Crystallization Phase Transitions and Phase Diagram of Langmuir Monolayers

V. M. Kaganer and E. B. Loginov

Institute of Crystallography, Russian Academy of Sciences, Leninskii pr.59, 117333 Moscow, Russia

Seven structurally distinct condensed phases in the phase diagram of water-supported Langmuir monolayers are explained in the framework of the Landau theory of phase transitions. The present treatment, which covers two-dimensional hexatic and solid phases and describes the transitions between them, involves the coupling of three order parameters. One of the parameters governs the collective tilt of the molecules, while the other two describe one-dimensional "weak crystallization" along the bond direction and normal to it with the herringbone ordering of the molecular backbone planes.

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Monolayers of amphiphilic molecules on the water surface (Langmuir monolayers) are two-dimensional fluids at high temperatures and two-dimensional solids at low temperatures. At least five structurally distinct phases are found over the intermediate temperature range. The first evidence for this rich polymorphism was the observation of kinks in the surface pressure—area isotherms [1–3]. Using the isotherm technique, various amphiphiles were found to show similar surface pressure—temperature phase diagrams containing at least seven phases. The theoretical phase diagram of the present paper, Fig. 1, essentially reproduces the generalized phase diagram of fatty acid monolayers [4], compiled from isotherm studies of acids with different chain lengths by matching up regions of the same shape with regular shifts of the temperature axis [5].

Although the interpretation of these kinks as phase transitions was for many years cast into doubt, recent x-ray diffraction experiments [6–14] have shown that all the regions of Fig. 1 have different structures. The LS phase is hexatic with sixfold symmetry and gives rise to just one triply degenerate first-order x-ray diffraction peak. The correlation length determined by the half-width of the peak is of 4–5 intermolecular distances [10]. Fluorescence microscopy of the domains in the coexistence region with the higher-temperature two-dimensional liquid phase L_1 (not included in Fig. 1) has revealed the sixfold axes of the domains [15]. The S phase can be considered to be derived from the LS phase by orthorhombic distortions accompanying the ordering of the short axes (backbone planes) of the molecules. It gives two peaks, one doubly degenerate and one nondegenerate, each with correlation lengths of about 30 intermolecular distances. The CS phase gives the resolution-limited peaks of a two-dimensional solid. As the surface pressure is lowered, transitions occur to the L_2, L'_2, and L''_2 phases whose molecules show collective tilt in addition to orthorhombic distortion. Symmetry arguments based on the present theory lead us to subdivide the L_2 phase into two phases, L_{2h} and L_{2d}, with herringbone ordered and disordered backbone planes, respectively, although the transition between them has not yet been observed

experimentally. The correlation lengths decrease slightly at the tilting transitions, but change drastically at the L'_2-L_{2h} transition. In the L_{2h} phase, the nondegenerate peak shows a correlation length of about 60 intermolecular distances whereas for the doubly degenerate peak the correlation length is about 4 times smaller. These differences in the correlation lengths find a natural explanation in the theory presented below.

The orders of the transitions were first determined by isotherm measurements and then confirmed with x-ray diffraction. The tilting transitions are found to be continuous whereas the other ones are first order. The phases L_2 (L_{2h} and L_{2d} in our notation) and L'_2 of fatty acids differ in direction of the tilt with respect to the bond orientations. Molecules tilt to the nearest neighbor in phase L_2 and to the next-nearest neighbor in phase L'_2, the swiveling transition between these phases being obviously of the first order.

Phase transitions in Langmuir monolayers have been the subject of a number of computer simulations and molecular models (see, e.g., Ref. [16], references and discussion therein). While these methods provide detailed information on the behavior of the monolayer at particular phase transitions, they do not give an overview. The Landau theory of phase transitions [17] gives a
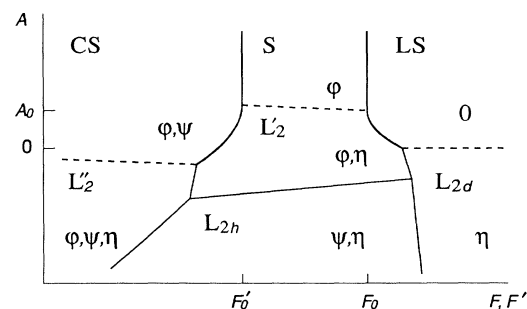

FIG. 1. Theoretical phase diagram. Nonzero order parameters are indicated for each phase. F, F' are the temperaturelike variables and A is the surface pressurelike one. Solid lines denote the first-order transitions; dashed lines indicate the second-order ones.

symmetry-based, model-independent description of possible structural changes in the system. It has been employed recently [18] to analyze some of the phase transitions in Langmuir monolayers. The transitions between four of the condensed phases (LS, S, L_2, and L_2') were explained by the coupling of two order parameters, describing the collective tilt of the molecules and the herringbone ordering of their backbone planes, respectively. However, the phases were treated as crystalline, and the considerable differences in correlation length were not taken into account.

Within the framework of the Landau theory, it is possible to consider changes of translational order from short range to long range as "weak crystallization" transitions. Landau himself used the amplitude of the periodic density wave appearing at the crystallization of a liquid as an order parameter to prove that the transition from liquid to crystal must always be first order [19]. Weak crystallization theory is applicable if the discontinuities at the transition point are small and if all the wave vectors involved in the transition have equal length. An example where both requirements are satisfied is the formation of smectic liquid crystals. Interest in weak crystallization theory was stimulated by Alexander and McTague [20], who argued that the bcc structure is preferred during the three-dimensional crystallization of a liquid. Albrecht et al. [21] considered crystallization of phospholipid monolayers. In the present work, the Landau theory of phase transitions in Langmuir monolayers is developed taking into account differences in the translational order of the phases, thus allowing comparison with the x-ray experimental data on both diffraction peak positions and their widths.

We consider the progressive ordering of a Langmuir monolayer starting from the least ordered condensed phase, i.e., the LS phase. As a liquid, even if anisotropic, it possesses continuous translation symmetry. In addition, it displays long-range orientational order of the point symmetry group C_{6v}, generated by a sixfold symmetry axis and two orthogonal symmetry planes normal to the plane of the monolayer. The collective tilt of the molecules is described by the in-plane components n_x, n_y of the unit vector $\mathbf{n}$ directed along the long axes of the molecules. It is convenient to convert to polar coordinates: $n_x = \eta \cos \beta$, $n_y = \eta \sin \beta$. The free energy expansion must be invariant with respect to reflection in symmetry planes (which changes the sign of n_x or n_y), and to the sixfold rotation (which transforms the azimuthal angle $\beta \to \beta + \pi/3$). The leading terms in the expansion are

$$\Phi_\eta = A\eta^2 + B\eta^4 - D\eta^6 \cos 6\beta . \qquad (1)$$

When $B > 0$, Eq. (1) describes a second-order tilting transition at $A = 0$. The last term in Eq. (1) is small in comparison with the other ones but is the lowest-order term depending on the angle β. For $D > 0$, minimization

of Φ_η over β gives $\beta = \pi m/3$ (m is integer). Hence the tilt occurs in the direction to the nearest neighbor, as at the observed transition LS-L_{2d}. If D changes sign, the tilt direction varies. We do not touch this problem which is considered, with fluctuation corrections, in Ref. [22]. Figure 2(a) illustrates symmetry of the phase ($\eta \neq 0, \beta = 0$).

The structural data are not consistent with 2D nematiclike ordering of the molecular backbone planes [18]. To demonstrate this, consider the nematic order parameter $\hat{Q}$—a symmetrical traceless 2D tensor. The two independent components of $\hat{Q}$ can be represented in polar coordinates as $Q_{xx} - Q_{yy} = \xi \cos \alpha$, $2Q_{xy} = \xi \sin \alpha$, where $\alpha = 0$ when the nematic director points along the bonds and $\alpha = \pi$ when the director is perpendicular to them. A sixfold rotation transforms the components of the second-rank tensor according to $\alpha \to \alpha + 2\pi/3$, and the free energy expansion is

$$\Phi_\xi = C\xi^2 - K\xi^3 \cos 3\alpha + L\xi^4 - V\xi\eta^2 \cos(\alpha - 2\beta). \qquad (2)$$

The induced nematic order $\xi \sim \eta^2$ at the LS-L_{2d} transition is described by the first and the last terms of Eq. (2). The free energy is minimum at $\alpha = 0$ for $V > 0$, in accordance with the observation for fatty acids. The spontaneous ordering from $\xi = 0$ to $\xi_0 = K/2L$ takes place as C decreases to $C_0 = K^2/4L$. The transition is first order due to the cubic term in Eq. (2). When $K > 0$ the minimum occurs at $\alpha = 0$, corresponding to the nematic order along the bond direction at the LS-S transition. At the tilting transition S-L_2' occurring at $\xi = \xi_0$ and $\alpha = 0$, β should be zero, as it has already been shown that $V > 0$. However, experimentally in the phase L_2' [9,10], the molecules tilt to the next-nearest neighbor, i.e., $\beta = \pi/2$. Therefore, the structural data for the two tilting transitions LS-L_2 and S-L_2' cannot be explained simultaneously with 2D nematic ordering.

Crystallization phase transitions are described by terms of the form $u_{\mathbf{k}_j} \exp(i\mathbf{k}_j \cdot \mathbf{r})$ in the expansion for the density function; weak crystallization is the limiting case when all the wave vectors taking part have equal length [19]. The only invariant terms in the free energy expansion over the corresponding order parameters ϕ_j are those combinations of the ϕ_j's with $\mathbf{k}$ vectors consti-
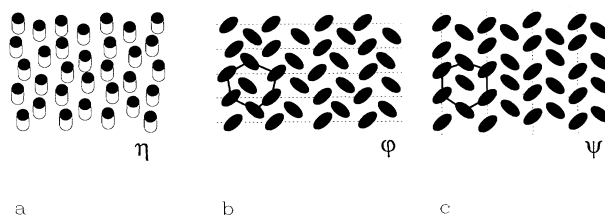

η   φ   ψ

a   b   c

FIG. 2. Molecular arrangements for collective tilt of the molecules (a) and one-dimensional crystallization with the crystallization waves along (b) and normally (c) to the bond direction.

tuting a closed polygon ($\sum_j \mathbf{k}_j = 0$). Since the experimentally observed phases possess orthorhombic symmetry, we can restrict ourselves by $\mathbf{k}$ vectors lying in the symmetry planes. The sixfold rotation C_6 generates the star consisting of six vectors $\mathbf{k}_{j+1} = C_6 \mathbf{k}_j$. The order parameter has six components ϕ_j, and since the density function $\sum_j u_{\mathbf{k}_j} \exp(i\mathbf{k}_j \cdot \mathbf{r})$ must always be real, it follows that $\phi_{j+3} = \phi_j^*$. It is convenient to designate $\phi_1 = \varphi_1 \exp(i\gamma_1), \phi_2 = \varphi_2 \exp(i\gamma_2), \phi_3 = \varphi_3 \exp(i\gamma_3), \phi_4 = \varphi_1 \exp(-i\gamma_1), \phi_5 = \varphi_2 \exp(-i\gamma_2), \phi_6 = \varphi_3 \exp(-i\gamma_3)$.

There exist two representations for each star $\mathbf{k}_j$, one which preserves the sign of the order parameter on reflection in the symmetry plane containing the wave vector, and one which changes it. The former representation gives the free energy expansion

$$\Phi = P\varphi^2 + Q\varphi_1\varphi_2\varphi_3 \cos(\gamma_1 + \gamma_2 + \gamma_3) \\ + R\varphi^4 + S(\varphi_1^4 + \varphi_2^4 + \varphi_3^4); \tag{3}$$

here $\varphi^2 = \varphi_1^2 + \varphi_2^2 + \varphi_3^2$. The cubic term in Eq. (3) gives rise to a first-order transition with equal amplitudes for all of the waves: $\varphi_1 = \varphi_2 = \varphi_3$. This therefore describes a first-order crystallization phase transition from a hexatic to a hexagonal crystal. It does not occur in Langmuir monolayers and so is not of interest for the present work.

The representation which changes the sign of the order parameter on the reflection mentioned above allows only even powers of the order parameter in the free energy expansion:

$$\Phi_\varphi = F\varphi^2 + G_1\varphi^4 + G_2(\varphi_1^4 + \varphi_2^4 + \varphi_3^4) \\ + H_1\varphi^6 + H_2\varphi^2(\varphi_1^4 + \varphi_2^4 + \varphi_3^4) \\ + H_3\varphi_1^2\varphi_2^2\varphi_3^2. \tag{4}$$

If φ^2 is kept fixed, the minimum of (4) with respect to the components φ_j depends on the sign of G_2. For $G_2 > 0$ one has $\varphi_1 = \varphi_2 = \varphi_3$. This case preserves the hexagonal symmetry and hence is not of interest for the present work. When $G_2 < 0$, the symmetry is broken: $\varphi_1 = \varphi, \varphi_2 = \varphi_3 = 0$, meaning that crystallization occurs only in one dimension. The ordered phase consists of equidistantly spaced rows of the molecules, with the order parameter alternating from one row to the next. Within a row, the molecules possess liquidlike order. The order parameter φ describes either antiferroelectric ordering of transverse vectors of the molecules or alternating orientations of the 2D nematic director. The latter case corresponds to the herringbone order commonly encountered in 3D packings of aliphatic chain derivatives [23] as well as in ordered smectic liquid crystals [24]. It is illustrated in Figs. 2(b) and 2(c) for crystallization directions parallel and normal to the bond direction. The dashed lines indicate periodicity, and the order within the crystalline rows is liquidlike.

The phases shown in Figs. 2(b) and 2(c) give rise to different low-order diffraction peaks. In Fig. 2(b), the bonds do not lie in the crystalline rows. This gives broad first-order diffraction peaks, reflecting the liquidlike order. In contrast, the diffraction pattern of the phase shown in Fig. 2(c) shows one narrow peak due to diffraction from the crystalline rows, while the doubly degenerate peak caused by the short-range translational order within the rows is broad. Comparing these results with the experimental data on the diffraction peak widths, we can attribute Fig. 2(b) to the phases S and L_2' whereas Fig. 2(c) corresponds to the phase L_{2h} possessing considerably different widths of the peaks. Clearly, one crystallization order parameter is inadequate, and it is necessary to deal with order parameters describing the transitions to phases with mutually orthogonal directions of crystallization.

We preserve the letter φ for the order parameter of the phase shown in Fig. 2(b). For one crystallization wave ($\varphi_1 = \varphi, \varphi_2 = \varphi_3 = 0$) Eq. (4) reduces to

$$\Phi_\varphi = F\varphi^2 - G\varphi^4 + H\varphi^6, \tag{5}$$

with $G = -(G_1 + G_2)$ and $H = H_1 + H_2 + H_3$. To obtain the first-order transition LS-S in Langmuir monolayers, we take the coefficients F, G, H to be positive. The coefficient F is considered to be temperature dependent whereas G and H are taken to be constant. As F decreases to the value $F_0 = G^2/4H$, a first-order transition occurs from $\varphi = 0$ to $\varphi = \varphi_0$ with $\varphi_0^2 = G/2H$. The transition from the hexatic phase to the phase shown in Fig. 2(c) is described by the order parameter ψ possessing the same symmetry and the same free energy expansion,

$$\Phi_\psi = F'\psi^2 - G'\psi^4 + H'\psi^6. \tag{6}$$

Accordingly, the first-order transition at $F_0' = G'^2/4H'$ gives $\psi_0^2 = G'/2H'$. The coupling between φ and ψ described by the product of the invariants, $\varphi^2\psi^2$, does not qualitatively influence the transitions and is omitted from subsequent consideration.

The coupling between the order parameter φ_j and the tilt is described by the invariant

$$\varphi_1^2\eta^2 \cos 2\beta + \varphi_2^2\eta^2 \cos(2\beta + 2\pi/3) \\ + \varphi_3^2\eta^2 \cos(2\beta + 4\pi/3). \tag{7}$$

Taking $\varphi_1 = \varphi, \varphi_2 = \varphi_3 = 0$, adding the product of the invariants φ^2 and η^2 and analogous coupling terms for the order parameter ψ one has finally

$$\Phi_{\varphi\psi\eta} = (I\varphi^2 + I'\psi^2)\eta^2 + (J\varphi^2 - J'\psi^2)\eta^2 \cos 2\beta. \tag{8}$$

The coupling between these three order parameters gives a large variety of phase diagrams, depending on the relationships between the coefficients in the free energy expansion. Our aim is to explain the experimental phase diagram of the monolayers of amphiphilic molecules. The variables in the theoretical phase diagram, Fig. 1, are the coefficients A, F, and F' of the lowest-order terms in the free energy expansions over corresponding order parameters; all other coefficients are taken to be constant. The most symmetrical phase, the hexatic LS, occurs when

A, F, and F' are sufficiently large. As F decreases to the value $F_0 = G^2/4H$, a first-order transition occurs at which the backbone planes order, giving the S phase. Based on the x-ray data, we have identified this transition as being one-dimensional crystallization with the crystallization wave along the bond direction [Fig. 2(b)]. The second-order tilting phase transition at the line $A = 0$ leads to the phase L_{2d} with short-range translational order. The tilting phase transition S-L_2' occurs at $\varphi \approx \varphi_0$ and $\psi = 0$. For $J > 0$ Eq. (8) gives $\beta = \pi/2$ (tilt to the next-nearest neighbor) in the L_2' phase, in agreement with the experiment. Then the lowest-order term of Eq. (1) transforms to $(A - A_0)\eta^2$ with $A_0 = (J - I)\varphi^2$. The line S-L_2' is shifted by A_0 with respect to the line LS-L_{2d}. The analysis of the transitions between these phases is quite similar to that performed in Ref. [18] for the transitions between crystalline phases since the free energy expansions are the same.

As the temperature decreases, the subsequent crystallization over the order parameter ψ occurs, giving rise to the transition S-CS at sufficiently large pressures ($A > A_0$). The phase CS possesses crystallization waves in two orthogonal directions and is therefore a 2D crystal. The transition CS-L_2'' is the tilting phase transition in the crystalline phase. The tilt is towards the nearest neighbor, as observed, when $J\varphi^2 < J'\psi^2$ in Eq. (8). The swiveling transition L_2'-L_{2h} occurs as the tilt angle η increases, driven by the competition between the order parameters φ and ψ. The free energy has local minima at $(\varphi \neq 0, \psi = 0)$ and $(\varphi = 0, \psi \neq 0)$. Just after S-L_2' transition the first minimum is obviously deeper. However, further behavior depends on the relative values of the coefficients in the free energy expansion. If the order parameter ψ were nonzero, the coupling (8) would give $\beta = 0$ for $J' > 0$ and would reduce F' in Eq. (6) to $\tilde{F}' = F' - (J' - I')\eta^2$. As the tilt angle η increases, $\tilde{F}'$ reaches the value F_0' and the free energy in the local minimum at $(\varphi = 0, \psi \neq 0, \beta = 0)$ becomes negative. Further increase of η makes this minimum deeper than the minimum at $(\varphi \neq 0, \psi = 0, \beta = \pi/2)$. The observed simultaneous change of the tilt direction and the correlation lengths at L_2'-L_{2h} transition is thus explained.

In summary, symmetry considerations of the Landau theory allow the hexatic phase to crystallize in only two ways: first, direct crystallization to a hexagonal 2D crystal and second, one-dimensional crystallization by ordering of some molecular degree of freedom (the backbone planes in the present case). The rich polymorphism of Langmuir monolayers is due to the coupling of 1D crystallization with the collective tilt of the molecules.

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