follows small-scale rugosity of the substrate. Large-scale pictures obtained by AFM reveal, within the bilayer, the existence of the same defects as those seen with optical microscopy (see Fig. 2). It should be noticed that no deterioration of the edge of the bilayer is evidenced in this picture; this shows that the horizontal stresses applied to the bilayer, while scanning, are weak compared to the cohesive interactions within the bilayer. The height of the bilayer could be deduced from such pictures and was found to be 54 ± 4 Å. This value is in good agreement with twice the length of the fully extended arachidic acid molecule which is 27 Å long. This result suggests an almost perpendicular orientation of arachidic acid molecules with respect to the substrate surface.

Finally, we also got high-resolution images which allowed us to obtain the 2D crystallographic structure of the LB film [Fig. 3(a)]. The Fourier transform of this image [Fig. 3(a) inset] demonstrates that arachidic molecules are arranged on a distorted hexagonal lattice slightly elongated along the scanning direction. From measurements of molecular spacings, one gets an area per molecule, $A_{\mathrm{AFM}}=20\pm3$ Å^2, which is in good agreement with the area deduced from isotherms, $A_{\mathrm{iso}}=20$ Å^2. At this point it is difficult to identify the origin of the distortion of the hexagonal lattice; this may be an intrinsic structural property of the bilayer, or may originate from tip-bilayer interaction while scanning. By digital filtering, keeping only the six spots of the Fourier-transformed image in the reciprocal space, the presence of a pair of dislocations is clearly evidenced in the center of the image [Fig. 3(b)]. It should be pointed out that such a filtering procedure cannot induce the observed defects. Indeed at least one of the dislocations can be seen on the raw image [on the left-hand side of Fig. 3(a)]. On the contrary, filtering without care leads to a perfect lattice structure thus hindering the presence of such defects. We were indeed able to obtain such a defect-free lattice by decreasing the size of the conserved frequency domains around the most intense spots of the 2D Fourier transform.

At the moment it is rather difficult to estimate the surface density of such defects and to rule out the presence of isolated dislocations. Clearly, one should need to get molecular-scale-resolved images of larger size. Nevertheless, the observation of such defects at a molecular scale is of high importance, since pairs of dislocations are the intrinsic defects of two-dimensional solids [19]. Indeed



(a)

(b)

FIG. 3. (a) Molecular-resolved image of a bilayer by AFM. Inset: The Fourier transform of this image exhibiting six spots of different intensities characteristic of a distorted hexagonal lattice. (b) In this image, only the spatial frequencies corresponding to the six spots of the Fourier-transformed image have been kept. A pair of dislocations is then clearly visible in the center of the image.

the creation of an isolated dislocation requires an infinite elastic energy which grows logarithmically with the size of the system; in contrast, the creation of a pair of dislocations requires a finite energy and does not disrupt molecular ordering at large scales. Thus, even at low temperatures, pairs of dislocations should exist in two-dimensional solid phases.

All these results show the ability of local probe microscopies to give at once a great deal of information about structural properties of LB films. In particular, these are the only techniques which allow a direct visualization of their crystallographic organization at the molecular level, together with their intrinsic defects. Furthermore, combining such AFM experiments with STM ones should allow a direct comparison between structures determined by both techniques and thus decide whether or not tunneling of electrons is possible through those organic layers.

The ability to observe clearly such topological defects should allow a new approach to the two-dimensional physics involved in such systems. In particular, the Kosterlitz-Thouless-Halperin-Nelson-Young theory has pointed out the role played by defects like dislocations and disclinations in the melting of a two-dimensional solid [20–22]. They predicted two continuous melting transitions for a 2D crystal instead of a single first-order transition as for three-dimensional solids. The 2D crystal first melts into a "hexatic" phase, which shows a short-range positional order and a long-range orientational order, by the unbinding of dislocations pairs. The second transition towards an ordinary isotropic fluid (characterized by an exponential decay of both translational and orientational order on the same length scale) then proceeds by unbinding of disclinations pairs. Although some evidence of these transitions has already been given by experiments and computer simulations, there is actually no consensus for the melting mechanism of a 2D solid. In this regard the pictures shown here suggest that LB bilayers do possess defects inherent to two-dimensional crystals. Further studies, particularly by varying temperature, could possibly help our understanding of two-dimensional melting mechanisms by direct visualization of structural defects.

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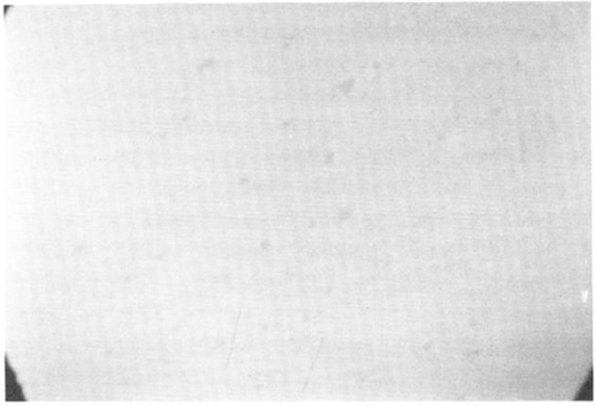

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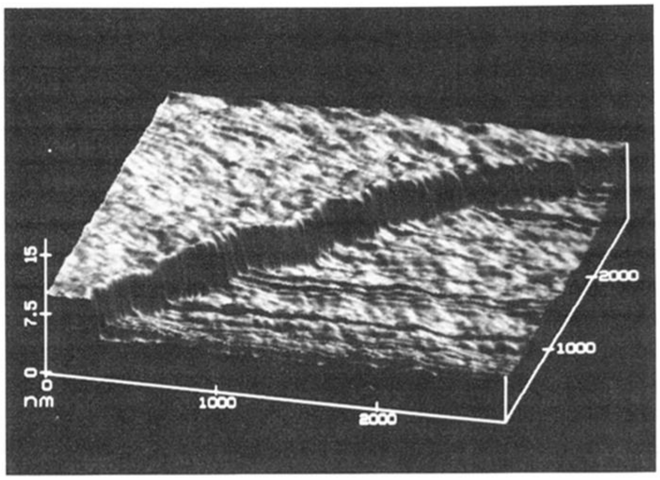

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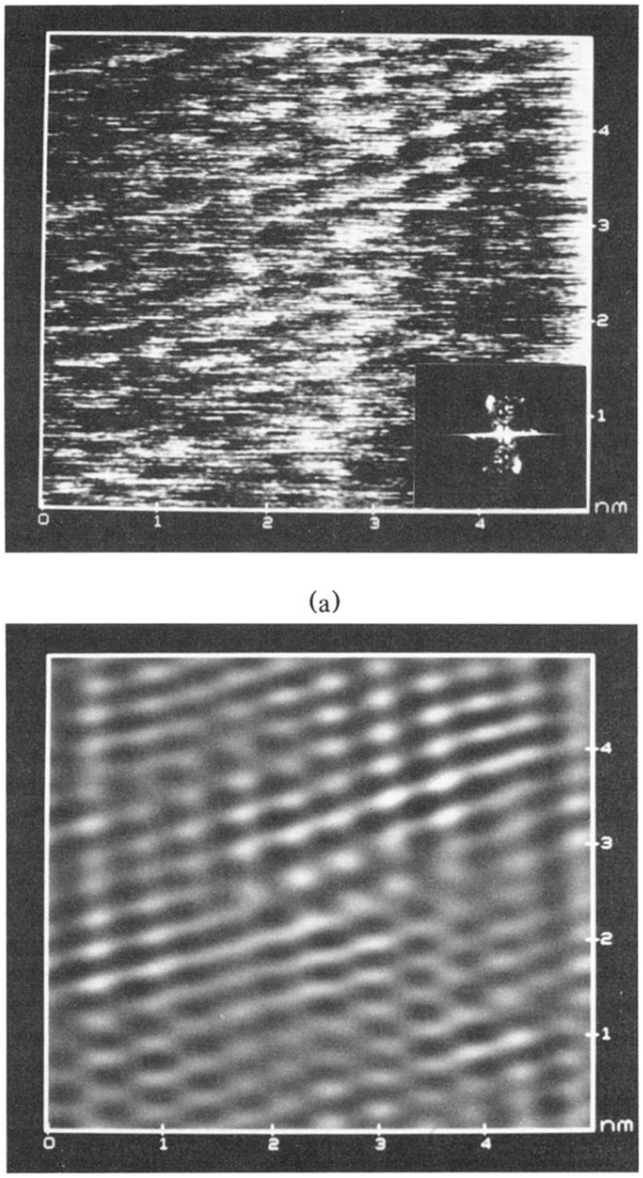

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