X-Ray Diffraction Studies of Organic Monolayers on the Surface of Water

P. Dutta, J. B. Peng,[a] B. Lin, J. B. Ketterson, and M. Prakash[b]
Department of Physics and Astronomy, Northwestern University, Evanston, Illinois 60201

P. Georgopoulos
Department of Materials Science and Engineering, Northwestern University, Evanston, Illinois 60201

and

S. Ehrlich
School of Materials Engineering, Purdue University, West Lafayette, Indiana 47907

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We have used synchrotron radiation to study organic monolayers on water ("Langmuir films"). At high monolayer pressures, lead stearate [$Pb(C_{17}H_{35}COO)_2$] shows a powder peak at 1.60 Å^{-1}, implying an area per unit cell of 17.8 Å^2 if the lattice is triangular. The correlation length is about 250 Å. Lignoceric acid ($C_{23}H_{47}COOH$) shows a similar peak even though no heavy ions are attached. When the pressure is reduced, the peak in lead stearate does not observably move or broaden; below the "knee" in the isotherm, however, the peak height decreases slowly with increasing area, implying a first-order melting transition.

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An amphiphilic molecule, such as a fatty acid or salt, has an ionic (hydrophilic) "head" attached to a long hydrocarbon (hydrophobic) "tail"; if insoluble, these molecules can be spread as monolayers ("Langmuir films") on the surface of water. In 1917, Langmuir[1] described an apparatus allowing a systematic variation of the area per molecule (A) with simultaneous monitoring of the two-dimensional pressure (π). Since then, a vast amount of π-A data on various materials has appeared in the literature,[2,3] and introductory discussions have found their way into undergraduate texts.[4] Although details vary, the isotherms of many materials show abrupt changes of slope, suggesting phase transitions. By consensus, the highest-density continuous section of the isotherm is called a solid. In the low-density limit one reasonably expects a gas phase; in between, a variety of phases (such as orientationally ordered and disordered, and striped) have been postulated[5] to explain the multiple singularities observed in some π-A diagrams.

However, although nearly seventy years have passed since the original isotherm studies, only indirect evidence of positional order and melting transitions has been available. Structure inferences from measurements of other macroscopic properties, such as the shear modulus,[6] are valuable but inevitably ambiguous (e.g., an amorphous solid supports shear but no long-range positional order; a polycrystalline solid may appear to have no shear modulus). A more microscopic picture comes from fluorescence micrographs (resolution $\simeq 2$ μm) by Möhwald and co-workers[7]: Using trace amounts of dye, they see dark patches indicating islands of a condensed phase that has expelled the dye. Electron diffraction data are unavailable because water cannot be introduced into a vacuum; although numerous x-ray studies have recently been performed of monolayers adsorbed on single-crystal substrates, Langmuir films present a greater technical problem. This is because water creates a large diffuse background, and also because the plane normal cannot be oriented to suit the experimenter's convenience. Much more is known about the structure of Langmuir-Blodgett monolayers[8] and multilayers,[9-11] but these are formed by transfer of monolayers from water to solid substrates. The structure and properties of such a film cannot be assumed to be the same as that of the monolayer on water; the latter is of particular interest because the isotherms suggest rich unexplored phase diagrams in many cases. (Of course, the surface tension of a Langmuir-Blodgett film cannot be easily monitored or changed.) Further, liquids supply "ideally smooth" substrates for the study of melting and other phase transitions in two dimensions.

Recently, we performed diffraction studies of the in-plane structure of Langmuir films at beam line X-18A of the National Synchrotron Light Source. A schematic of our experimental apparatus (not to scale) is shown in Fig. 1. We used a 6×6-in.^{2} Teflon trough, with three unobstructed sides (on the fourth side, x rays are blocked by a barrier used to change the monolayer area). In order to allow x rays to be incident at grazing angles, the trough must be overfilled so that there is an inverted meniscus. Our subphase was either ultrapure water (for acid monolayers) or an $8\times10^{-5}M$ solution of lead acetate (for lead-salt monolayers). To make a monolayer, we prepared a 1.87×10^{15}-molecules/μl solution of either stearic or lignoceric acid in heptane, and dropped about 50 μl onto the surface with a micropipette. The heptane

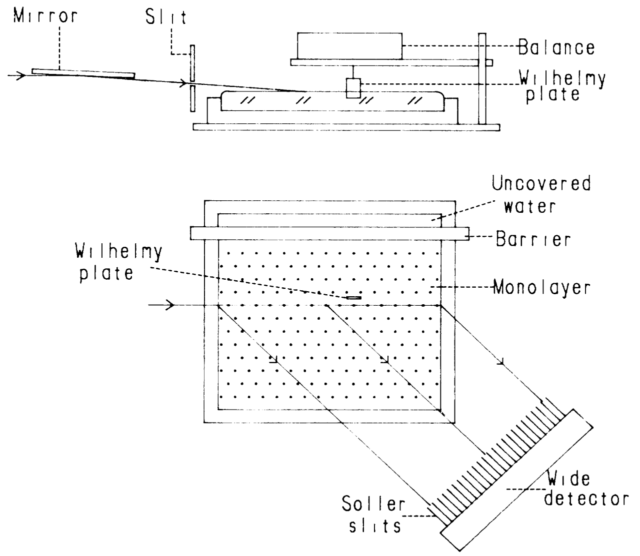

FIG. 1. Schematic of experimental setup, viewed from the side (top) and from above (bottom). The vertical angle of incidence is much smaller than it appears, and the size of the mirror and its distance from the rest of the apparatus are much larger.

spreads rapidly and evaporates, leaving the acid distributed over the surface. If there are lead ions in the subphase, the insoluble lead salt is produced in the monolayer.

The surface pressure was measured with a Wilhelmy technique[12] using filter paper suspended from an overhanging Cahn model RM electrobalance. Thus, by our moving the barrier and reading the pressure, isotherms can be determined directly on the x-ray trough. Any attempt to reduce the area below about 19 Å^2 per chain leads to irreversible collapse into a three-dimensional phase; this limiting area is determined by the lateral dimensions of hydrocarbon chains. This well-known collapse behavior is very different from that of (say) physisorbed monolayers on solid substrates: The Langmuir films sustain metastable pressures much higher than the pressure of a monolayer in equilibrium with bulk material ("equilibrium spreading pressure"), and the transition to the bulk phase is marked by a catastrophic drop in pressure without intervening multilayer stages. Films that can be compressed to pressures higher than the equilibrium spreading pressure (typically, a few dynes per centimeter), and whose pressures increase upon compression, must be monolayers.

We performed the diffraction experiment on a Huber model 424 horizontal-scanning diffractometer placed on an adjustable-height table. The table was loaded with cinder blocks to reduce vibration, and layers of cork and plastic foam were placed under the trough for the same reason. The water surface was always mirror smooth during counting (the diffractometer software allowed for pauses between motor movements and counting; we found 5 sec more than adequate). The radiation from the synchrotron ring was monochromatized to $\lambda = 1.24$ Å with a flat double-crystal monochromator, and part of it was then reflected downwards with a 40-cm strip of float glass. The reflected beam (at an angle of $\approx 10^{-3}$ rad to the horizontal) was well separated from the direct beam by the time it reached the diffractometer, and could be isolated by horizontal slits. After coarse adjustments to the height of the trough, the water surface was brought into the beam by our adding or removing water while monitoring the beam intensity past the trough. In later runs we also used a cathetometer (resolution: 0.02 mm) to help us reproduce the water level after cleaning. At these small incident angles, the x rays illuminate a strip across the entire water surface; to collect as much diffracted intensity as possible, we used an 8-cm-wide detector with custom-made vertical Soller slits. Slits with angular acceptances of 0.5° and 0.1° (FWHM) were used during the experiments (in the region of the observed peak, these acceptances correspond to diffraction vector resolutions of 0.04 and 0.008 Å^{-1}).

Before a monolayer was spread, we observed a smooth scattered background; there were no features resembling the monolayer peaks reported below. The background changed every time we cleaned and added fresh water, probably because the water level could not be reproduced exactly. We performed diffraction scans on several separately prepared monolayers of lead stearate, with pressures initially in the range 18–25 dyn/cm. These pressures are well within the high-pressure incompressible section of the π-A diagram (the isotherm is shown later as part of Fig. 3; the monolayers collapse at 30–35 dyn/cm). Results from all the samples were consistent; we saw a single peak at a diffraction vector of 1.60 Å^{-1} (Fig. 2). The peaks vanished when the monolayers were swept from the surface with the barrier. The existence of a barrier limits our ability to rotate the trough without interrupting either the incident or the diffracted beam; we turned the sample over a 25° range and saw no changes in the peak intensity. We saw no other diffraction peaks either at higher or at lower angles (0.7 to 3.5 Å^{-1}).

The peak shown in Fig. 2 was determined with our higher resolution (8×10^{-3} Å^{-1} FWHM); counting time was 1–2 min per point, depending on the current in the synchrotron ring, and the monitor count was 4×10^5. The subtracted background varied from 330 to 310 counts across the range shown. The peak is obviously wider than the resolution function. The solid line in Fig. 2 is a fit with the three-dimensional finite-size (Gaussian) structure factor[13]; it gives a correlation length of about 250 Å. No satisfactory fit can be obtained with the power-law structure factor appropriate for an *infinite* two-dimensional solid.[15] The dotted line is a fit with the structure factor predicted for a *finite* two-dimensional solid[14]; the fitted correlation length is 280 Å and η is ap-

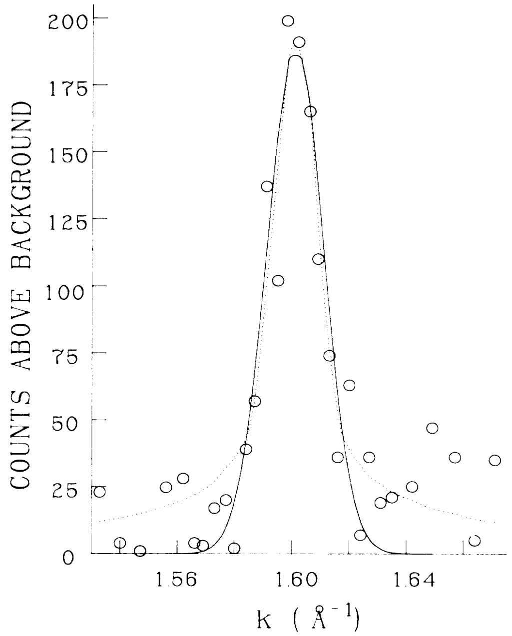

FIG. 2. Diffraction peak from a monolayer of lead stearate on water at a surface pressure of 18 dyn/cm. Counting time: approximately 1 min/point. The solid line is a fit with a Gaussian structure factor (Ref. 13); the dotted line uses the finite two-dimensional factor (Ref. 14).

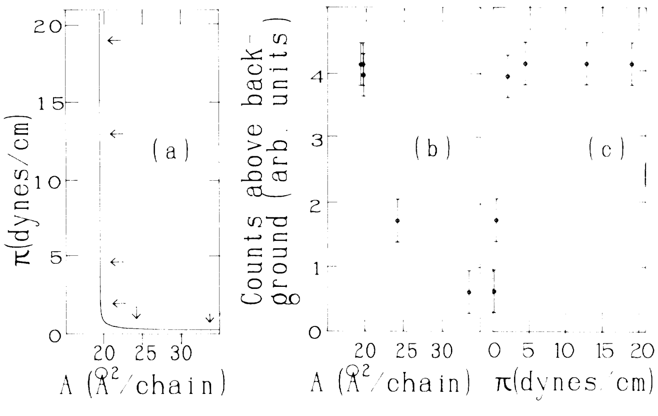

FIG. 3. (a) Pressure-area isotherm at room temperature for a lead stearate monolayer, indicating points at which diffraction data were obtained. (b) Peak height (peak counts minus hand-interpolated background) vs area per chain. (c) Same peak heights plotted vs monolayer pressure.

proximately 0.2. Both fits are essentially equivalent in the body of the peak; obviously, the peak shape is dominated by finite-size effects rather than by the effects of two dimensionality.

While we cannot deduce the structure of the monolayer from this single peak, we can say that it corresponds to the first peak of a triangular structure if the area of the unit cell is 17.8 Å^2. (The side of the triangle would then be 4.53 Å.) The peak cannot reasonably be ascribed to the lead ions, since lead is divalent and the area per ion cannot be much lower than 35–40 Å^2. However, the calculated area per unit cell *is* reasonable if the scattering is due to an array of vertical hydrocarbon chains: The average area from the π-A diagram is about 19 Å^2/chain and, since the monolayer could form dendritic domains not completely covering the surface (as seen in fluorescence micrographs[7]), the average area is only an upper limit to the single-crystal value. We also saw a peak similar to that in Fig. 2 from lignoceric acid. (Our attempts to study stearic acid were fruitless because it is too soluble to last through our long scans; lignoceric acid is 33% longer and thus much less soluble.) Therefore, although we initially used lead stearate in the expectation that lead ions would enhance the scattered intensity, it seems clear that the scattering is dominated by the hydrocarbons and that the introduction of heavy ions (undesirable in many cases) is unnecessary. The lead ions may be invisible because the aqueous environment causes them to be disordered or to have a high effective Debye-Waller factor; they may also be "screened" by the chains and by water molecules. The peak in lignoceric acid has essentially the same width as that for lead stearate but is slightly shifted, to 1.57 Å^{-1}. This may mean that the divalent lead ions pull the chains closer together, but it is also possible that longer chains are more likely to have "kinks" and thus will occupy slightly larger areas on the average.

For one monolayer, we determined the peak height at several positions along the π-A curve [Fig. 3(a)]. We saw no change in peak position or peak width in the entire range studied (~0–19 dyn/cm in pressure; 19–34 Å^2/chain in area). Because the isotherm has a "step-function" shape, we have plotted the same peak intensity data versus area per chain [Fig. 3(b)] and versus pressure [Fig. 3(c)]. It can be seen that the peak intensity is essentially constant in the high-pressure, constant-density section of the isotherm. It drops once we pass the "knee" of the isotherm, but only slowly as a function of area. It appears, therefore, that there is a first-order melting transition with a coexistence region starting at the knee. There should be an increase in the slope of the isotherm at the end of this region but, because the pressures in this region are smaller than our error in measuring them, such a feature is not expected to be visible.

We have thus demonstrated the feasibility of direct structural studies of Langmuir films. We have determined that positionally ordered phases exist in monolayers of lead stearate and lignoceric acid, and our data indicate that the melting of lead stearate monolayers is a first-order transition.

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[a] Permanent address: University of Science and Technology of China, Hefei, Anhui, People's Republic of China.

[b] Present address: Oak Ridge National Laboratory, Oak Ridge, TN 37830.

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