STRUCTURES AND SHEAR RESPONSE OF LIPID MONOLAYERS

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Introduction

Of the many systems now classified as 'soft condensed matter', lipids are some of the best known and most studied. Lipids occur most commonly in membranes, but the artificially created lipid systems known as Langmuir films (on water) and Langmuir-Blodgett films (on solid substrates) are in some ways better-defined and more easily controlled systems with which to address many of the same questions. Studies of these systems have a long and distinguished history, but in the past decade there has been an explosion of activity in this area, driven by the availability of new or more powerful experimental probes but also in part by the hope of producing new structured molecular materials and devices.

Today the focus of device-oriented research is shifting to self-assembled (chemisorbed) films, because it is recognized that these films are somewhat more stable under application conditions. This trend has resulted in a generally more appropriate view of Langmuir and Langmuir-Blodgett films as *model systems* with which to study the properties of organized molecular assemblies. These films are part of a larger class that includes membranes, lamellar paraffins and liquid crystals as well as self-assembled films, but with certain experimental and conceptual advantages (such as the ease with which the density may be varied, and the tethering to a flat plane).

The state of the field as recently as ten years ago bears little relationship to what we know today. Lipid monolayers were traditionally studied using classical methods such as isotherm measurements, surface viscometry, surface potential measurements, etc. In the past few years, probes such as optical spectroscopies (e.g. sum-frequency generation, polarized second-harmonic generation); various microscopies (e.g. fluorescence and polarized fluorescence, Brewster angle, atomic force); and scattering techniques (in particular, X-ray diffraction using synchrotron radiation) have given us increasingly direct *microscopic* information about molecular orientations and packing. For example, we now know as a result of combined isotherm, microscopy and X-ray diffraction studies that systems as 'simple' as saturated fatty acids and alcohols form a large number of ordered structures on the surface of water within a fairly narrow temperature range. One

can then ask why such structures are formed, and thus hope to establish how molecules and preparation conditions can be chosen to achieve specific structures and thus specific properties. Of course these are more difficult goals, and must be addressed with a combination of theory (largely in its infancy) and further experiments.

This report describes our continued studies of the phase diagrams of Langmuir monolayers, and our efforts to understand the variables that affect the structures formed. It also describes our studies of the structure of a transferred monolayer, and how this evolves as further layers are added. Finally, we describe our studies of the mechanical response of Langmuir-Blodgett films using a small-strain torsion balance at the center of a circular trough.

II. 'Ov' phase of fatty acid Langmuir monolayers

In 1993, using Brewster angle microscopy to study fatty acid Langmuir monolayers, Overbeck and Möbius¹ observed changes in texture within a region previously labeled the L₂ phase (distorted hexagonal, tilt towards a near neighbor²). These observations were quickly confirmed by Schwartz and Knobler³ using polarized fluorescence microscopy. While a change of texture is not in itself an unambiguous signal of a transition to a new phase, it is significant that these changes occurred reproducibly and reversibly when entering or leaving a specific region of the phase diagram.

One of the long-unanswered questions in the Langmuir monolayer field was whether the features seen in isotherms are really phase transitions. Earlier work supported by this grant played a substantial part in establishing that the features of carefully-obtained isotherms are not spurious, but always correspond to changes of structure clearly identifiable using X-ray diffraction. Here we were faced with a different question: whether there can be Langmuir monolayer phase transitions when, as in this case, there is *no* observable sign in the isotherm data.

Using glancing incidence X-ray diffraction, we found that the postulated boundary does indeed mark a phase transition to a phase now labeled 'Ov'. The tilt *angle* does not change across this transition, but the tilt *direction* changes from near-neighbor (NN) to next-nearest neighbor (NNN). For the data leading to these conclusions, see ref. 4. Contrary to a recent claim,⁵ our very detailed studies have found no evidence of an intermediate tilt direction in this region of the phase diagram.

The X-ray data also provide a microscopic 'reason' for the absence of a feature in monolayer isotherms. Fig. 1 shows the lattice parameters in the horizontal plane, in terms of the sides of the triangle formed by three neighboring molecules, and also the lattice parameters measured in a plane that is normal to the molecules ('normal plane'). It can be seen that in the normal plane, the triangle is equilateral on both sides of the transition, and shows no observable discontinuity at the transition. In other words the monolayer is in a 'tilted rotator' structure, and the transition

¹ G.A. Overbeck and D. Möbius, *J. Phys. Chem.* **97**, 7999 (1993)

² e.g. P. Dutta, in "Phase Transitions in Surface Films 2", edited by H. Taub, G. Torzo, H.J. Lauter and S.C. Fain (Plenum Publishing Co., New York, 1991) pg. 183

³ D.K. Schwartz and C.M. Knobler, *J. Phys. Chem.* **97**, 8849 (1993)

⁴ M.K. Durbin, A. Malik, R. Ghaskadvi, M.C. Shih, P. Zschack and P. Dutta, *J. Phys. Chem.* **98**, 1753 (1994)

⁵ I.R. Peterson, R.M. Kenn, A. Goudot, P. Fontaine, F. Rondelez, W.G. Bouwman and K. Kjaer, preprint

does not affect how the molecules pack with respect to each other. Only the tilt direction changes. Since the tilt angle does not change, the transition results in a discontinuous change in the horizontal-plane lattice parameters but no change in the *area* of the horizontal triangle (and thus no change in the area/molecule measured by isotherms).

Fig. 1. LEFT: schematic diagram showing tilted molecules in a distorted-hexagonal lattice and defining terms used in this report. RIGHT: Lattice constants in the horizontal and normal planes as a function of pressure for C_{19} acid monolayers at 30°C . Note that $a = a_p$ above the transition because the tilt is normal to this bond.

The appearance of a new phase with NNN tilt, quite separate from the L_2' phase known to have this tilt, is somewhat unexpected. Saturated fatty acid monolayers now show at least two NNN-tilted phases, two NN-tilted phases, and three untilted phases! However, the structure was indirectly confirmed by Fisher and Knobler,⁶ who found that in acid-alcohol mixtures the phase boundaries move until the L_2' and Ov regions merge into one region, which means that they have the same symmetry.

III. Langmuir monolayers of acid-alcohol and acid-acid mixtures

Mixed monolayers have been of interest for many years, in part because 'real' systems such as membranes are mixtures, and because Langmuir monolayers offer a way to study thermodynamic aspects of mixing in two dimensions.⁷ We initiated our recent studies of mixtures with a different goal: during the preceding three-year project period, we had studied the phase diagrams of acid and alcohol monolayers, and now we wanted to attempt to understand why these phase diagrams are different and to deconvolute if possible the roles of the head and tail groups in forming particular structures.

⁶ B. Fischer and C.M. Knobler, *J. Chem. Phys.*, to be published

⁷ e.g. I.S. Costin and G.T. Barnes, *J. Colloid Interf. Sci.* **51**, 106 (1975); K.J. Bacon and G.T. Barnes, *J. Colloid Interf. Sci.* **67**, 70 (1978)

At the simplest level, x-ray diffraction provides, more reliably and microscopically, information that is otherwise obtained from isotherms. We have shown,⁸ for example, that C₂₁ acid and C₂₁ alcohol monolayers are miscible, because the diffraction peaks from the mixture are distinct from those of the constituents. Our data also yield the microscopic area/molecule (free of errors due to defects, voids, etc.), and show that the density of a mixture is higher than the weighted densities of the constituents.⁹ Such data can be used in calculating the free energy of mixing, etc.

Fig. 2: Lattice constants in the perpendicular plane, a_p (open symbols) and a_p' (filled symbols), as a function of pressure along a 15°C isotherm, for pure C₂₁ acid (triangles), 80% C₂₁ acid + 20% C₂₁ alcohol (squares), and a 70%-30% mixture (circles). Vertical dashed lines mark phase transitions seen in isotherm data.

More detailed information is contained in actual lattice spacings. It is well-known by now that the molecular tilt decreases as the pressure is increased, and that this is the primary reason for the decrease in horizontal area/molecule within any given phase. (The tilt distorts the horizontal lattice, stretching it in the direction of the tilt.) It is therefore illuminating to look at the spacings in the normal plane rather than the horizontal plane. Only a sample of our data can be shown here (Fig. 2). Since the normal-plane distortion is always along a symmetry direction, there are only two unequal nearest-neighbor distances a_p and a_p' (see schematic in Fig. 1 for definition), whose pressure dependence at 15°C is shown for several compositions. It can be seen that the normal-plane spacings are the same in each phase, *independent of composition and pressure*; only the

⁸ M.C. Shih, M.K. Durbin, A. Malik, P. Zschack and P. Dutta, *J. Chem. Phys.* **101**, 9132 (1994)

⁹ M.K. Durbin, M. C. Shih, A. Malik, P. Zschack and P. Dutta, *Colloids and Surfaces*, to be published

phase transition pressures change. The shift is particularly strong for the NN-NNN boundary ('swiveling transition'); for more than 40% alcohol, and thus for pure alcohol as well, there is no NN-tilted phase at positive pressures. It is also significant that the direction of the distortion is different in the NN phase, where $a_p > a_p'$, and the NNN phase, where $a_p' > a_p$. Clearly there is a reorientation of the molecular backbone planes at this transition.

Because of the strong dependence of the swiveling transition pressure on composition, and because the alkane chain packing in the normal plane shows no observable pressure dependence, we conclude that the swiveling transition is driven by the head group lattice, which undergoes a structural transition that is accompanied by a rotation of the hydrocarbon chains about their axes. The chains then 'fall over' and pack in the best way possible given that the backbone orientations are fixed by the head groups. This picture requires that the head-head interactions not only be different for acid and alcohol groups (which is obvious) but that they be anisotropic. Many theoretical models and molecular dynamics simulations assume isotropic head-head interactions, and this would not explain the behavior at the swiveling transition. (For a complete discussion including similar results for acid-acid mixtures with different chain lengths, pressure-temperature phase diagrams for various acid-alcohol and acid-acid mixtures, and X-ray diffraction data along isobars, see Ref. 8-9.)

In a related investigation, we have been working with V.M. Kaganer of the Institute of Crystallography, Russian Academy of Sciences, to analyze trends in existing pure fatty acid monolayer data from several sources. Earlier mean field theory work by Kaganer and Loginov has been very successful in simulating many features of the observed phase diagram; However, their prediction of a phase transition from ordered to disordered backbone planes *within* what is now thought of as a single L_2 phase has not been credibly verified.⁵ As discussed above, the horizontal-plane lattice is distorted in the tilt direction; by extrapolating the lattice distortion as a function of tilt angle, to zero tilt angle, we find¹⁰ that at higher temperatures (e.g. C_{19} acid at 30°C, which corresponds to C_{21} acid at about 40°C) there is no 'intrinsic' distortion, while at lower temperatures the extrapolated lattice distortion is non-zero and varies only weakly with temperature. This implies a phase transition between a 'rotator' with disordered backbone planes, and a lower-temperature structure with ordered backbone planes.

IV. Structures of transferred monolayers and multilayers (LB films)

Does the Langmuir-Blodgett deposition process transfer the monolayer from the surface of water without changing it in any way? There has never been any good reason to think so, but in the absence of evidence to the contrary, it has often been assumed that this unlikely event occurs. We investigated this issue by transferring single monolayers to glass substrates from phases with different structures on the water surface: a tilted phase with distorted-hexagonal lattice (L_2); an untilted distorted-hexagonal phase (S); and an untilted hexagonal phase (LS). We found¹¹ that while there are some small quantitative differences between films transferred from the three different phases, they are all qualitatively identical (untilted molecules, hexagonal lattice). More details are in ref. 11.

¹⁰ V.M.Kaganer, I.R.Peterson, R.M.Kenn, M.C.Shih, M.K.Durbin and P.Dutta, *Chem.Phys.Lett.* **102**, 9412 (1995)

¹¹ M.C. Shih, J.B. Peng, K.G. Huang and P. Dutta, *Langmuir* **9**, 776 (1993)

Fig. 3: 'Rod' (K_z) scans at the in-plane peak positions for 1-, 3- and 5-layer LB films of lead stearate. The $\{11\}$ peak position is $K_{xy}=1.525\text{\AA}^{-1}$ and the $\{20\}$ peak is at $K_{xy}=1.71\text{\AA}^{-1}$. There is only one rod scan for the monolayer sample because it has only one radial peak. The solid lines are intensities calculated using the proposed structure (see ref. 12), while dotted and dashed lines are calculated from alternative structures.

Tippmann et al¹² also found that the first monolayer in a fatty salt LB film is hexagonal, but that a multilayer film is distorted hexagonal. How does the structure evolve as more layers are deposited? Is the first layer structure changed by the deposition of subsequent layers? It turns out that it is possible to answer this question by looking at 'rod' scans from lead stearate LB films as a function of thickness, and also that it is possible to distinguish the scattering from the alkane chain from the scattering from the heavy lead atoms even though the peak positions in the radial direction coincide. We studied 1-layer, 3-layer and 5-layer LB films on glass substrates (even numbers of layers are stable only under water). These films contain 1, 2 and 3 lead ion layers, respectively. Reflectivity data (see ref. 13) confirm that the film thicknesses correspond to the number of layers. Rod scans at the diffraction peak positions, however, show intensity oscillations with widths that correspond to two layers in a 3-layer film, and four layers in a 5-layer film. Clearly, therefore, the first layer retains its different structure. Moreover (see Fig. 3) we find an extra set of intensity oscillations along the rod for the 5-layer film, corresponding to interference between the second and third lead ion layers (the first lead layer has a different structure and thus

¹² P. Tippmann, R.M. Kenn and H. Möhwald, *Thin Solid Films* **210**, 577 (1992)

¹³ A. Malik, M. K. Durbin, A. G. Richter, K. G. Huang and P. Dutta, *Phys. Rev. B* (rapid communication), to be published

these oscillations do not appear in the 3-layer film). We have fitted the observed intensity oscillations using a simple structure factor calculation, and thus we have determined not only the structure within a plane (which is well known¹⁴), but the relative positions of adjacent alkane layers (other than the first layer) and the positions of the lead atoms relative to the alkane lattice. For more details see refs. 13 and 15.

V. Viscoelastic response of Langmuir monolayers

There is a long history of channel viscometry and other viscosity measurements on Langmuir monolayers. Such measurements are obviously based on the assumption that the monolayers are fluid. Our x-ray studies over the past two project periods have shown that this is not the case; some phases have resolution-limited diffraction peaks, while others have broader peaks but are clearly not classical fluids. Thus some of the 'viscosity' data in the literature may be on solid films stressed beyond the elastic limit. Even in phases that do not support static shear, the mechanical response can be expected to be viscoelastic rather than purely viscous.

We have developed a circular trough with an elastic perimeter, to compress monolayers in a shape-preserving manner so that no shear stress is applied during compression. The outer radius of the monolayer is typically 8-10 cm. At the center is a torsion balance with a circular "float" (radius 1 cm), which can be driven at various frequencies and at amplitudes as small as 0.005°. The driving force is electromagnetic, using a small coil that moves with the float, and the deflection is sensed electromagnetically as well. Further details are given elsewhere;¹⁶ here we show a sample of the results obtained. From the response of the float we can determine the stress and strain and thus calculate the complex shear modulus $G = G' + iG''$:

Fig. 4 LEFT: real part of shear modulus of a C_{21} acid monolayer as a function of rotor amplitude at 1Hz. RIGHT: Real and imaginary parts of shear modulus as functions of pressure.

¹⁴ J.F. Stephens and C. Tuck-Lee, *J. Appl. Cryst.* **2**, 191969; M. Prakash, P. Dutta, J.B. Ketterson and B.M. Abraham, *Chem. Phys. Lett.* **111**, 395 (1984)

¹⁵ A. Malik, M. K. Durbin, A. G. Richter, K. G. Huang and P. Dutta, submitted to *Thin Solid Films*

¹⁶ R. Ghaskadvi, J.B. Ketterson and P. Dutta, in preparation

It can be seen from Fig. 4 (left) that there is a strain limit (amplitude limit $\sim 0.02^\circ$ for the monolayer dimensions given above) beyond which the shear response becomes nonlinear (amplitude-dependent). G'' shows the same behavior. These results are for a specific monolayer at a specific temperature, but the strain limit is rather small, and it is clear that the interpretation of the extensive channel viscometry data in the literature is problematic.

We have also looked at the shear response in the small-strain linear limit as a function of pressure. Fig 4 (right) shows that at the L2"-S transition between an NNN-tilted phase and an untilted phase, G' shows a discontinuous jump while G'' does not. Since this particular transition is not first order (no flat section in isotherms; no discontinuity in lattice parameters or molecular tilt, only in their first derivatives) the reason for the discontinuity in G' is unclear. It may be that the molecules "lock in" in such a way as to substantially increase the shear modulus of the untilted phase, but it is surprising that this cannot be seen as a discontinuity in X-ray data.

VI. Publications supported by this grant, 1993-present

"Atomic force and fluorescence microscopy of Langmuir-Blodgett monolayers of L- α -dimyristoylphosphatidic acid", J.M. Mikrut, Y. Kim, P. Dutta, J.B. Ketterson and R.C. Macdonald, *Phys. Rev. B* **48**, 14479 (1993)

"Thin films: X-ray diffraction", P. Dutta, in *Encyclopedia of Advanced Materials*, edited by S. Mahajan (Pergamon Press, 1994)

"X-ray diffraction study of a recently identified phase transition in fatty acid Langmuir monolayers", M.K. Durbin, A. Malik, R. Ghaskadvi, M.C. Shih, P. Zschack and P. Dutta, *J. Phys. Chem.* **98**, 1753 (1994)

"Lattice structures and molecular tilts in Langmuir monolayers of saturated fatty acid-alcohol mixtures", M.C. Shih, M.K. Durbin, A. Malik, P. Zschack and P. Dutta, *J. Chem. Phys.* **101**, 9132 (1994)

"Tilted phases of fatty acid monolayers", V.M. Kaganer, I.R. Peterson, R.M. Kenn, M.C. Shih, M.K. Durbin and P. Dutta, *Chem. Phys. Lett.* **102**, 9412 (1995)

"Structures of head and tail group monolayers in multilayer Langmuir-Blodgett films", A. Malik, M. K. Durbin, A. G. Richter, K. G. Huang and P. Dutta, *Phys. Rev. B* (rapid communication), to be published

"Isotherm and X-ray diffraction studies of mixed monolayers". M.K. Durbin, M. C. Shih, A. Malik, P. Zschack and P. Dutta, *Colloids and Surfaces*, to be published

"Order in Langmuir-Blodgett films of lead and cadmium stearate", A. Malik, M. K. Durbin, A. G. Richter, K. G. Huang and P. Dutta, submitted to *Thin Solid Films*

"Shear response and X-ray diffraction studies of monolayer phases", P. Dutta, to be published in Proceedings of the International Symposium on Micelles, Microemulsions and Monolayers (edited by D.O. Shah)

VII. Talks covering grant-supported work, 1993-present

P. Dutta, invited talk, ACS meeting, Denver, CO, 1993

M.K. Durbin, contributed talk, APS March meeting, Seattle, WA, 1993

P. Dutta, invited talk, International Workshop on Monolayers at the Air-Water Interface, Heron Island, Australia, 1994

M.K. Durbin, contributed talk, APS March meeting, Pittsburgh, PA, 1994

R. Ghaskadvi, contributed talk, APS March meeting, Pittsburgh, PA, 1994

M.K. Durbin, contributed talk, APS March meeting, San Jose, CA, 1995

R. Ghaskadvi, contributed talk, APS March meeting, San Jose, CA, 1995

P. Dutta, invited talk, International Symposium on Micelles, Microemulsions and Monolayers, Gainesville, FL, 8/95

M.K. Durbin, contributed talk, Seventh International Conference on Organized Molecular Films, Ancona, Italy, 9/95

R. Ghaskadvi, contributed poster, Seventh International Conference on Organized Molecular Films, Ancona, Italy, 9/95