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Invited Lecture

Mesophases in monolayers of fatty acids and phospholipids

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Langmuir monolayers at the air/water interface are distinguished by their richness of phases. These can be assigned to smectic categories, although the dominant competing interactions are not yet well elaborated. For single chain compounds, there are van der Waals attractions of the chains and repulsive forces of the head groups competing in determining the local structure. For larger molecules like phospholipids there appear also to be important dipolar interactions of the head groups. In order to study these interactions, we report surface X-ray diffraction studies of films of fatty acids and phospholipids at the air/water interface, with varying environmental parameters, as well as head group size and shape. We observe a wealth of mesophases and also the influence of molecular chirality on the structure. The defined control of the monolayer structure can be made use of to control crystal formation by diffusion from the subphase and nucleation at the interface. This is studied spectroscopically, microscopically and *via* electron diffraction of transferred films of cyanine dyes. In that case one observes epitaxy between the dye crystal and surfactant layer, and the relative lattices can be varied via suitable dye mixtures. A very peculiar interfacial influence results from the orientation of molecular dipoles at the interface. This causes long-range repulsive interactions leading to periodic superlattices in two phase coexistence regions. These forces are observed and quantified via fluorescence microscopy.

1. Introduction

This contribution is not only intended to prove that many amphiphilic monolayers are lyotropic liquid crystals but also that these systems are good models for studies of general features of liquid-crystalline phases. Qualitatively, this becomes obvious by looking at the general structure of the molecules that are considered in this work (see figure 1). Most amphiphiles possess aliphatic chains with many internal degrees of freedom. If these chains determine the packing, one expects phases known for alkane crystals. Yet, there may be other molecular moieties like the head groups of phospholipids which order in a different way. This may cause frustration and by varying the geometries of head and tail one can study this in detail. Investigating the systems at the air/water interface presents the advantage that they are adjacent to a smooth and soft water surface. However, one can also prepare them on a periodic lattice formed by inorganic ions or a dye crystal adsorbing at the charged monolayer.

Obviously monolayers resemble one layer of smectic liquid crystals, and indeed many systems like phospholipids exhibit smectic phases as bulk samples, but there are also important differences:

The high surface tension confines the molecules strictly in one plane with an interface definable to an accuracy of better than 1 Å.

The environmental parameters and specially the two-dimensional molecular density can be varied over a broad range, while maintaining the layer structure.

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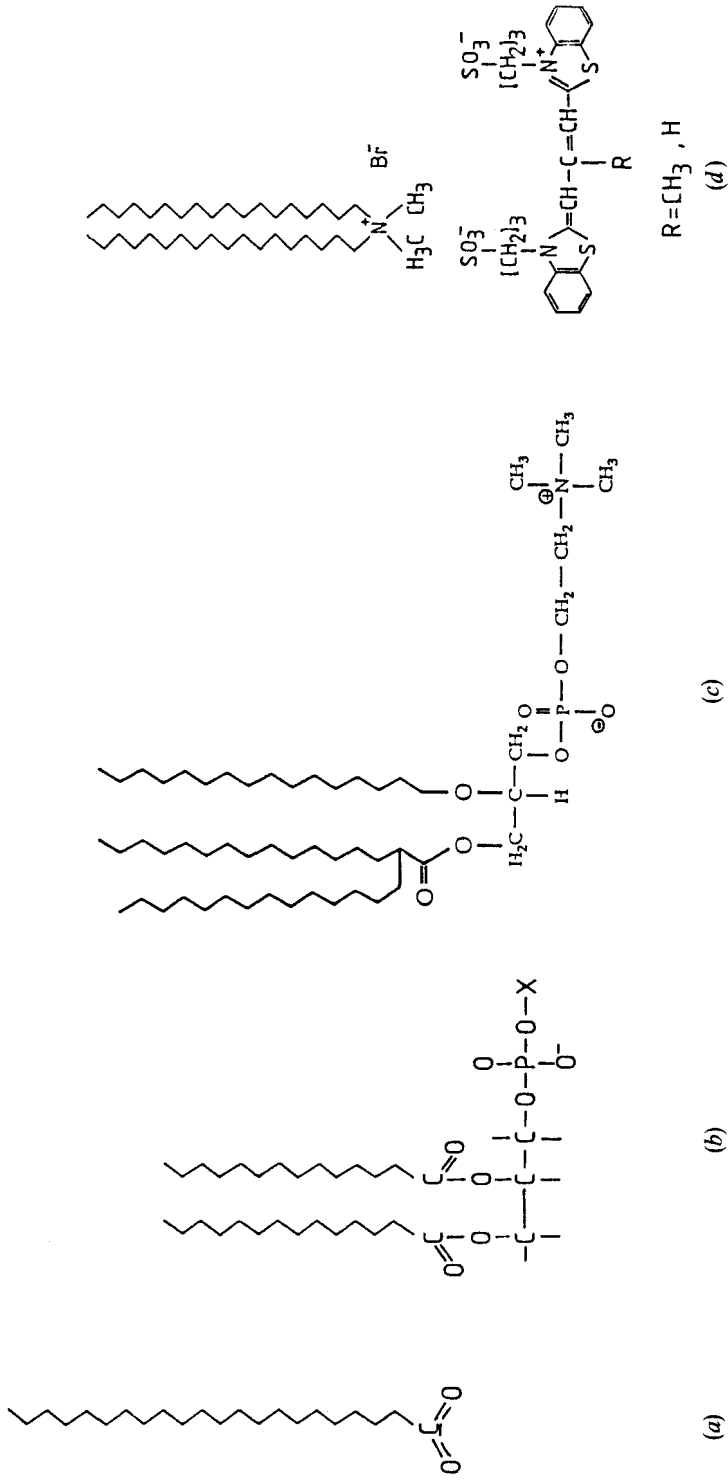


Figure 1. Molecules concerned in this work: (a) single chain fatty acid, (b) diacylphospholipid, (c) branched chain phospholipid and (d) charged amphiphile and cyanine dye crystallizing at an interface.

Polar molecules are arranged at an interface that breaks the symmetry and causes long-range repulsive interactions.

2. Techniques

The above features could have been written down more than 10 years ago, but there would have been little direct proof at the structural level. This has changed considerably in the past decade by development of suitable surface sensitive techniques, and three of the most powerful will be made use of in this presentation.

The scattering of an X-ray beam hitting the surface at glancing angle measured as a function of horizontal angle (wave vector transfer Q_h) yields information on the lattice formed by the aliphatic tail projected on the surface [1]. Measuring the diffraction intensity of a Bragg spot along the surface normal (Bragg rod), one derives the tilt angle t of the tails with respect to the surface normal. In particular, if the tails are uniformly tilted at an angle t with respect to the surface normal and a projection normal to a lattice plane (Q_h^{\max}), the diffraction intensity as a function of the normal wave vector transfer Q_z assumes a maximum at [2]

$$Q_z^{\max} = Q_h^{\max} \cdot \tan t$$

The tilt angle can additionally but less precisely be derived by measuring the film thickness. This, as well as the normal density profile ρ_z , is derived by measuring the X-ray reflectivity R normalized to the Fresnel reflectivity R_F via [1]

$$\frac{R}{R_F} = \frac{1}{\rho_{H_2O}^2} \left| \int \frac{d\rho}{dz} \exp(iQ_z z) dz \right|^2$$

Since dye probes like most impurities are soluble preferentially in one of two or more coexisting phases, domains can be observed and followed by fluorescence microscopic inspection of the surface [3–5]. The technique has sometimes been challenged due to the dependence on dye probes. However, recent developments in Brewster angle microscopy [6, 7] have confirmed the results. The latter technique images the light reflection of a surface at the Brewster angle. The reflection depends on the thickness and also the refractive index anisotropy of a surfactant layer. Therefore, it not only visualizes the domain structure, but also yields information on tilt angle and orientational order.

Although applicable only to films on thin solid supports, transmission electron diffraction has become a powerful tool [8]. As the electron beam can be focused on selected areas of diameters below 10 μm , it is applicable to single domains and therefore corresponds to single crystal diffraction.

3. Structure at the molecular level in ordered phases

3.1. Fatty acids

Figure 2 depicts the phase diagram of behenic acid with the phase boundaries derived from careful isotherm measurements [9]. This diagram is typical for many simple surfactants. It has been shown that varying the chain length essentially shifts the temperature scale and going from the acid to an ethyl ester or methyl ester, the head group predominantly shifts the pressure scale, but the qualitative features are not affected [10].

The assignment of the phases to a molecular arrangement has been made by means of X-ray analysis [11]. Figure 3 shows the diffraction intensity as a function of in-plane

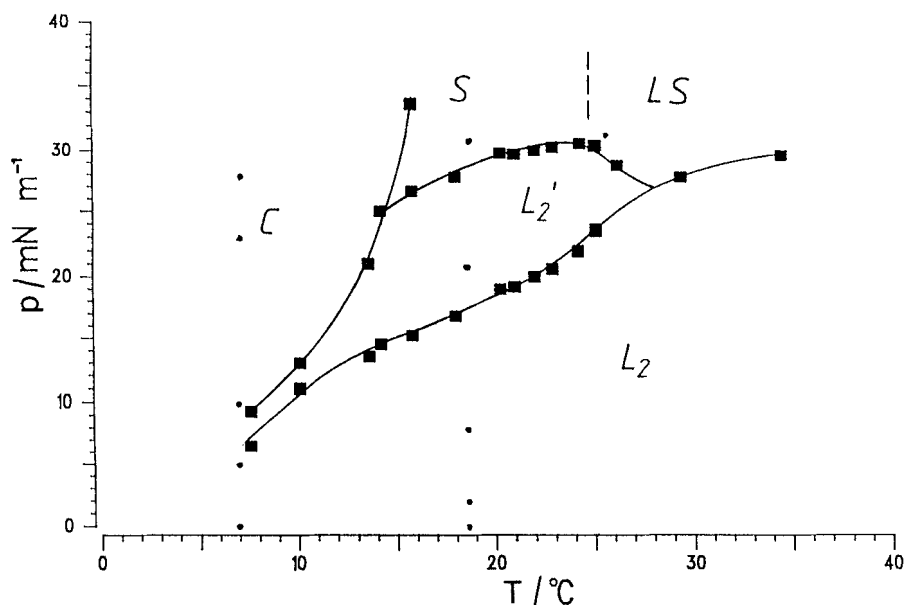


Figure 2. Phase diagram for behenic acid ($\text{pH}=5.5$).

wave vector transfer (right) and normal wave vector transfer (left) for the two Bragg peaks for a behenic acid monolayer in four different phases. The two diffraction peaks correspond to the (1, 1) and to the (0, 2) reflections of a centred rectangular lattice given by the projection of the chains on the surface. The narrow peak with resolution limited width is typical for a crystalline phase, justifying the designation of this phase as crystalline solid (C). In this phase the projected molecular area is rather low (18.6 \AA^2), close to that of low temperature phases of alkanes [12]. The aliphatic tails are normal to the surface, since for both peaks the Bragg rods are maximal for $Q_z = 0$. For the other phases, the Bragg peaks are much broader and from the widths one derives positional correlation lengths between 10 and 50 lattice spacings. This supports the notion of Peterson [13] that these are mesophases. They can be distinguished by their symmetry, reflected in the Bragg rods. For a tilt towards a nearest neighbour chain, one expects one spot not to realize the tilt, since the projection on the surface is parallel to the lattice plane, but the other Bragg rod exhibits a maximum for $Q_z^{\text{max}} > 0$. This obviously holds for the L_2 phase. For a tilt towards a next nearest neighbour, both rods should exhibit maxima for $Q_z > 0$, which is measured for the L_2' phase. In contrast to this, $Q_z^{\text{max}} = 0$ for both Bragg peaks of the S phase proving a vertical tail orientation. The three mesophases L_2 , L_2' and S distinguished by the chain tilt exhibit the same chain cross section of $19.2 \pm 0.1 \text{ \AA}^2$. This is between the values observed for alkane crystals ($< 18.6 \text{ \AA}^2$) and for alkane phases with free rotation about their long axes ($\sim 19.8 \text{ \AA}^2$). It is best described as a rotator II phase with a librational motion about the long axes.

At higher temperatures, for behenic acid [11] and near room temperature for the shorter arachidic acid, one also encounters the free rotator phase with a cross section per molecule of 19.8 \AA^2 [14]. There, if the chains are vertical, the chain lattice is hexagonal. Expanding the film, the chains uniformly tilt towards a nearest neighbour. Figure 4 compares the tilt angle as a function of molecular area determined from the Bragg rods and from X-ray reflectivity analysis, yielding the thickness l in the most condensed (l_0) and expanded (l) states according to [15] $l/l_0 = \cos t$.

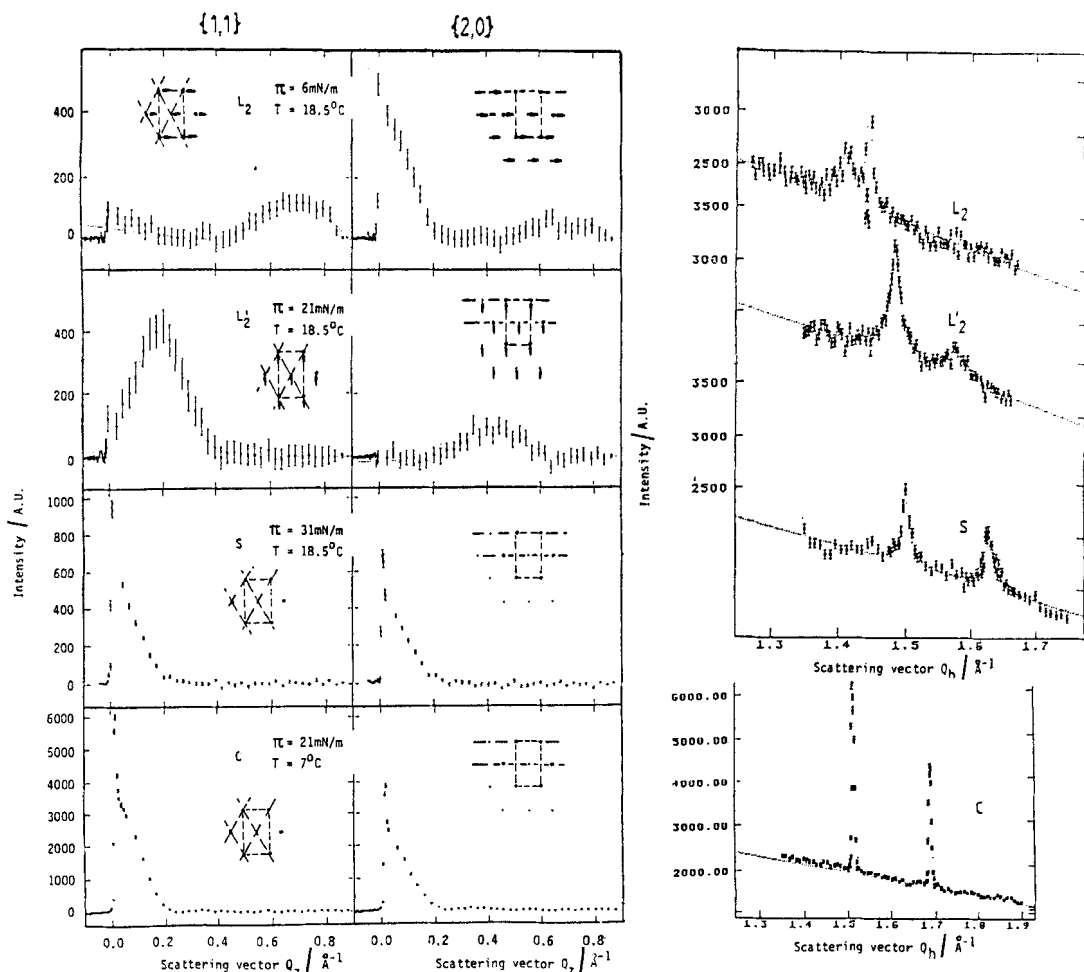


Figure 3. X-ray scattering intensity as a function of horizontal wave vector transfer Q_h (right) and normal wave vector transfer Q_z (left) for behenic acid monolayers in the phases L_2 , L'_2 , S and C (pH 5.5).

Obviously the values obtained by both techniques agree and obey a cosine law showing that within one phase, compression does not increase the density but merely the tilt angle. Figure 4 contains one most interesting subtlety: the transition from the untilted to the tilted state appears to be continuous. Recent calculations [16] have shown that this cannot be explained merely by optimizing of van der Waals interactions. Expanding parallel rods grafted on a plane, the distance between the rods can be reduced by tilting. This increases attraction, but the ends of adjacent rods lose contact. The latter energy cost dominates for low t , and hence the transition should be of first order. If, however, one takes into account an attractive interaction of tails and surface, the above energy expense can be compensated. The latter depends on the lattice statistics, and this explains why the transition is of second order on going from the nearest neighbour state to the untilted state and of first order on going from next nearest neighbour to untilted [17].

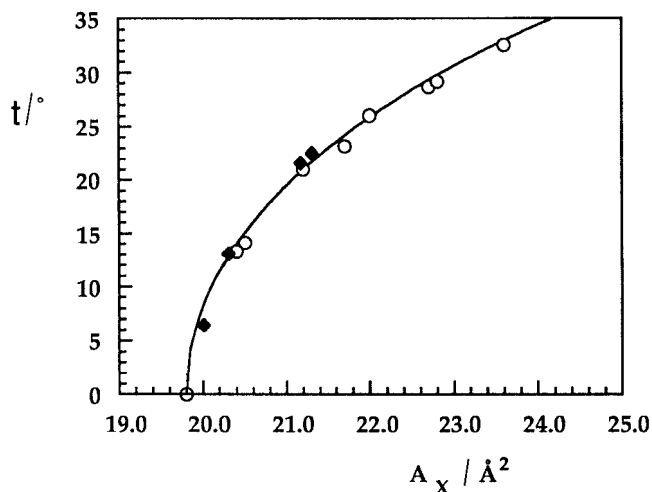


Figure 4. Tilt angle t as a function of molecular area for arachidic acid monolayers (pH 5.5, $T = 20^\circ$) determined from the Bragg rods (\blacklozenge), Q_z^{\max} , and from reflectivity data (\circ) l_T/l_T^0 . The full curve is expected if the cross section per molecule is 19.8 \AA^2 , independent of lateral pressure.

3.2. Phospholipids

X-ray studies on phospholipids have not yet been published that systematically, and therefore the sequence of phases is not yet well known. Still the following statements are valid at this stage [18]:

There exist many mesophases with a cross sectional area per chain near 19.8 \AA^2 , there are nearest neighbour and next nearest neighbour phases with the tilt angle varying on compression and without tilt at high pressures.

Phospholipids are distinguished from the first class of compounds as (at least) two chains are coupled by a head group. In addition the head group is large, which may cause packing restraints. Unfortunately, diffraction signals from head groups have never been measured, probably due to static or dynamic disorder. Also, there are no peaks corresponding to a doubling of the unit cell observable. The latter would be the case if two chains are coupled in a laterally periodic way. However, there is an interesting influence of head group chirality on the chain arrangement which will be explained by means of figure 5.

Measuring diffraction as a function of Q_h , one realizes two peaks for the racemate and three peaks for the enantiomerically pure compound [19]. The two peaks again correspond to a centred rectangular lattice, and as one peak is maximal for $Q_z = 0$, the other for $Q_z > 0$, there is a nearest neighbour tilt. For the pure compound, the peak with $Q_z^{\max} > 0$ is split into two, and this corresponds to a transition from a rectangular into an oblique cell.

The symmetry reduction must arise from a force acting at an angle with respect to the otherwise rectangular cell. The force very probably results from the head groups, and this in turn requires orientational order of the head groups. This conclusion is supported by the finding that the symmetry break does not exist in a racemic mixture.

Partly motivated by biophysical questions, branched chain phospholipids have been prepared and studied [20]. When the branch is as long as the main chain, one may

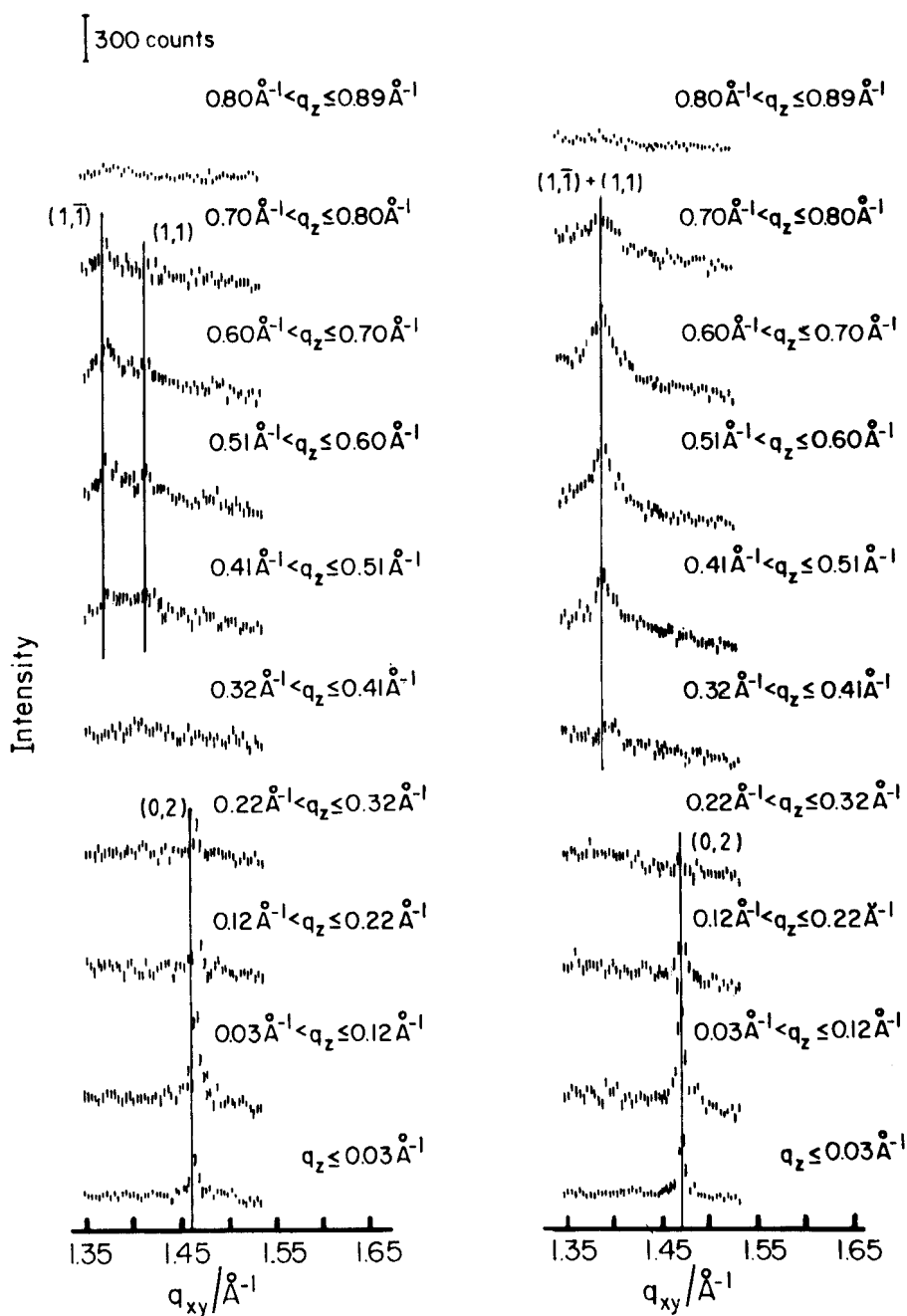


Figure 5. X-ray scattering intensity as a function of in-plane wave vector transfer q_{xy} for different intervals or normal wave vector transfer q_z for monolayers of dipalmitoylphosphatidylethanolamine at low pressures. (a) Enantiomerically resolved compound L-DPPE at 1 mN m^{-1} and (b) racemic DL-DPPE at 2 mN m^{-1} .

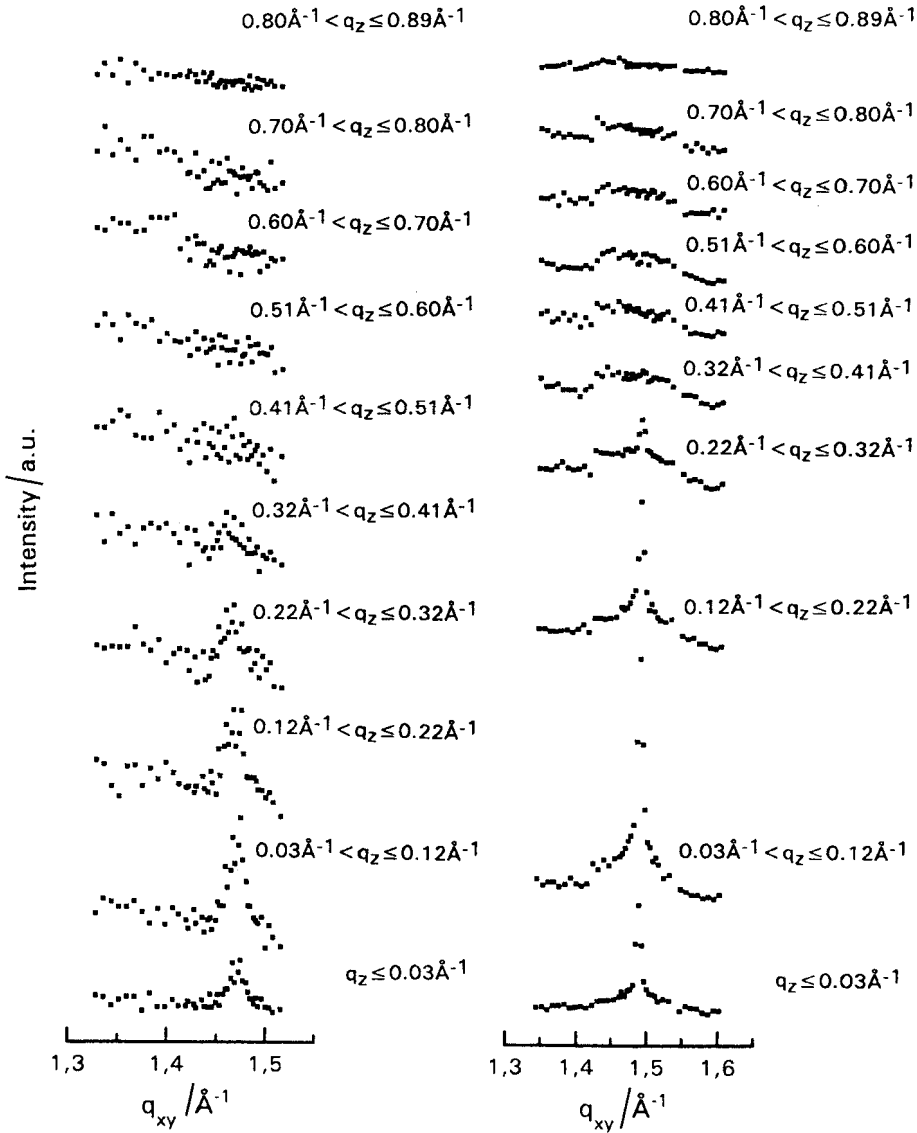


Figure 6. X-ray scattering intensity as a function of in-plane wave vector transfer q_{xy} for different intervals of normal wave vector transfer q_z for monolayers of the branched chain lipid (see figure 1(c)) at two different pressures ($T = 15^\circ\text{C}$), (a) 10.5 mN m^{-1} and (b) 40 mN m^{-1} .

consider these as lipids with three or four chains per head. Thus, the molecular area is given by the area per chain and this determines the packing. Figure 6 indeed shows that there are phases with uniform chain tilt and the tilt angle is reduced on compression [21]. The latter is again deduced from the finding that the value $Q_z^{\text{max}} > 0$ is smaller at higher pressures.

3.3. Surfactants on periodic support

It has recently been shown that an ion lattice under a fatty acid monolayer may affect the tail arrangement [22]. The resulting lattice is oblique with arguments as given above for chiral phospholipids. This system appears to be unique, as the inorganic

lattice is formed only with Cd ions and only under very special conditions. Hence, it is not possible to investigate the interplay between two structures.

Recently, motivated by research into preparing two-dimensional dye aggregates with well-defined properties, we discovered a promising route in this direction [23]. Preparing a charged monolayer, conditions can be selected to crystallize cyanine dyes at the interface after electrostatic attraction. The systems can be transferred on to a thin amorphous support, and figure 7 shows electron diffraction data for two systems [24]. They differ slightly in the dye structure, where a hydrogen at the methine is replaced by a CH_3 group. The electron diffraction pattern reveals ten independent sharp reflections attributed to the dye crystal and up to 3 independent broad reflections from the chains. The orientations of the groups of reflections are related; hence there is epitaxy between the two lattices. With many reflections, the lattices of the dyes can be determined rather precisely. In both examples there are two molecules per unit cell forming a different angle α between the long axes (see figure 8). The electronically strongly coupled dyes are arranged in a coplanar manner in rows, the spacing along these rows corresponding to the distance between the rows in the diffraction pattern [23]. Obviously, the two different dyes exhibit different structures and by preparing a mixed system it is possible to tune the dye lattice [24].

The chain lattice very probably is incommensurate with that of the dye, and usually one observed two spots which are brighter than the others. This can be understood assuming a distorted hexagonal arrangement and a tilt towards a nearest neighbour. In that case there is one plane, which does not experience the tilt displaying maximum intensity. Looking at the diffraction patterns again, this plane can be parallel or perpendicular to the rows of dyes. At this stage we should state that these studies are far from being systematic. In particular, it appears possible to vary the lateral density of lipids above a dye crystal. This indicates very weak coupling between the two lattices.

4. Structure at the μm level

Whereas the last chapter has considered phases with chain order, we now consider the transition into these phases from an isotropic liquid. This first order transition,

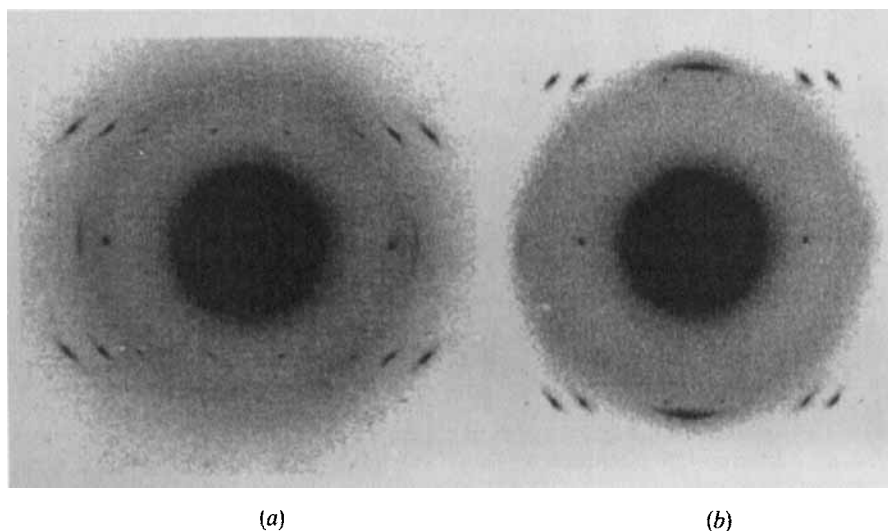


Figure 7. Electron diffraction spot for the surfactant (2 blurred spots) and cyanine crystal with (a) $R = \text{H}$ and (b) $R = \text{CH}_3$ (see figure 1(d)).

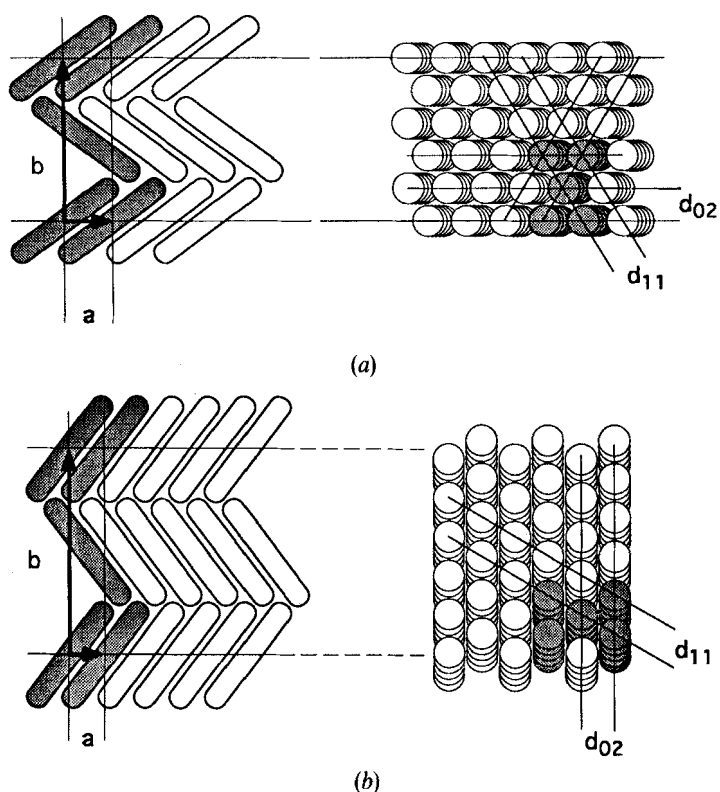


Figure 8. Arrangement of dye crystals see (a) along the surface normal and (b) with aliphatic tails tilted into two different directions for the two systems of figure 7.

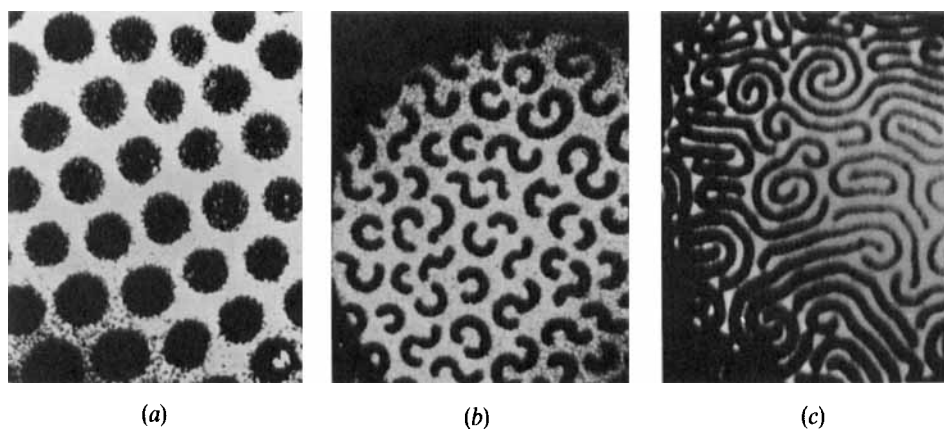


Figure 9. Fluorescence micrographs of monolayers containing 1 mol% of a dye probe in the fluid/ordered coexistence region: (a) Dimyristoylphosphatidic acid (DMPA) at low surface charge density. (b) and (c) DMPA at high charge density with 1 mol% cholesterol added. The short axis is about 100 μm .

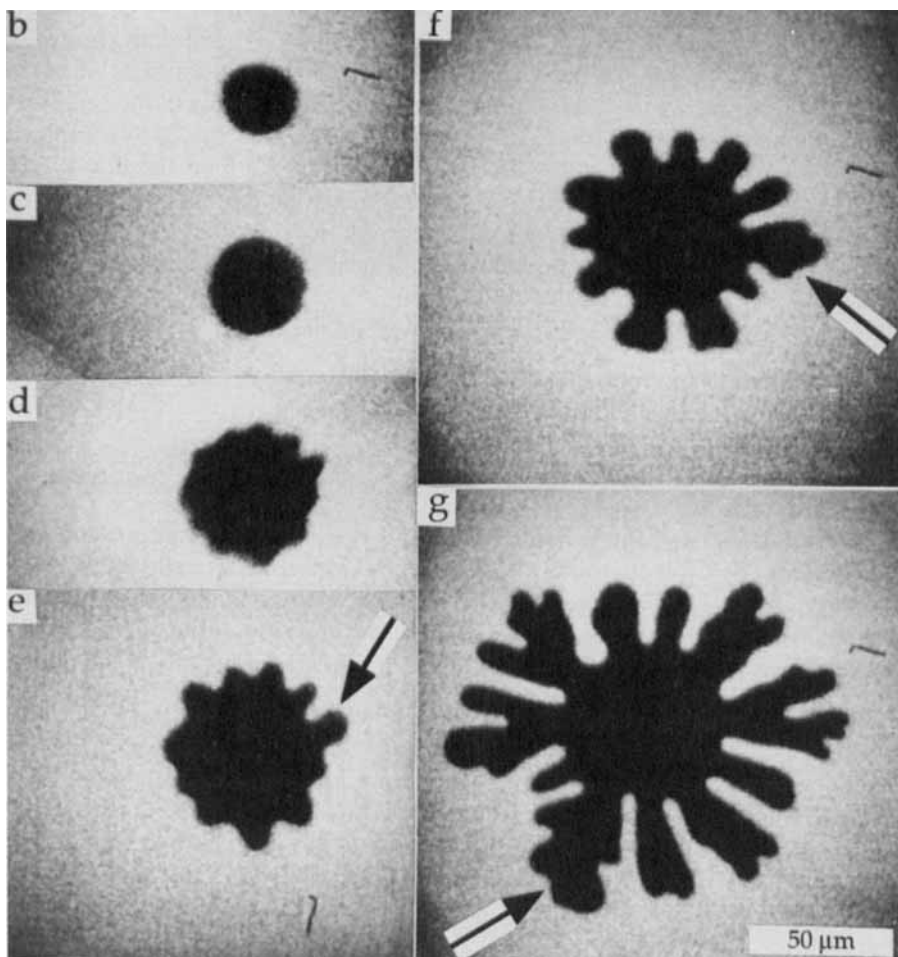


Figure 10. Growth of a domain of a branched chain lipid isolated under an electrode. The time to obtain g exceeds 1 hour.

often called the main transition, is distinguished by a nearly horizontal part of the pressure/area isotherm. Looking at the surface through a fluorescence microscope one can see formation of the ordered phase (dark) in this range, because the dye probe is preferentially dissolved in the disordered phase (bright) [3–5] (see figure 9). Interestingly, one frequently observes a very regular arrangement of lamellar or circular domains, and these can be qualitatively understood as follows [25–28]: The two coexisting phases differ by their density of dipoles normal to the surface, and this difference has been measured from surface potential measurements to be about 100 mDebye/nm² [29]. Consequently, adjacent domains repel and may form a Wigner lattice if they are of uniform size. Domains may be of uniform size either if they experience the same growth conditions or, as is in some cases encountered for monolayers, if the size is an equilibrium feature. The latter can result for a two-dimensional system, since the repulsive dipolar energy of a domain increases logarithmically with size [30]. Hence, an equilibrium size may be established from a competition between boundary energy (tending to increase the size) and electrostatic

energy (reducing the size). Thinking along this line, it is also possible that minimization of electrostatic energy enforces non-compact shapes [30, 31]. Hence shape transitions into lamellar or elliptical shapes have been predicted from calculations [30]. They can be observed after varying ionic conditions, temperature [32] or, as in the example of figure 10, domain size [33]. In this example, a single domain is isolated by a dedicated electrode system above the surface. Slowly compressing the film, the domains are observed to grow and, on exceeding a certain size, a shape instability develops. Numerical simulations predict a series of first order phase transitions between different shapes [34]. These are apparently not observed, as generally one instability enslaves all other modes.

These types of studies have remained an active field of research for various reasons:

All aspects of structure formation are theoretically and experimentally fully assessable in a two-dimensional system,

there are special features connected with the interfacial nature which may be relevant for many systems, including surface-induced ordering of liquid crystals

inspection of shapes may yield insight into the microscope nature and defect structures. This was realized very early on by inspecting faceted structures, and very recently it has also been possible to decide on director orientation within the domains by polarized microscopy [35] or by inspection of the dye distribution along defect lines [36].

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