Anisotropy of the Line Tension and Bulk Elasticity in Two-Dimensional Drops of a Mesophase

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Using Brewster angle microscopy to study Langmuir monolayers of fatty acids at the air-water interface, we have observed a boojum pattern in two-dimensional drops of a tilted liquid condensed phase. In a boojum, the in-plane molecular orientation turns continuously and points with the same molecular orientation are located on straight lines, crossing at a defect point expelled from the drop. We have observed a distortion of the drops in the neighborhood of these points. We have studied the distortion of the drops and the distance of the defect point to the drop boundary, and deduced several ratios between elastic constants, anisotropic line tension, and elastic constants of the medium.

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Thanks to polarized fluorescence microscopy and Brewster angle microscopy [1], a rich variety of molecular patterns has been observed in the tilted liquid condensed phases of fatty acids or ester monolayers spread at the air-water interface. According to x-ray diffraction experiments [2], in these hexatic phases, the molecules are located on a locally hexagonal or distorted hexagonal lattice; the orientational order of the intermolecular directions is long range, but the positional order of the molecules is only short range. In some of these phases the molecules are tilted from the surface normal. The tilt angle is fixed in each phase, however, the in-plane molecular orientation, i.e., the tilt-azimuthal angle of the molecules, varies according to the phase texture. In addition, the tilt-azimuthal direction is fixed with respect to the intermolecular directions. Several patterns have been observed in these tilted phases [3–8]. It has been shown that most of the condensed phases of fatty acids and esters are similar to smectic phases of liquid-crystal films. Indeed, similar patterns have been visualized in the smectic phases [9,10]. The shape of drops of an hexatic phase and the arrangement of the molecules inside them result from the competition between the elastic energy relative to the texture inside the drops, the isotropic line energy of the interface between the drops, and the surrounding isotropic phase and the conditions at the boundary of the drops, i.e., the anisotropic line energy.

Microscopy at the Brewster angle [1] allows the observation of phase coexistences. The intensity of the reflected light depends on the thickness of the layer and on its density. Moreover, the optical anisotropy of the film is observed by adding an analyzer in the path of the reflected light. In the tilted liquid condensed phases, each azimuthal orientation of the molecules corresponds to a shade of grey on the image.

We have observed the coexistence between two-dimensional drops of the tilted liquid condensed phase L_2 (tilt toward a nearest neighbor) and the gaseous phase in a Langmuir monolayer of palmitic acid spread on water at pH 5.5, at room temperature. Commercial palmitic acid contains impurities (less than 1%). They formed round drops (of much less reflectivity than the dense drops but more bright than the gas), most of the time located around liquid condensed drops. We have recrystallized the palmitic acid from Merck (the purest we could find) twice, and performed a chromatography. A high proportion of the impurities have thus been eliminated.

Observed with an analyzer, the drops of the L_2 phase have a boojum pattern [Figs. 1(a) and 1(b)]. The tilt-azimuthal angle of the molecules turns continuously, and curves of the same in-plane molecular orientation are straight lines crossing at a defect point rejected outside the drop. The expulsion distance was observed to depend on the size of the boojum. In the large drops (300 μm in diameter), the defect point is close to the drop boundary (20 to 30 μm). On the contrary, in the small drops (60 μm in diameter), the defect point is far from the border of the drop (110 to 120 μm). The in-plane orientation of the molecules was determined. In the very large drops, the in-plane molecular direction $\mathbf{c}$ is normal to the gas/L_2 interface all around the drop boundary, except just in the vicinity of the defect point. In contrast, in the small drops, $\mathbf{c}$ is normal to the drop boundary only in the neighborhood of the point A of the x axis [Fig. 1(c)], i.e., on the opposite part of the drop with respect to the defect point. We have also noticed a slight elongation of the drops and a cusp in the direction of the defect (Fig. 2). The small drops are more elongated than the large ones which are nearly circular. Our observations show that the cost in defect core energy is probably high, since the defect point is rejected outside the drop. Furthermore, the expulsion of the defect far from the border lowers the cost in elastic energy inside the drop [9]. However, the expulsion leads to a violation of the boundary conditions which tend to align the molecules normal to the gas/L_2 interface [3]. The boundary conditions would be perfectly satisfied if the defect point was on the border of the drop; when it is rejected outside, they are no longer satisfied on the side of the drop which is the closest to the defect point.

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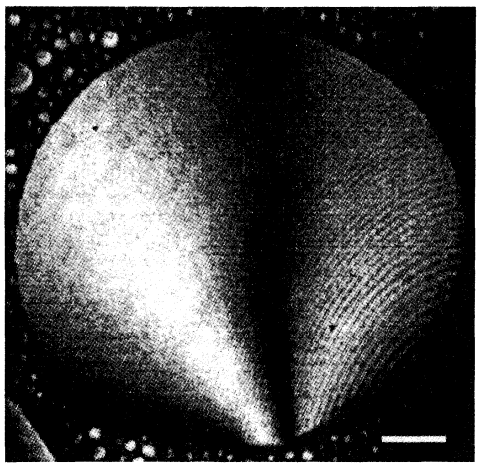
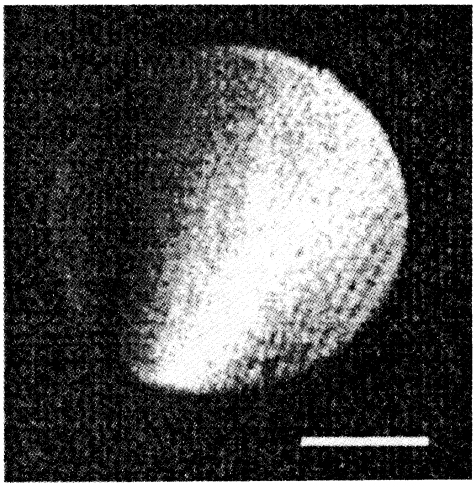


(a)



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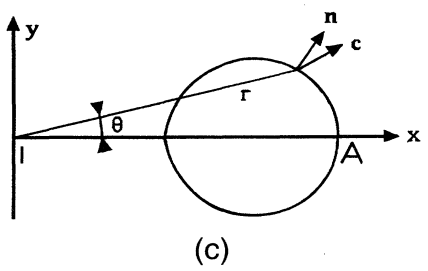

(c)

FIG. 1. Images of two drops of L_2 phase in the gaseous phase. Their radius are (a) $R = 196\ \mu$m and (b) $R = 74\ \mu$m. (c) Diagram of a drop.

Consequently, there is a cost in anisotropic line energy of the gas/L_2 interface. The deformation of the drops allows these boundary conditions to be satisfied better. Actually, the small drops whose boundary conditions are not well satisfied are more elongated in the direction of the defect point than the large drops which are slightly distorted. Our observation of this distortion implies that the anisotropic part of the line energy of the gas/L_2 interface is strong with respect to its isotropic part otherwise, the drops would remain round.

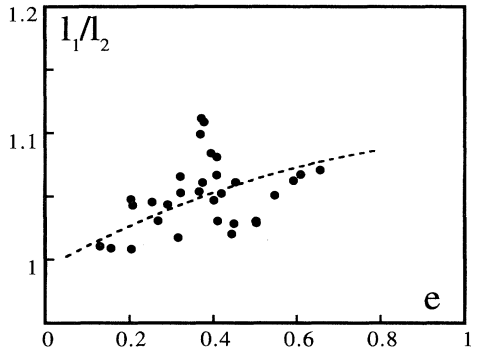

FIG. 2. Experimental drop elongation l_1/l_2 versus the ratio $e = d/(l_1 + d)$. l_1 and l_2 are the diameters of the drop, respectively, in the direction of the defect point and in the perpendicular direction.

In order to have information on the ratio between the anisotropic and isotropic line tensions and also on the elastic constants of the boojum texture observed, we have adapted a model used to calculate elastic constants in similar boojums of the smectic I phase in liquid-crystal films [9]. The tilted dense phase is described by the unit vector in the direction of the in-plane molecular orientation $\mathbf{c}$: $\mathbf{c} = \cos\phi\mathbf{x} + \sin\phi\mathbf{y}$ where ϕ is the tilt-azimuthal angle. The terms of the free-energy density must be consistent with the symmetries of a tilted Langmuir monolayer which are different from that of a liquid-crystal film. The Langmuir film is not symmetric with respect to the plane (x, y) of the head groups, a term linear in $\nabla \cdot \mathbf{c}$, representing a splay of the molecules is possible. However, the term $\nabla \cdot \mathbf{c}$ by itself is a total divergence that can be included in the boundary conditions (i.e., line tension). Moreover, here, the molecules of palmitic axis are not chiral so the free energy must be invariant in symmetries with respect to the vertical planes: a spontaneous flexion of the order parameter is forbidden, i.e., a term linear in $\nabla \times \mathbf{c}$. The expression of the free-energy density F_2 in terms of the order parameter $\mathbf{c}$ is then

$$F_2 = \frac{K_s}{2}(\nabla \cdot \mathbf{c})^2 + \frac{K_b}{2}(\nabla \times \mathbf{c})^2, \qquad (1)$$

where K_s and K_b are two Frank constants; K_s is a splaying energy of the order parameter $\mathbf{c}$, and K_b is a bending energy. The bulk free energy F_b is the integral of F_2 over the area of the boojum. F_2 can be written in terms of $K = (K_s + K_b)/2$ and $\beta = (K_s - K_b)/(K_s + K_b)$ remarking that $K_s = K(1 + \beta)$ and $K_b = K(1 - \beta)$. K_s and K_b must be positive, so that $-1 \leq \beta \leq 1$. We must now minimize the free-energy density F_2 with respect to the tilt-azimuthal angle ϕ in order to determine the allowed textures of the molecules inside the drops. Unless assuming that $K_s = K_b$ (i.e., $\beta = 0$), this equation is very complicated. However, as in Ref. [9], we utilize solutions that correspond to the texture we have observed. In the

boojums, the tilt-azimuthal angle ϕ of a molecule is independent of its distance r to the defect point and only depends on the angle θ between $\mathbf{r}$ and the x axis [Fig. 1(c)]. Hence, we can try a solution of the form $\phi = s\theta + \phi_0$. ϕ_0 is a constant and s is the winding number of the defect point: This is the angle of rotation of the order parameter $\mathbf{c}$ around any closed circuit encircling the defect, divided by 2π. One obtains the following solutions: (1) if $\beta = 0$, i.e., $K_s = K_b$, all the values of the winding number s are allowed, and (2) if $\beta \neq 0$, the allowed values of s are $s = 0$ (the domain is uniform), $s = 1$ ($\mathbf{c}$ is radial or tangential), and $s = 2$ which describes the arrangement of the molecules observed here. For instance, in the large drops in which the defect point is very close to the drop, we can observe that the order parameter $\mathbf{c}$ rotates through 2π when moving along half of any closed path encircling the defect (i.e., when θ rotates through π). The molecules being perpendicular to the drop boundary in these drops, the tilt-azimuthal angle ϕ is equal to 2θ. Therefore the solution $\phi = 2\theta$ corresponding to the boojum texture that we have observed is predicted by this model free energy. The expression of the minimum free-energy density is then

$$F_2 = 2K[1 + \beta\cos(2\theta)]/r^2. \quad (2)$$

The total free energy is the sum of the bulk elastic free energy, i.e., the integral of the free-energy density F_2 over the area S of the boojum and of the line energy of the gas/L_2 interface. This line energy depends on the angle α between the order parameter $\mathbf{c}$ and the unit vector $\mathbf{n}$ normal to the boundary of the boojum. It can be expanded in a Fourier series in α. Respecting the symmetries of the Langmuir monolayer [11], we will only keep the first two terms, $F_1 = \int dl\{\lambda_0 - \lambda_1 \mathbf{c}\cdot\mathbf{n}\}$. λ_0 and λ_1 are, respectively, the isotropic and anisotropic line tensions. The interfacial energy is then minimized when the in-plane molecular orientation is normal to the drop boundary as observed on the images. λ_1 characterizes the strength of the normal boundary conditions.

First, by taking advantage of the variation of the expulsion distance of the defect point with the size of the drops, we have determined the ratio between the anisotropic line tension λ_1 and the elastic constant K and also obtained an estimation of β. To achieve this, the free energy was calculated supposing that the drops are circular, given that their elongation is small. The minimization of the free energy with respect to the ratio $\rho = R + d$ (R is the radius of the drop and d the expulsion distance of the defect point) at fixed drop area gives the following relation between K, λ_1, and β [9]:

$$\lambda_1/K = (2/\rho)[\beta + \rho^2/(\rho^2 - R^2)]. \quad (3)$$

For different values of β, we have determined the value of λ_1/K that gives the best agreement between the experimental points ρ/R as a function of the radius R of the drop and the corresponding theoretical curves (Fig. 3). The best fit is obtained for $\beta = 1$ and $\lambda_1/K = 3.6 \times 10^4\ \mathrm{m}^{-1}$. However, the fits obtained for $0.3 < \beta < 1$ are in correct agreement with the experimental points and give $2.5 \times 10^4 < \lambda_1/K < 3.6 \times 10^4\ \mathrm{m}^{-1}$. Consequently, $K_s > K_b$, an unexpected result because the boojum texture presents more splay than bend. However, it is likely that it is the strength of the boundary conditions that imposes the texture, rather than the relative values of K_s and K_b.

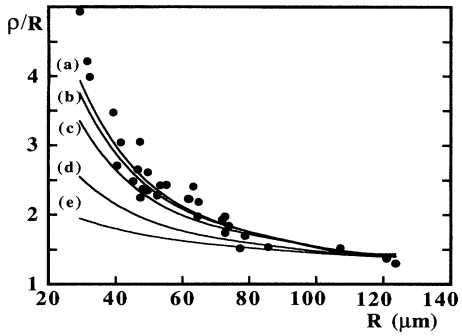

FIG. 3. Experimental values of ρ/R vs R and theoretical curves corresponding to different values of β and λ_1/K. (a) $\beta = 1$ and $\lambda_1/K = 3.6 \times 10^4\ \mathrm{m}^{-1}$, (b) $\beta = 0.5$ and $\lambda_1/K = 2.8 \times 10^4\ \mathrm{m}^{-1}$, (c) $\beta = 0$ and $\lambda_1/K = 2.2 \times 10^4\ \mathrm{m}^{-1}$, (d) $\beta = -0.5$ and $\lambda_1/K = 1.8 \times 10^4\ \mathrm{m}^{-1}$, and (e) $\beta = -1$ and $\lambda_1/K = 1.2 \times 10^4\ \mathrm{m}^{-1}$.

Further, we have studied the elongation of the drops in order to determine the ratio λ_1/λ_0 between the anisotropic and the isotropic line tensions. The shape and the texture of a drop are that minimizing the free energy. Writing that the variation of the free energy corresponding to a small change of the shape of the drop at equilibrium vanishes, one obtains the generalized Gibbs-Thomson equation [16]:

$$\lambda/R + \lambda'/R_\perp - \lambda''/R_\parallel = \Delta\Pi + F_2, \quad (4)$$

where $\Delta\Pi$ is a constant and λ' and λ'' are, respectively, the first and second derivatives of the line tension λ with respect to the angle α between the molecular direction $\mathbf{c}$ and the normal to the boundary $\mathbf{n}$. $1/R_\perp = \partial\phi/\partial s$ and $1/R_\parallel = \partial\phi/\partial n$ are "radii of curvature" for the molecular orientation (s being the curvilinear abscis of the drop boundary and n the position on the normal). The variation of the free energy associated to a change $\delta\mathbf{c}$ of the texture gives two equations, the first one is the Euler-Lagrange equation for the texture and the second one is an equilibrium equation of the torques exerted on the gas/L_2 interface:

$$[K_s\mathbf{n}\cdot(\nabla\cdot\mathbf{c}) + K_b(\nabla\times\mathbf{c})\times\mathbf{n} - \lambda_1\mathbf{n}]\times\mathbf{c} = 0. \quad (5)$$

In the case of a boojum texture ($\phi = 2\theta$), Eqs. (4) and (5) are, respectively, $\lambda_0/R + (2\lambda_1/r)\cos(\theta) = \Delta\Pi + (2K/r^2)[1 + \beta\cos(2\theta)]$ and $(2K/r)[\sin(\theta' - \theta) + \beta \times \sin(\theta' - 3\theta)] = \lambda_1\sin(\theta' - 2\theta)$. r is the distance from the defect point and θ', the angle between $\mathbf{n}$ and the symmetry axis $0x$. In the particular case where $\beta = 0$, these two equations describe a family of circular drops, as was remarked by Rudnick and Bruinsma [17]. To explain the appearance of an elongation of the drop and a cusp, it is needed $\beta \neq 0$ or the introduction of a third term in

the Fourier series in α of the line tension, $\lambda_2 \cos(2\alpha)$ [17]. In these two cases, the boojum texture ($\phi = 2\theta$) does not satisfy Eqs. (4) and (5) on the drop border and a deviation from this texture is requested. In the experiments, it is observed with good accuracy that the curves of the same in-plane molecular orientation are straight lines, but it is more difficult to conclude on the position of the intersection of these lines, in particular in the case of small drops. For $\beta = 0$, the Euler-Lagrange equation reduces to a Laplacian so that the calculation of the distortion of the boojum texture can be performed at first order in λ_2/λ_1. However, as $\beta > 0$ was deduced from the experimental curve $(\rho/R, R)$, it seems more natural to explain the drop elongation with $\beta \neq 0$ (and $\lambda_2 = 0$). In this case, the calculation of the distortion of the boojum texture is much more complex because the Euler-Lagrange equation is very complicated. We have kept the boojum texture and calculated numerically (from Eq. (4) or from the equation $\lambda_0/R + 2\lambda_1 \cos(\theta)/r = \Delta\Pi + \lambda_1[1 + \beta \cos(2\theta)] \sin(\theta' - 2\theta)/[\sin(\theta' - \theta) + \beta \sin(\theta' - 3\theta)]r$ deduced from Eqs. (4) and (5)) the shape of the drop, for different values of β. We have obtained a drop elongated in the direction of the defect point for $\beta > 0$ and a flattened drop for $\beta < 0$. This result is in agreement with the positive value of β found above. However, we found a too small elongation to explain the experimental results, probably because we have not calculated the deviation of the texture from the boojum texture ($\phi = 2\theta$).

In our calculation of λ_1/K and β, we have not considered the long-range electrostatic interactions between the vertical components of the dipoles carried by the molecules. These interactions induce the deformation of the drops which are close to each other. Since we have studied isolated drops, these interactions between neighboring drops can be neglected; however, dipolar interactions inside each drop must be considered. Contrary to the isotropic line tension, these forces tend to increase the drop elongation [12]. The dipolar electrostatic interactions can be divided into two parts [13]. The first one, called "short range," corresponds to the electrostatic interactions acting on a distance smaller than b. The second part, called "long range," contains the electrostatic interactions acting on a distance larger than b. If $b \ll R$, the curvature radius of the drop, the short-range part can be included in the line tension λ due to the other short-range forces which become $\lambda - \lambda_e(b)$. $\lambda_e(b)$ increases logarithmically with b. On the contrary, the long-range part cannot be included in the line tension but induces a pressure variation inside each drop which depends on the complete configuration of the drop. An estimation of $\lambda_e(b)$ for a drop of the L_2 phase in the gas gives $\lambda_e \approx 8 \times 10^{-13}$ N for $b = 1$ μm. These values have to be compared to the line tension λ measured in similar systems, $\lambda \sim 5 \times 10^{-12}$ N [14,15]. The larger b, the more the electrostatic forces are taken into account in λ_e. However, when b becomes too large, an exact description of the drops in the vicinity of the cusp is no longer possible. Supposing that the long-range part of the electrostatic forces could be included in the line tension, it would induce a variation $\delta\lambda_e \approx 4 \times 10^{-13}$ N of this line tension for the largest drops. This gives an upper estimation of the importance of these forces in our system. Note that they are at least 10 times smaller than the line tension.

In conclusion, from the distance of a drop with a boojum texture to its virtual defect point, we have deduced the ratio between the elastic constant and the anisotropic line tension $2.8 \times 10^{-5} < K/\lambda_1 < 4 \times 10^{-5}$ m and the coefficient β, $0.3 < \beta < 1$, the positive value of which indicates that the elastic energy relative to the splay is higher than that relative to the bend. The best fit is obtained for $\beta = 1$ and $K/\lambda_1 = 2.8 \times 10^{-5}$ m, a large value meaning that probably λ_1/λ_0 is small. We have observed an elongation of the drops, up to about 7% for small drops, in the direction defect point and a cusp. This deformation is compatible with the positive value of β.

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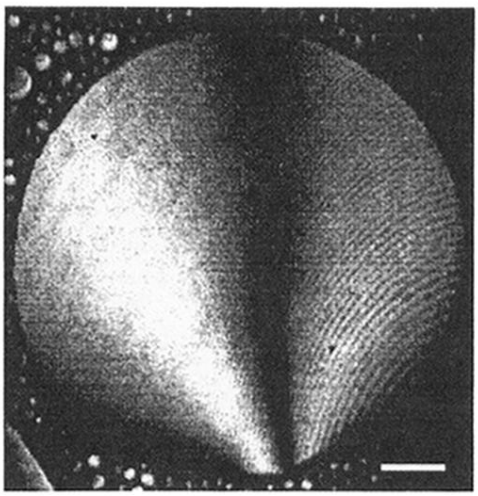

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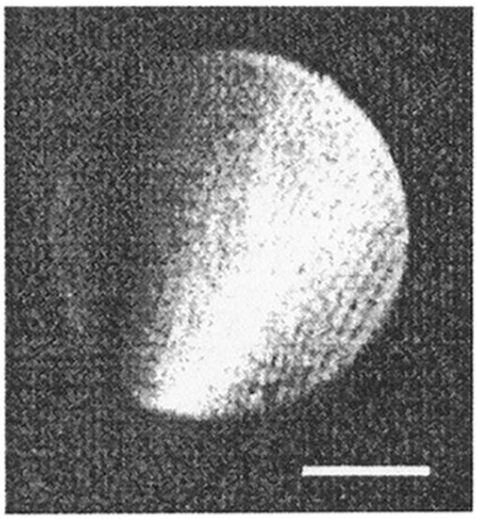

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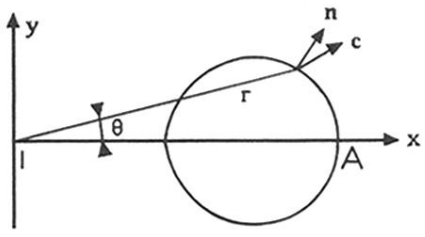

(c)

FIG. 1. Images of two drops of L_2 phase in the gaseous phase. Their radius are (a) $R = 196\ \mu$m and (b) $R = 74\ \mu$m. (c) Diagram of a drop.