Collective Reorientation in Isolated Smectic-C Langmuir Monolayer Droplets Induced by Line Tension Anisotropy

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We report a reorientational phenomenon that takes place inside confined smectic-C (SmC) domains in a phase-segregated Langmuir film. Observations of texture changes by means of Brewster angle miscroscopy (BAM) refer to an azobenzene derivative whose monolayer behavior depends strongly on its molecular cis/trans configuration. Well-developed droplets of a trans-rich mesophase adopt mixed bend/splay structures whose splay sign is reversed through complete droplet reordering when varying the surface pressure. Numerical simulations of a simple relaxational model based on a free-energy functional fully reproduce the experimental observations.

Introduction

Langmuir monolayers, monomolecular films of insoluble surfactant species spread at the air−water interface, are particularly suited systems for looking for dynamical aspects of mesoscopic self-organization.[1,2] Interest in this kind of softly condensed material is being continuously renovated both from fundamental and practical purposes. Potentialities offered by assembled monolayers are equally appreciated by investigators aiming at discovering new bottom-up designing strategies, for instance, to develop chemical or biochemical sensors, or for those who look at them to gain insight into the structural properties of cellular membranes. From a more fundamental point of view, Langmuir monolayers provide one of the most genuine examples of 2D physicochemical systems.

Unusual physical properties of 2D condensed systems are already apparent in the variety of mesophases that they adopt when varying either of their basic state variables, that is, the temperature and the surface pressure.[3] Some of these phases display textures, when observed using polarized light, that reflect the coherence in the spatial distribution of the local optical axis of the amphiphilic constituent molecules.[4] Here, we report a reorientational phenomenon, followed experimentally as a well-resolved texture change, which occurs inside individual domains in Langmuir monolayers at low molecular densities and is induced by controlled changes in the surface pressure. Supporting simulations, obtained with a dynamical model built on a Landau-type expansion of the free energy of the confined material, are reported in the last part of this letter.

Our experimental observations correspond to a monomolecular film of the azobenzene derivative 4-[4-[(4-octylphenyl)azo]-phenoxy]butanoic acid, 8Az3COOH in the shorthand notation used later on. Two features of this amphiphilic compound are worth mentioning. First, it is photosensitive, a property that is associated with the light-induced transition between the trans and cis isomeric forms of the azo group in the molecule.[5] In turn, this configurational change dramatically modifies the amphiphilic nature itself and the dielectric properties of the species as a surfactant. More precisely, cis molecules are crumpled, rather than stretched, with higher dipolar moment at the azo moiety compared to trans molecules. We recall in passing that such a photoisomerizable nature endows this material with a great potential for the study of nonequilibrium self-organization phenomena.[6−8]

Second, and even more important to understand the phenomena here described, the trans isomer forms mesophases at relatively high values of area per molecule, compared with the known situation for alkane amphiphiles with similar chain length.[9] This favors the assembling of labile monolayers that display long-range orientational order but substantial positional disorder.[10] Thus, by selecting conveniently prepared monolayers of this material, with respect to its trans/cis configurational state (see below), and by working at particularly chosen conditions of temperature and surface pressure, we will benefit from the advantages of dealing with textured yet labile phases, free of the rigidity imposed by the hexatic positional order commonly found in mesophases of lipid monolayers.[3]

Experimental Methods and Results

The synthesis of the azobenzene derivative 8Az3COOH follows previously reported procedures.[11] Solutions ($\simeq$1 mM) were prepared using chloroform (J. T. Baker, p.a. grade) and spread over ultrapure water contained in a custom-built Teflon trough.[12] After spreading, a minimum of 5 min was allowed for the solvent to evaporate and the system to equilibrate. The trough was thermostated at 35.0 $\pm$ 0.2 °C. Imaging of the monolayer was performed with a custom-built Brewster angle microscope.[12] Such a device, based on a reflection polarizing microscope, allowed us to visualize the molecular ordering of birefringent layers.[13,14] Quantitative analysis of the digitized BAM images allowed us to resolve the molecular tilt and azimuth at mesoscopic length scales.[12] For the material at hand, with our BAM configuration, the reflectivity as a function of the molecular azimuth is a smooth function, with three maxima and three minima. The existence of highly symmetric textures, such as the ones reported here, is crucial to unambiguously extract the 2D azimuth field from the BAM images.

The protocol to prepare the spreading solution turns out to be crucial. If the solution is stored, deposited, and further
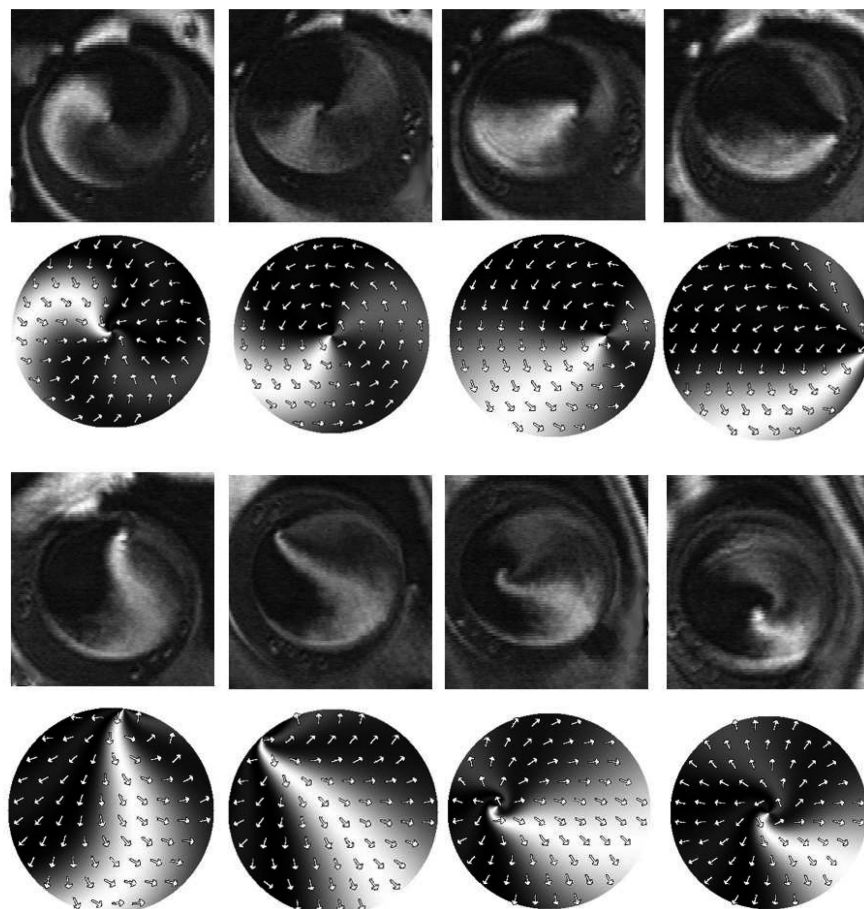
Figure 1. Sequence of BAM images for a splay-in to splay-out transition after a decrease in the surface pressure from 7.5 to 3 mN/m at 35 °C. The width of the BAM images is 207 μm. Below each image, the estimated azimuth field is shown. This process needs around 3 min to be completed. The defect movement either outward or inward lasts around 30 s.

manipulated in the dark or under dim red light, then the amphiphilic molecules are essentially trans. At 35 °C, monolayers display a characteristic flickering of their reflectivity, look quite fluid, and show extended textures that are compatible with a smectic-C (SmC) ordering (positional disorder).[15] We preferred, however, to proceed differently by forcing a situation of phase segregation to look for reorientational processes inside individual domains. To this end, the azobenzene solution was exposed, prior to deposition, to room light. A mixture of cis and trans isomers was then achieved, as revealed by UV−vis absorption spectroscopy. After deposition, and by keeping the monolayer in the dark, we observed small droplets of a birefringent phase (as viewed with the BAM), appearing in a matrix of a dark-gray, untextured isotropic phase. Further growth occurred by a fast coalescence dynamics that in about 30 min led to an average droplet diameter up to 250 μm. Although further droplet growth is unavoidable, either via coalescence or caused by the cis to trans thermal isomerization, both processes are, at this stage, slow enough to allow for extended observation and manipulation of individual droplets. Parallel observations[11] permitted us to conclude that the isotropic, barely condensed, and highly fluid medium was rich in cis component, whereas the assembled confined domains were essentially composed of the trans isomer. Experimental evidence[11] indicates that phase separation is practically complete.

Analysis of the inner structure of these droplets reveals that their SmC-like textures are organized around a point singularity near the center. Assuming that the polar tilt has a uniform value (except likely near the core defect),[16] the typical configuration

of well-developed droplets is consistent with a central bend distortion, progressively adapted to a splay arrangement near the boundaries (similar textures are also found in the context of chiral thin films).[17] Furthermore, the presence of both clockwise and counterclockwise bend deformations near the central singularity is consistent with the achiral nature of the 8Az3COOH species. The key observation we want to report here refers, however, to dynamical changes in the splay sign induced by controlled variations of the surface pressure Π. When the monolayer is kept at low Π values, $\Pi \leq 3$ mN m^{-1}, the splay distortion corresponds to molecules with their tails directed outward (splay-out in the shorthand notation used hereafter). Under compression, albeit maintaining the smectic order, $\Pi \leq 13$ mN m^{-1}, the splay distortion near the outermost droplet corona evolves to adopt the reverse configuration, that is, molecular tails pointing inward (splay-in). The original splay-out configuration is recovered after returning back to the initial low pressure state of the monolayer. A simple intuitive reasoning should be enough at this point to interpret these observations. In more condensed states, the stretched and apolar tails of trans molecules inside but close to the droplet boundary would tend to avoid the interaction with the highly polar and bent chains of the cis molecules predominant in the outer phase.

Although in our experiments we have identified different pathways underlying such a reorientational dynamics, depending essentially on the droplet size, we shall focus here in the most generic scenario, as displayed in Figure 1. It corresponds to intermediate-size droplets (between ca. 150 and 250 μm) and proceeds in the following way (here chosen to go from splay-

in to splay-out). First, a swiveling reorientation takes place that permits the entire droplet to attain an almost pure bend texture without any apparent motion of the central singularity. Subsequently, the defect moves toward the boundary of the droplet, keeping its own structure and the field of distortions around it. This outward motion terminates when the defect reaches the boundary, and the droplet adopts the common texture typical of a boojum. Rather than remaining anchored to the outer contour, the defect then starts to rotate along the boundary an unpredictable number of times, until it moves inward, again dragging the orientation of the molecules around it and leading the texture to reshape according to the final splay-out conformation. Figure 1 presents the whole sequence of BAM images and the corresponding reconstructed azimuth field for the reorientation process just described.

Our experiments confirm that the signs of the defect rotational motion, when tight fitted to the boundary, and that of the central bend distortion coincide or differ, depending on whether the splay contribution of the final mixed texture is splay-out or splay-in, respectively. Indeed, both clockwise and counterclockwise rotations are simultaneously observed because, as mentioned above, both chiralities of the central bend distortion coexist.

Theoretical Section

Our model, previously proposed to analyze equilibrium textures,[18] is built on a free-energy-based continuum description of the droplet-like domains, admitted size-fixed, with a perfectly circular shape that is independent of any inner texture changes. Furthermore, we assume a uniform tilt angle distribution, avoid considering any variable for the cis/trans composition, and neglect droplet−droplet interactions. The single-order parameter left is then the azimuth variable φ of the trans molecules, in terms of which elastic interactions are computed from local deformations of the in-plane $\vec{\mathbf{c}}$ molecular director [$\vec{\mathbf{c}} = (\cos \varphi, \sin \varphi)$]

$$\mathscr{F}_{elas} = \int \left[\frac{K_s}{2} (\vec{\nabla} \cdot \vec{\mathbf{c}})^2 + \frac{K_b}{2} |\vec{\nabla} \times \vec{\mathbf{c}}|^2 \right] dx \, dy \qquad (1)$$

where K_s and K_b stand, respectively, for the splay and bend elastic constants.[19,20] In what follows, we will assume, in accordance with our experiments, that $K_s > K_b$, that is, bend distortions are favored. We supplement this bulk term with the interfacial energy between the confined phase and the isotropic medium. At lowest orders such boundary term reads[4]

$$\mathscr{F}_b = \int [\alpha - \beta(\vec{\mathbf{c}} \cdot \vec{\mathbf{n}})] dl \qquad (2)$$

where $\vec{\mathbf{n}}$ stands for the boundary normal unit vector and α denotes the isotropic line tension. Notice that $\beta > 0$ (respectively, $\beta < 0$) favors tails of molecules at the interface pointing outward (respectively, inward) from the droplet boundary.

Reorientational dynamics, occurring in a time scale determined by a viscosity-like and material-dependent parameter, γ, is readily formulated in terms of the total free energy $\mathscr{F} = \mathscr{F}_{elas} + \mathscr{F}_b$

$$\frac{\partial \varphi}{\partial t} = -\frac{1}{\gamma} \frac{\delta \mathscr{F}}{\delta \varphi} + \zeta \qquad (3)$$

where ζ represents a small amplitude thermal noise added to favor complete relaxational processes, thus avoiding spurious frustrated texture dynamics.
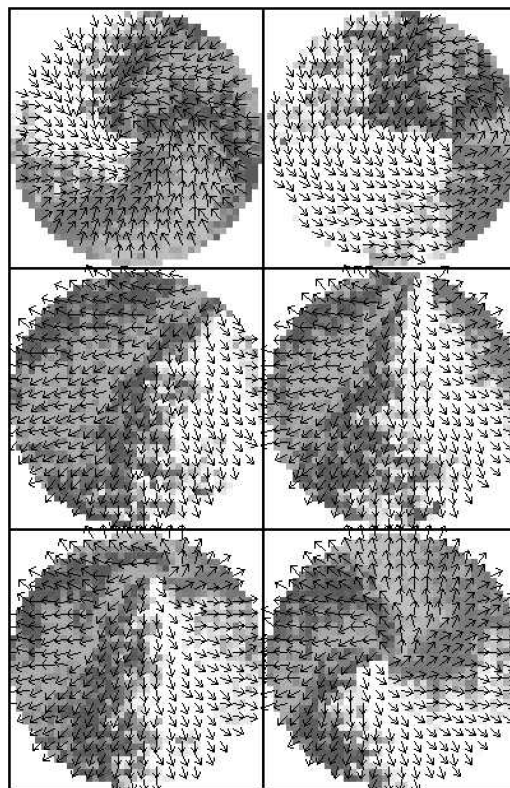

Figure 2. Sequence for the dynamics of an initially centered bend defect in a droplet with $R = 2$, elastic constants $K_s = 0.1$ and $K_b = 0.02$, and β gradually increased from −0.1 to +0.1. The arrows represent the azimuthal molecular orientation, and the gray color scale is equivalent to the one resulting from BAM observations. These results were obtained from the numerical resolution of eq 3 using arbitrarily $\gamma = 1$ and a moderate noise that follows the fluctuation−dissipation relation $< \zeta_i(t)\zeta_j(t') > = 0.01 \, \delta_{ij}\delta(t - t')$. Equation 3 is numerically solved in a 2D circle discretized in square boxes of sufficiently small size $\Delta x \ll R$.

We have numerically solved eq 3 (see caption of Figure 2 for details), trying to reproduce the reorientational dynamics observed in our experiments. For simplicity, we choose here to enforce pressure variations solely through changes in the model boundary parameter β. According to our arguments above, β is assumed to crossover from being negative at high pressures to positive at low compression. This correspondence, however, has to be considered only as qualitative, singularly when varying the monolayer lateral pressure, because such changes, in relation to the state of the assembled molecules at the droplet boundary, are likely to be mediated by a complex combination of several intermediate kinetic processes in the monolayer. Figure 2 depicts the numerical simulation after prescribing, for simplicity, a symmetric positive linear ramp variation in β. In a qualitative description, the resulting reorientational dynamics is remarkably similar to the experimental one; for example, the stability/instability of central defects (see below), the outward-inward displacement of the defect, and the sense of its rotational motion are well captured by the relaxational model presented here.

Additional numerical calculations may help to extract some useful insight toward understanding the relaxational phenomenon just described. A series of equilibrium noise-free textures were computed for eccentric bend-like defects in terms of their distance to the center of the droplet. Results are summarized in Figure 3. Clearly, at nonzero values of β, both for positive and negative determinations, the minimum free energy is achieved for centered defects, whereas approaching null values of β the

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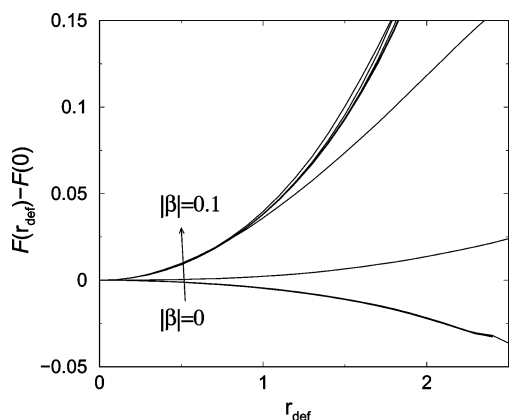*J. Phys. Chem. B, Vol. 108, No. 45, 2004* **17277**

Figure 3. Energy curves for relaxed noise-free structures as a function of the distance of the bend defect to the droplet center, r_{def}. The droplets have a size $R = 3$, the elastic constants are the same as those in Figure 2, and $|\beta|$ is varied from 0 to 0.1.

defect expulsion is favored. This result supports our observations above concerning the outward motion of the central singularity at the intermediate stage of the droplet texture evolution.

Conclusions

In this letter, we have reported that the reorientational dynamics of SmC droplets in Langmuir monolayers of an azobenzene derivative are induced by surface pressure changes. This process involves a sign reversal of the splay texture following the transient displacement of the central defect. BAM imaging techniques of such monolayers provide a well-defined characterization of the collective reordering phenomenon at the mesoscopic level. The experimental observations are captured by a simple model based on elastic and surface interactions. Surface pressure variations are modeled as modifications of a line tension anisotropy parameter at the droplet boundary,

reflecting the low affinity of trans molecules inside the condensed domains with respect to the cis isomers in the outer liquid phase.

References and Notes

(1) Whitesides, G. M.; Grzybowski, B. *Science* **2002**, *295*, 2418.
(2) Mikhailov, A. S.; Ertl, G. *Science* **1996**, *272*, 1596.
(3) Kaganer, V. M.; Möhwald, H.; Dutta, P. *Rev. Mod. Phys.* **1999**, *71*, 779.
(4) Fischer, T. M.; Bruinsma, R. F.; Knobler, C. M. *Phys. Rev. E* **1994**, *50*, 413.
(5) Rau, H. *Photochemistry and Photophysics*; CRC Press: Boca Raton, FL, 1990.
(6) Tabe, Y.; Yokoyama, H. *Langmuir* **1995**, *11*, 4609.
(7) Tabe, Y.; Yokoyama, H. *Mol. Cryst. Liq. Cryst.* **2001**, *358*, 125.
(8) Tabe, Y.; Yamamoto, T.; Yokoyama, H. *New J. Phys.* **2003**, *5*, 132.
(9) Knobler, C. M. *Adv. Chem. Phys.* **1990**, *77*, 397.
(10) Durbin, M. K.; Malik, A.; Richter, A. G.; Yu, C. J.; Eisenhower, R.; Dutta, P. *Langmuir* **1998**, *14*, 899.
(11) Crusats, J.; Albalat, R.; Claret, J.; Ignés-Mullol, J.; Sagués, F. *Langmuir* **2004**, *20*, 8668.
(12) Ignés-Mullol, J.; Claret, J.; Sagués, F. *J. Phys. Chem. B* **2004**, *108*, 612.
(13) Hénon, S.; Meunier, J. *Rev. Sci. Instrum.* **1991**, *62*, 936.
(14) Hönig, D.; Möbius, D. *J. Phys. Chem.* **1991**, *95*, 4590.
(15) Feder, A.; Tabe, Y.; Mazur, E. *Phys. Rev. Lett.* **1997**, *79*, 1682.
(16) Tabe, Y.; Shen, N.; Mazur, E.; Yokoyama, H. *Phys. Rev. Lett.* **1999**, *82*, 759.
(17) Kraus, I.; Meyer, R. B. *Phys. Rev. Lett.* **1999**, *82*, 3815.
(18) Reigada, R.; Abad, E.; Crusats, J.; Claret, J.; Ignés-Mullol, J.; Sagués, F. *J. Chem. Phys.* in press, 2004.
(19) Young, C. R.; Pindak, R.; Clark, N. A.; Meyer, R. B. *Phys. Rev. Lett.* **1978**, *40*, 773.
(20) Langer, S. A.; Sethna, J. P. *Phys. Rev. A* **1986**, *34*, 5035.