

## Skeletonization as a Probe of Interlayer Correlations in Langmuir–Blodgett Films

M. L. Kurnaz and D. K. Schwartz\*

Department of Chemistry, Tulane University,  
New Orleans, Louisiana 70118

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### Introduction

In 1937 Katherine Blodgett demonstrated that immersing certain Langmuir–Blodgett (LB) films in benzene for short periods of time “skeletonized” the films.<sup>1</sup> She determined, using optical interference methods on optically-thick multilayers, that the refractive index of the skeletonized films was reduced but the film thickness remained approximately equal to that of the original film. She hypothesized that the skeletonization removed some molecules, resulting in gaps throughout the films but that the overall film retained its integrity.

Since the films successfully skeletonized are prepared at a pH lower than necessary for full conversion of free acid to soap, it is reasonable to assume that the molecules removed by dissolution in benzene correspond to the free acid and that the molecules converted to soap remain in the film. The kinetics of this skeletonization process and the optical constants of the resulting films have been previously studied.<sup>1–5</sup> However, the details of the mixing of acid and soap molecules and, hence, the structure of the skeletonized film have remained a mystery.

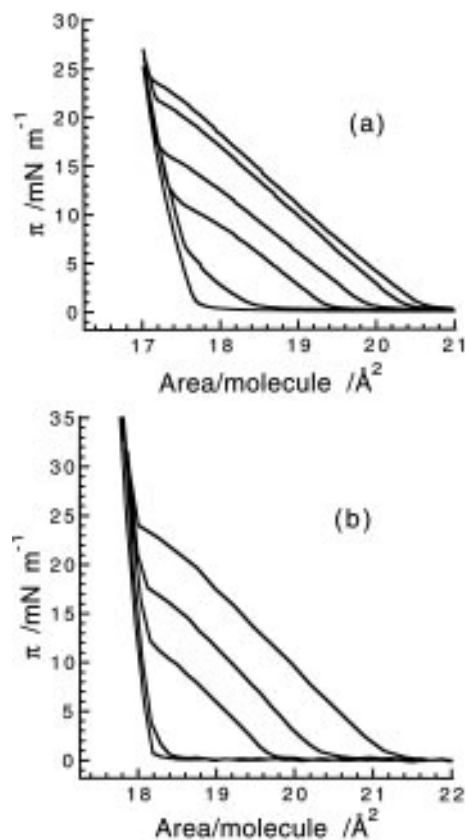
### Experimental Details

Arachidic (eicosanoic) acid was spread from chloroform solution to an area of about 40 Å<sup>2</sup>/mol on a 5 × 10<sup>−4</sup> M CdCl<sub>2</sub> or CaCl<sub>2</sub> solution (Millipore Milli-Q UV+ water was used) contained in a Teflon NIMA LB trough held at 22 ± 0.5 °C. The pH was adjusted between 4.8 and 5.6 by addition of HCl, to 6.2 by addition of NaHCO<sub>3</sub>, and to higher pH by addition of NaOH. Three molecular layers were transferred to mica substrates by successive vertical dipping at 1.6 or 5 mm/min while the monolayer was held at constant surface pressure ( $\pi$  = 25 or 30 mN/m). Mica substrates were freshly cleaved immediately before use. For CdA<sub>2</sub>, transfer ratios were typically 100 ± 5% at pH ≤ 5.8; however, at higher pH, the third layer had a transfer ratio of about 80% at 1.6 mm/min and 100% at 5 mm/min. For CaA<sub>2</sub>, transfer ratios were 100 ± 5% at pH ≥ 6.9. At lower pH the first layer transferred well; however, the transfer ratio of the second layer was very low or even negative indicating that the first layer was partially removed. We did not, therefore, study CaA<sub>2</sub> films at pH < 6.9.

Films were skeletonized by immersion in gently-stirred benzene. AFM images of films immersed for 1–2 min showed the same general characteristics as the images shown below; however, a number of loosely-attached “blobs” were also observed. After immersion in benzene for longer times, 10–30 min, this contamination was removed and good images of the surface were reproducibly obtained. Imaging was performed using a Nanoscope III atomic force microscope (AFM) under ambient conditions using a 15 μm × 15 μm scanner and a silicon nitride tip on an integral cantilever with spring constant 0.12 N/m in contact mode. Images were obtained from at least five macroscopically-separated areas on each sample. Representative images are presented below.

\* To whom correspondence should be addressed: tel, 504-865-5573; fax, 504-865-5596; e-mail, dks@mailhost.tcs.tulane.edu.

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**Figure 1.** (a) Isotherms obtained of arachidic acid deposited on a 5 × 10<sup>−4</sup> M CdCl<sub>2</sub> solution at pH = 4.8, 5.0, 5.2, 5.4, 5.8, and 6.2 respectively, top to bottom. Note that the diagonal region representing the L<sub>2</sub> phase becomes less prominent with increasing pH until it finally disappears. The “lift-off” point, i.e., the area at which the surface pressure begins to deviate from zero, is an indicator of the relative fractions of arachidic acid and the cadmium soap. (b) Isotherms of arachidic acid on a 5 × 10<sup>−4</sup> M CaCl<sub>2</sub> subphase at pH = 5.7, 6.4, 7.0, 7.5, and 7.8 respectively.

### Results

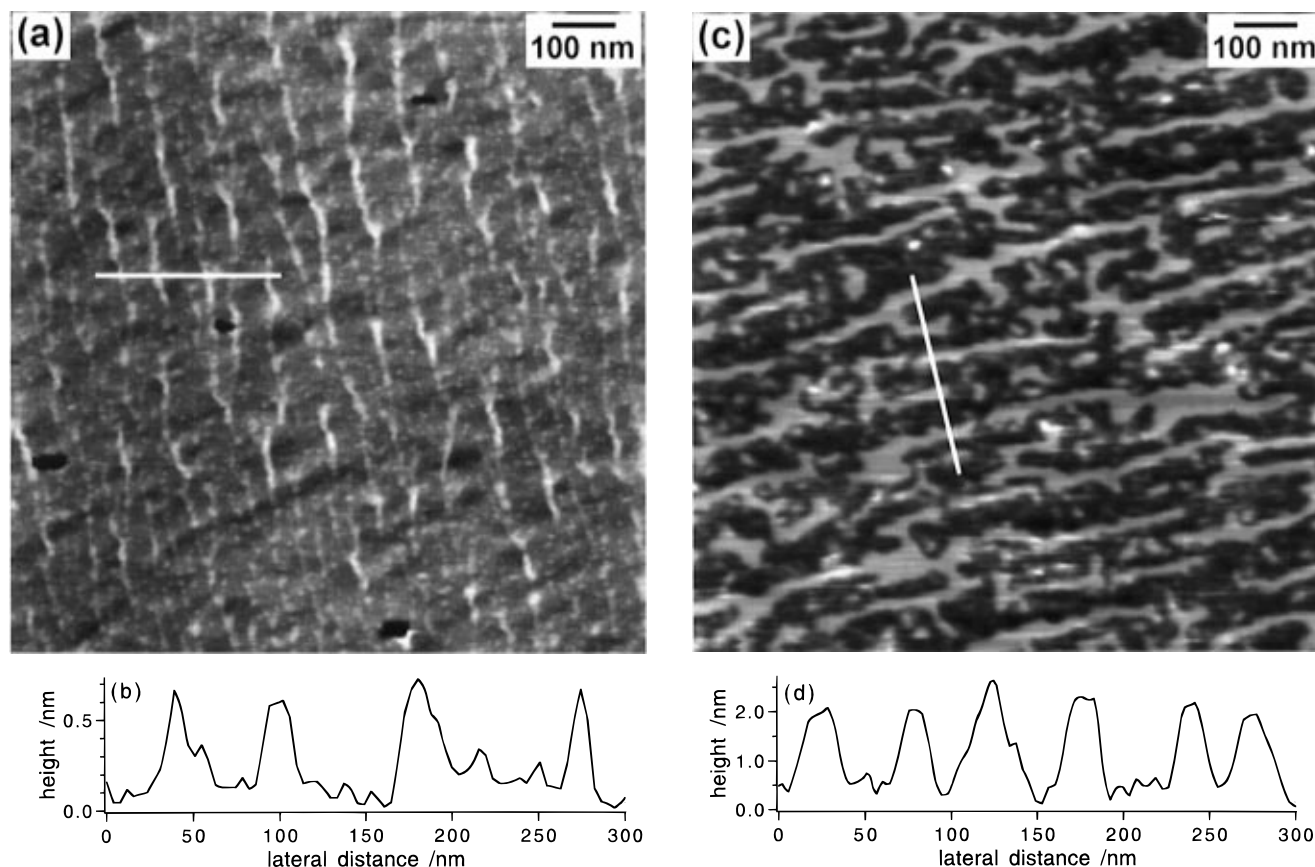
The surface pressure–area isotherms, using either Cd<sup>2+</sup> or Ca<sup>2+</sup>, show qualitatively similar systematic variation as a function of pH (see Figures 1). At low pH, the fatty acids are un-ionized and the isotherms are indistinguishable from an isotherm of arachidic acid on pure water (with no cation present). The region of intermediate slope between about 21 and 18 Å<sup>2</sup>/mol, corresponding to the L<sub>2</sub> phase,<sup>6</sup> ends at a kink at about 24 mN/m which signals a transition to the LS phase. As the pH is increased, the L<sub>2</sub> phase is observed over a smaller range of  $\pi$  and area/mol until at high enough pH the L<sub>2</sub> phase is altogether absent. A further increase in pH does not result in any additional change in the isotherm. This evolution occurs for Cd<sup>2+</sup> over a pH range of 4.8–6.2 and for Ca<sup>2+</sup> over a range of 5.7–7.8. These isotherms are consistent with fatty acid salt isotherms in the literature.<sup>7,8</sup>

The surface morphology of a CdA<sub>2</sub> film is distinctly different for a film prepared at pH = 5.0 (Figure 2), where the acid is only about 10% converted to soap, and pH = 5.8 (Figure 3), where the acid is about 80% converted to soap. At pH = 5.0 narrow ridges (0.4–0.8 nm high) are observed aligned in the dipping direction (Figure 2a). These films were extremely delicate and were successfully

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**Figure 2.** AFM images of three-layer LB films of arachidic acid/cadmium arachidate,  $1\ \mu\text{m} \times 1\ \mu\text{m}$ , deposited at pH = 5.0, before and after skeletonization. (a) In the “as-prepared” film, narrow ridges about 0.6 nm high are visible separated by about 50 nm. The ridges are aligned with the dipping direction. (b) The height profile associated with the line drawn on (a) displaying the heights of typical ridges (0.4–0.8 nm). (c) After skeletonization, ridges about 2–2.5 nm high (aligned with the dipping direction) are observed separated by about 50 nm. (d) the height profile associated with the line drawn on (c) displaying the heights of typical ridges.

imaged only at forces less than about 1 nN. We were unable to obtain molecular resolution images. Figure 2c shows a film prepared at pH = 5.0 that has been “skeletonized” (soaked in benzene) to remove the free acid molecules from the film.<sup>1</sup> As in the unskeletonized film at the same pH, parallel ridges, approximately 50 nm apart, are aligned in the dipping direction. However, the ridges are 2–2.5 nm above the lower adjacent areas. This height difference is consistent with the length of a single molecule (fully extended length is 2.8 nm) and implies that monolayer patches of arachidic acid have been removed.

At pH = 5.8 pits and holes of various depths appear scattered on the surface of CdA<sub>2</sub> films (Figure 3a). There are a significant number of holes  $2.5 \pm 0.3$  nm deep as well as holes  $5.0 \pm 0.5$  nm deep. These monolayer and bilayer deep defects have been previously observed<sup>9–15</sup> and are present as well in films prepared at higher pH. However, there are numerous irregular shallow pits (0.8–1.5 nm deep) in the surface of the pH = 5.8 film that do not appear at higher pH. Molecular resolution images

can be obtained routinely on the flat raised regions of these films.<sup>16,17</sup> After skeletonization (Figure 3c), the morphology appears as a maze of high regions separated by lower trenches. The height profile in Figure 3d shows that the raised areas are about 5–6 nm higher than the lower adjacent areas. This implies that bilayer patches of arachidic acid have been removed during skeletonization.

At values of pH between 5.0 and 5.8 alternating bands of the low pH and high pH textures are observed perpendicular to the dipping direction. This has been described previously.<sup>18</sup> The relative fractions of high areas and low areas on the surface show a systematic dependence on pH that is generally consistent with the relative proportion of free acid and soap expected from the isotherms.

For CaA<sub>2</sub>, however, the change in surface morphology with pH is quite subtle. Figure 4a shows a film prepared at pH = 6.9 where the acid is approximately 45% converted to soap. In addition to scattered bilayer-deep holes an apparently random and meandering network of two different surface heights is observed. The height difference between high and low regions is only 0.2–0.3 nm and the domains are typically 20–50 nm wide. After skeletonization (Figure 4c), labyrinthine domains are still observed. However, a significant part of the top layer has been removed and the height difference between the

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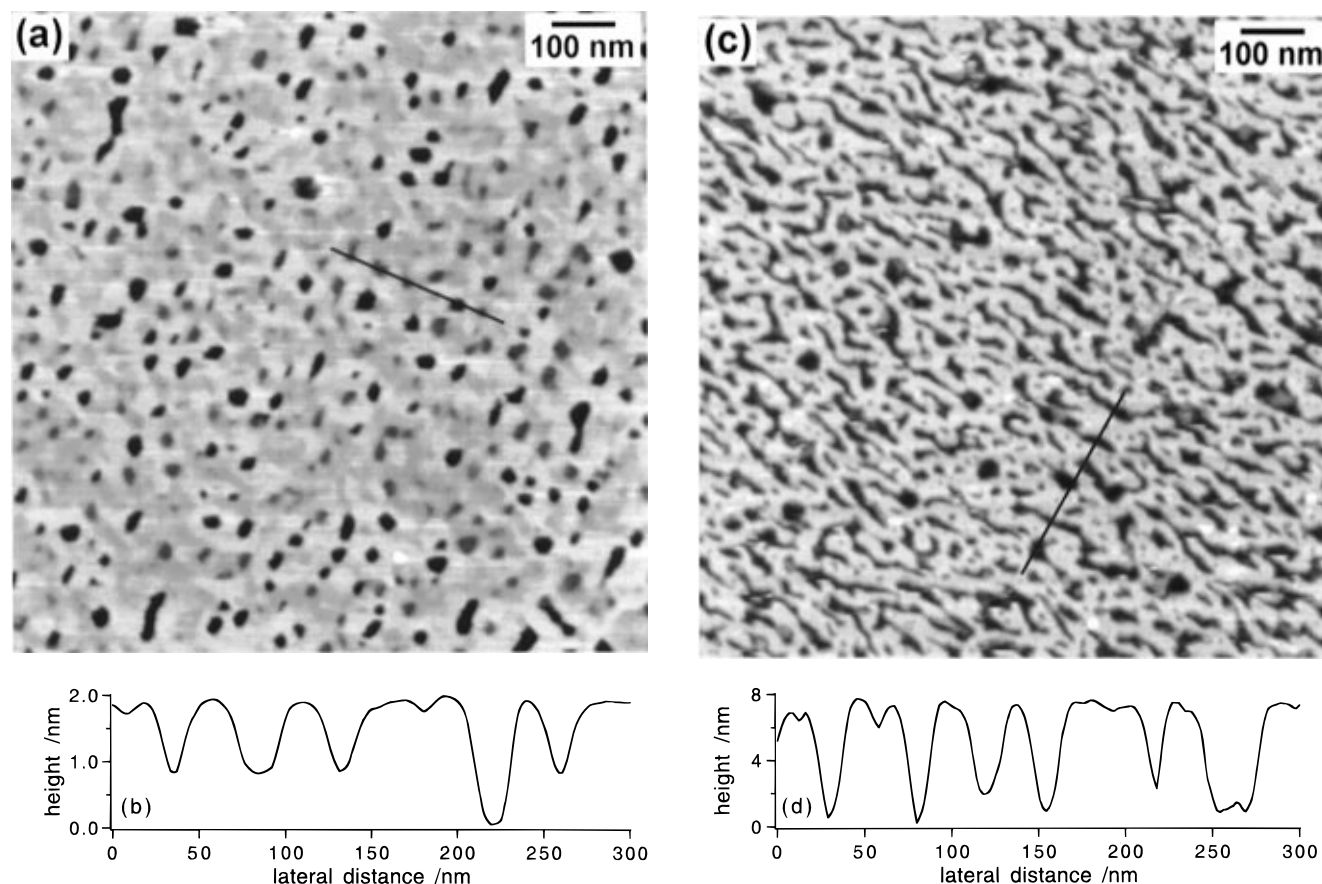
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**Figure 3.** AFM images of three-layer LB films of arachidic acid/cadmium arachidate,  $1\ \mu\text{m} \times 1\ \mu\text{m}$ , deposited at pH = 5.8, before and after skeletonization. (a) Before skeletonization, numerous holes are visible with depths of about 2.5 nm or 5.5 nm corresponding to monolayer and bilayer defects. In addition, pits  $1.2 \pm 0.3\ \text{nm}$  deep are observed. (b) The height profile associated with the line drawn on (a) displaying the depths of several pits and one monolayer hole. (c) After skeletonization, trenches 5–6 nm deep are observed. (d) The height profile associated with the line drawn on (c) displaying the depths of typical trenches.

highest remaining regions and the neighboring lower areas is about 3 nm, consistent with the height of a monolayer. Monolayer and bilayer-deep trenches are observed in the fraction of the surface from which the top layer was apparently removed by skeletonization.

Figure 5 shows images obtained on  $\text{CaA}_2$  prepared at pH = 7.5 (90% converted to soap). Surprisingly, the surfaces of films prepared at this pH are qualitatively the same as at the lower pH. In all cases, a network of domains differing by about 0.3 nm in height is observed on the as-prepared film. The lower regions appear to cover slightly less of the surface with increasing pH and the lateral dimension of the low domains increases slightly. However, the respective surface coverage of high and low regions are not consistent with the proportions of free acid and soap predicted by the isotherms (Figure 1b). Increasing the pH even more (as far as 9.3) does not result in any additional change in surface morphology.

The skeletonized films did not appear to have reorganized in such a way as to become thicker than three layers as has been observed in films left immersed in aqueous solution.<sup>19</sup> The largest height differences measured from the highest to lowest parts of an image were in the range 8–9 nm. By increasing the normal force exerted by the AFM tip, we were able to dig holes through the film to a uniformly flat surface that we believe is bare mica. The height difference between the bottom of these “dug” holes and the highest parts of the film was also in the range 8–9 nm.

## Discussion

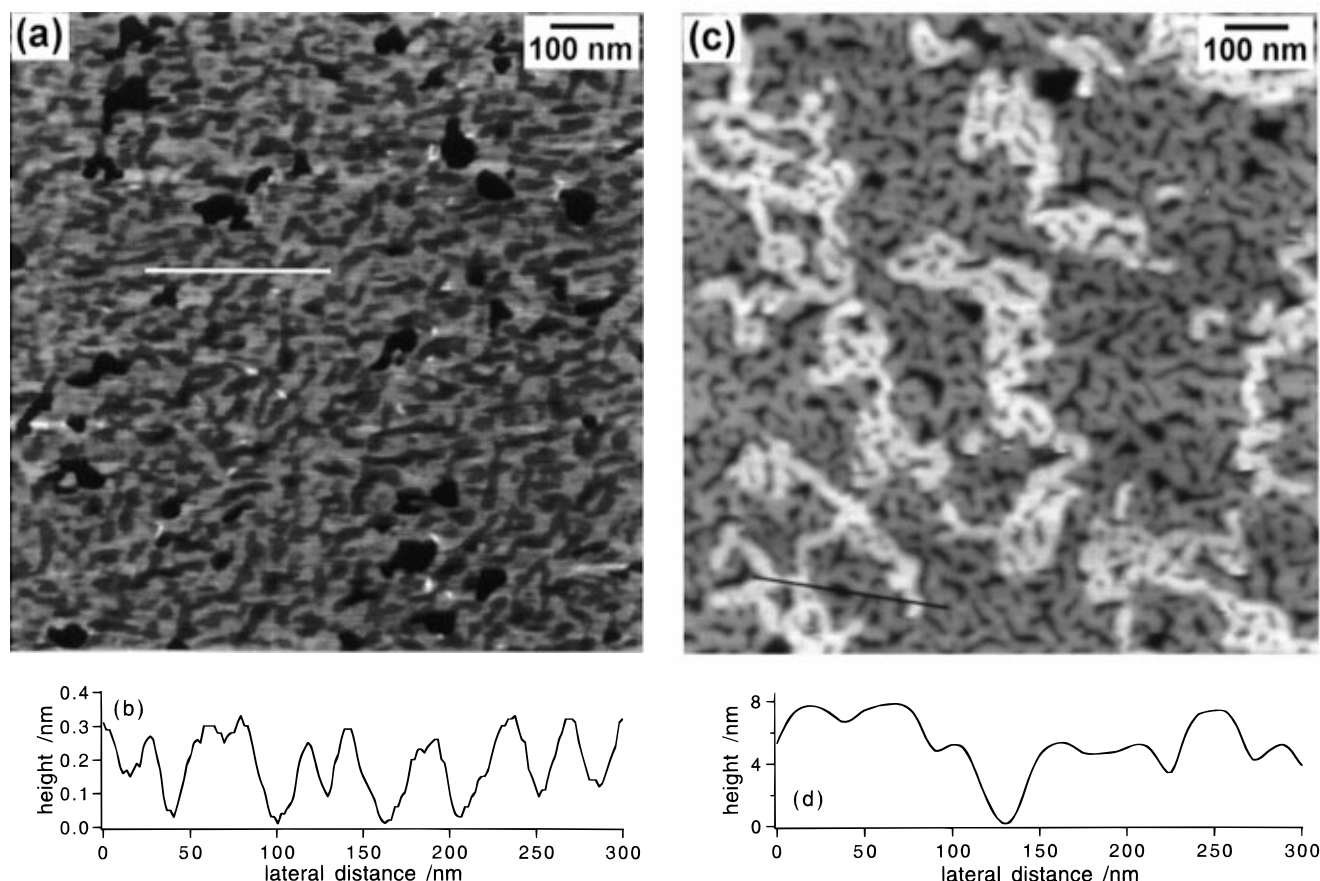
The systematic trend of the isotherms with pH shown in Figure 1 has traditionally been interpreted as due to an increasing fraction of soap in the monolayer. An order parameter defined with respect to the “lift-off” area of the isotherm is in excellent agreement with the mole fraction of cadmium and calcium soap incorporated in an LB film directly measured by surface analytical techniques such as X-ray photoelectron spectroscopy, Fourier transform infrared spectroscopy, and neutron activation analysis.<sup>20,21</sup> Since coexistence of multiple structures was not observed using grazing incidence X-ray diffraction on monolayers of calcium and copper(II) fatty acid salts on the water surface, we assume that the phase separation occurs during transfer.

The images of  $\text{CdA}_2$  surfaces are consistent with phase separation of acid-rich and soap-rich phases since the relative surface coverage of high and low areas varies in the expected way with pH. We suggest that the differences in surface morphology at low and high pH are due to the phase-separated domains being correlated only within the topmost monolayer at low pH and across at least a bilayer at high pH. Several observations are consistent with this hypothesis. The height difference between domains is 1.2 nm at high pH, approximately equal to the expected difference in bilayer thickness between the C form of arachidic acid (4.4 nm)<sup>22,23</sup> and the untitled CdA structure

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**Figure 4.** AFM images of three-layer LB films of arachidic acid/calcium arachidate,  $1 \mu\text{m} \times 1 \mu\text{m}$ , deposited at pH = 6.9, before and after skeletonization. (a) The surface of the film before skeletonization appears as a random labyrinthine pattern of high and low regions with a typical lateral dimension of 20–40 nm. Scattered bilayer holes are also observed. (b) The height profile associated with the line drawn on (a) demonstrating that the domains have a height difference of 0.2–0.3 nm. (c) After skeletonization, most of the top layer has been removed. The remains of the top layer retains a labyrinthine morphology. Most of the underlying layer is still present and marked by monolayer and bilayer trenches. (d) The height profile associated with the line drawn on (c) showing the height difference of about 3 nm between the remains of the top layer and the underlying layer as well as the depth of a bilayer hole (6 nm) in the underlying layer.

(5.6 nm).<sup>24–26</sup> At low pH the height difference is only about half this value. Furthermore, when the free acid is removed by skeletonization, trenches one monolayer deep are observed at low pH, implying that regions of arachidic acid in the top layer were sitting on top of regions of the cadmium salt not removed by skeletonization. However, at high pH, entire bilayers are removed, implying that the phase separation is correlated through at least a bilayer. Also, mechanical stability and the ability to obtain molecular resolution AFM images in CdA (which can be done only at high pH) has been previously shown to be connected with the headgroup–headgroup interface in combination with the cation.<sup>16</sup>

We cannot, however, correlate the details of the phase separation in CaA<sub>2</sub> with the relative proportion of acid and salt expected at a given pH. In particular, at pH  $\geq 8$  the film should be composed completely of calcium soap. However, we observe coexistence of surface regions with different heights at pH as high as 9.3. It is likely, therefore, that the coexisting areas are due to different molecular arrangements. For example, the chains may be tilted by

different angles from the layer normal resulting in a difference in surface height. This phenomenon has been previously observed in magnesium<sup>27</sup> and barium<sup>28,29</sup> fatty acid salts.

Nevertheless, the skeletonized CaA<sub>2</sub> films have a distinctly different appearance than the skeletonized CdA<sub>2</sub> films at high pH. In particular, the dominance of monolayer height differences between the remaining parts of the top layer and adjacent lower areas in CaA<sub>2</sub> implies that monolayer patches of material are removed by skeletonization. We suggest, therefore, that the structure of CaA<sub>2</sub> films is correlated primarily within a given layer and that the correlations do not extend to the neighboring layer. This implies that the primary role of the Ca<sup>2+</sup> ion is to bind arachidate ions within a layer. This is in contrast to the predominance of bilayer height differences in skeletonized CdA<sub>2</sub> which are clear evidence that domains extend at least two layers deep. This may be associated with an interlayer bridging role of the Cd<sup>2+</sup> ion. These conclusions are consistent with direct measurements of crystal structure correlations made by grazing incidence X-ray diffraction. Tippmann-Krayer *et al.*<sup>26</sup> determined that the molecular lattice in CdA<sub>2</sub> multilayers was correlated 6–7 nm in the surface normal direction,

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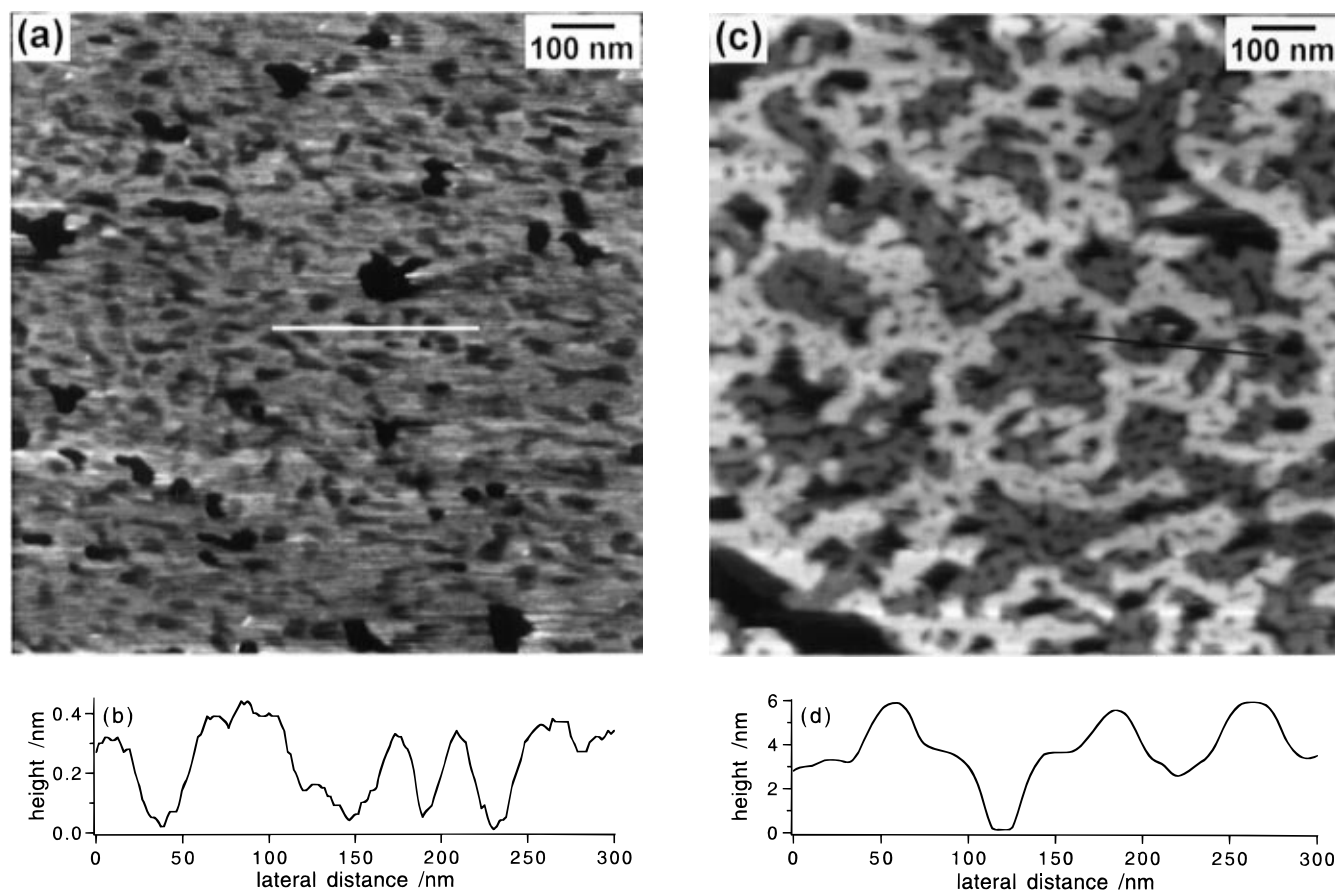
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**Figure 5.** AFM images of three-layer LB films of arachidic acid/calcium arachidate,  $1\ \mu\text{m} \times 1\ \mu\text{m}$ , deposited at pH = 7.5, before and after skeletonization. (a) Before skeletonization coexisting low and high domains are observed as well as occasional bilayer holes. (b) The height profile associated with the line drawn on (a) demonstrating that the domains have a height difference of 0.2–0.3 nm. (c) After skeletonization, much of the top layer has been removed and the underlying layer is marked by monolayer and bilayer trenches. (d) The height profile associated with the line drawn on (c) showing the height difference of about 3 nm between the remains of the top layer and the underlying layer as well as the depth of a monolayer trench (3 nm) in the underlying layer.

consistent with slightly more than a bilayer. However, a recent study by Malik *et al.*<sup>30</sup> on  $\text{CaA}_2$  has shown that crystalline correlations are only within each layer of a multilayer film.

### Conclusion

Phase separation at small (20–50 nm) length scales is observed by AFM in mixed LB films of arachidic acid and calcium or cadmium arachidate. In  $\text{CdA}_2$  the surface structure of the films is consistent with gradual conversion of free acid to soap as a function of pH. Skeletonization of these films appears to remove patches of monolayer at low pH and bilayer at high pH. In  $\text{CaA}_2$  coexisting labyrinthine domains appear at values of pH between 6.9

and 9.3. The behavior of the surface structure with pH is not consistent with phase separation of acid and soap but with coexisting regions of two different molecular arrangements. In contrast to  $\text{CdA}_2$ , skeletonization appears to remove monolayer patches of the film. This implies that interlayer correlations are effectively absent in  $\text{CaA}_2$  while correlations extend to the adjacent layer in  $\text{CdA}_2$ .

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