Light-Induced Layer by Layer Thickening in Photosensitive Liquid Crystal Membranes

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(Received 5 January 2005; published 7 July 2005)

Photosensitive smectic membranes of pure liquid crystal (LC) were studied under white light illumination. A thickness increase is observed in the illuminated film area. Appropriate light and thermal conditions lead to a thickening layer by layer process. This unusual phenomenon is opposite to the well-known step-by-step thinning transitions under heating. We give a phenomenological interpretation for thickening based on layer transport of LC matter towards the illuminated area.

DOI: 10.1103/PhysRevLett.95.027802 PACS numbers: 61.30.−v, 42.70.Df, 64.70.Md, 68.15.+e

Smectic membrane behavior is in many aspects determined by surface and fluctuation phenomena [1,2]. The latter effects become important near phase transitions. The surface stabilizes the smectic phases with positional order. In bulk samples the smectic structures exist near the free surface above the transition temperature between smectic and phases without positional ordering (nematic, cholesteric (N^*), isotropic liquid). Various original behaviors resulting from competition between surface and bulk ordering in films have already been reported: formation of two-dimensional emulsions [3–5], induction of polar characteristics , and structural phase transitions [7]. One of the most striking phenomena is the layer by layer thinning transitions. Stoebe *et al.* [8] discovered that smectic membranes do not melt at heating; moreover, the temperature range of the existing membranes increases with decreasing membrane thickness. For a given thickness (determined by the number of smectic layers N), a critical temperature T_N exists, at which one smectic layer is lost. Thinning transitions have been extensively studied experimentally and theoretically [8–13]. Membrane structure instability occurring near T_N gives rise to the thinning process. This instability is created by a decrease of the surface correlation length with temperature leading to a net decrease of the smectic order parameter in the film. To return to a stable state, the membrane thickness is reduced, for the free surfaces can stabilize more effectively the layered structure of the resulting thinner $(N - 1)$-layer membrane. To our knowledge, thinning is so far the only known mechanism that transfers a smectic membrane from an unstable to a stable state.

In this Letter, we report the first observation of the reverse phenomena, namely, the ''thickening'' transitions in photosensitive smectic-C^* (SmC^*) membranes leading to their structural stabilization. This new process occurs under white light illumination instead of temperature change. *Trans*-to-*cis* photoisomerization takes place under illumination of the liquid crystal (LC) azobenzene molecules [14]. In the bend-shaped *cis*-isomer form, the molecules are nonmesogen and then act as impurities in the smectic phase. In bulk LC cells, this leads to the shift of the phase transitions towards low temperatures and even to a modification of the LC phase sequences [15]. Recent studies have reported the influence of light on isotropic droplets' nucleation in smectic films [5,16,17]. In our nondoped photosensitive films, illumination generates not only N^* droplets, but also for the first time, smectic platforms (additional SmC^* layers created in the illuminated area). We have more particularly put into evidence under proper conditions a layer by layer regime for the platform formation. It will be compared to the known thinning process.

The studied smectic films have been prepared with two LC materials denoted $12F_2A$ and $7F_2A$ [14]. The $12F_2A$ phase sequence is: K (57.6 °C) SmC^* (106.6 °C) N^* (114.0 °C) BP; the $7F_2A$ one is: K (78.5 °C) SmC^* (86.0 °C) TGB_C (88.5 °C) N^* (120.5 °C) BP. The films are drawn in the SmC^* phase over 3–5 mm holes in glass plates. The setup enables simultaneous optical observations (polarizing microscope, color CCD camera) and reflectivity measurements. The number of smectic layers N is determined via optical reflectivity spectra measurements [1]. In the studied films N ranges from 15 to 400. Photoinduced transformations occur for light intensities in between 5–100 klx. The droplet nucleation observed in our nF_2A compounds can occur separately from the thickening process or at a certain stage of this process.

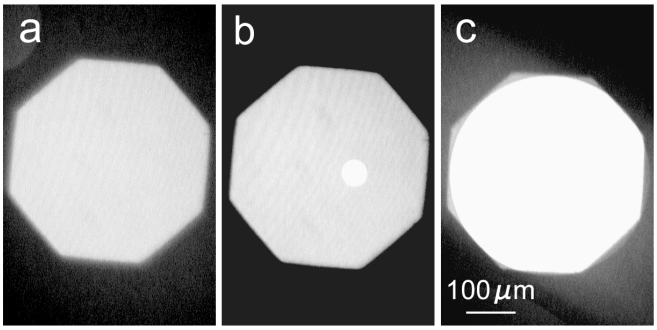

FIG. 1. Photosensitive smectic film (76 °C, $7F_2A$ compound). (a) Before illumination, homogeneous thickness. (b) Under illumination, platform nucleation after $t_0 = 12$ s. (c) Illuminated area S_{ill} completely invaded by the platform at $t = 29$ s.

The droplets' nature and kinetics will be presented elsewhere.

Under illumination, smectic platforms can be formed in the initially homogeneous film. A platform nucleation and growth is shown in Fig. 1. The platforms consist of an integer number of layers ΔN that appear and add to the N-layer membrane background [Fig. 1(b)]. Usually, their size tends to expand with time to finally match the illuminated area S_{ill} [Fig. 1(c)]. Platform nucleation occurs for operating temperatures ranging from 12 °C to 2 °C below bulk transition temperature. The nearly periodic stripes present in the film [Figs. 1(a) and 1(b)] are related to the **c**-director rotation in the SmC^* film plane [18]. Unlike lens-shaped N^* or isotropic droplets, the platforms have a flat surface with abrupt borders; their homogeneous color (or contrast for $N + \Delta N < 30$) is determined by N [1]. We call them "platforms" to differentiate them from the smectic islands obtained when cooling LC droplets [19]. The islands have first a staircase shape and they finally flatten to disappear after a few tens of minutes. The platform formation has been observed systematically for various defect-free membranes of the $n\mathrm{F_2A}$ series and with an initial $N < 200$. Platforms can last a few hours. A light intensity threshold value does exist below where no thickening process is possible. This threshold seems to be related to two processes. The first one is the *cis*-isomer relaxation in S_{ill}; the second is the *cis*-isomer flow outside S_{ill} and the *trans*-isomer backflow from the nonilluminated part of the membrane.

The generation of platforms with fixed ΔN (Fig. 1) can be replaced by an impressive layer by layer thickening regime (Fig. 2). Micrographs 2(a)–2(f) show the nucleation and growth at constant intensity of the first 7 elementary platforms, one after the other. The typical exposure time t_0 inducing layer by layer thickening can vary in between 0.5 and 50 s ($t_0 = 16.6$ s, Fig. 2). We can roughly estimate that t_0 is inversely proportional to the light intensity. Every consecutive elementary platform nucleates with an initial size of the order of 1 μm. This critical size above which thickening takes place is much less than the one observed for dislocation loops with thinning (≈ 50 μm) [20,21]. The nucleation occurs always in the middle of the previously formed 1-layer platforms; it is effectively easier to nucleate in the thicker part of the film and far from the platform border. The growth of 10 additional layers with a roughly circular contour leads to a "Babel-tower" configuration [Fig. 2(f)]. Each additional layer tends to fill progressively the whole surface S_{ill}. After nucleation of the 11th elementary platform, a N^* droplet has started forming in S_{ill}, preventing the formation of a complete 10-layer platform. Figure 3 gives the area growth versus time at constant illumination of the 2nd 1-layer platform (A_2 curve) as well as the sum of all 1-layer platform areas (S_{tot} curve). In practice, every newly formed elementary platform expands through S_{ill} with the same uniform velocity. Their growth velocity is not altered by the presence of the other new layers. A_2 growth is curtly stopped as soon as S_{ill} has been reached (see saturated part of A_2 curve). Above a value about 0.037 mm^2, A_2 dependence with time becomes linear. The onset (Fig. 3) gives the time evolution of the number of new 1-layer platforms ΔN. Their rate of appearance is increased as soon as the 1st elementary layers match the S_{ill} size. In general, the area growth is slowed down or the formation of a new elementary platform is stopped when decreasing the light intensity. The platforms keep on existing for several hours provided they are not swallowed by the meniscus. Platform formation seems to be an irreversible process. S_{tot} is proportional to

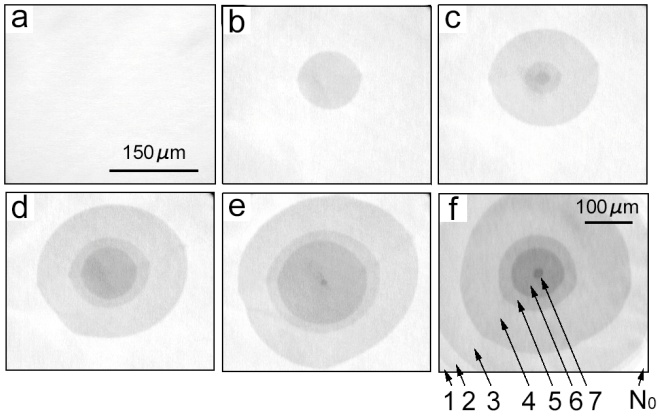

FIG. 2. Layer by layer thickening in S_{ill} with initially $N_0 = 82$ layers (96 °C, $12\mathrm{F_2A}$). (a) S_{ill} at $t = 0$ s. 1st 1-layer platform nucleated at $t_0 = 16.6$ s. (b),(c),(d),(e),(f): new layers appearing one by one in the middle of the 1st one, at $t - t_0 = 1$, 2, 3, 3.5, and 7 s, respectively. (f): numbers 1–7 denote the order of appearance of the successive layers. 150 μm bar holds for (a)–(e) and 100 μm for (f).

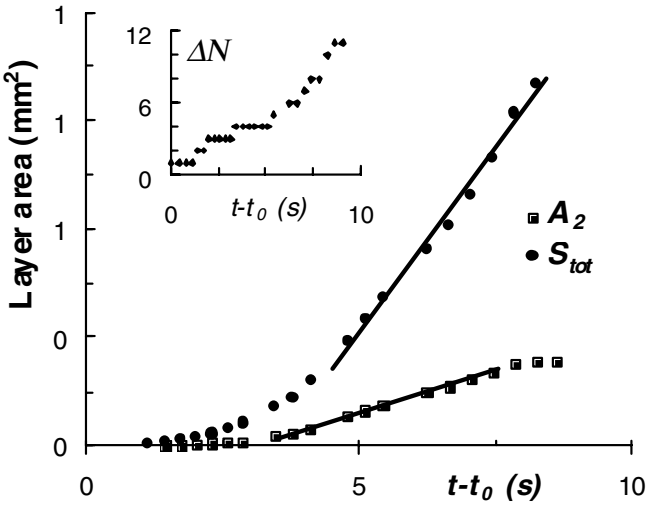

FIG. 3. Plot of 1-layer platform areas versus $t - t_0$ (96 °C, $12\mathrm{F_2A}$). A_2 curve (squares): area of the 2nd newly formed layer. S_{tot} curve (circles): sum area of all new layers. Inset: number of new layers ΔN appearing in S_{ill} versus time.

the quantity of new LC matter Q that has entered S_{ill}: $Q \sim S_{tot}d$, with d as the layer thickness. The linear variation with time of S_{tot} means that thickening occurs with constant LC matter flow in S_{ill}. Below the illumination threshold, whatever the stage of the thickening process was, the thickness and size expansion of the ΔN-layer platforms remain unchanged. Unlike dislocation loops created during the thinning process, the newly formed platforms do not tend to grow up to the meniscus size. Note that the size of S_{ill} (about 0.243 mm^2) is much less than the total membrane area (about 7 mm^2). Moreover, the linear variation of the platform area with time differs from that of the dislocation loops, which is nearly quadratic far above the critical radius [20,21]. Comparison between the thickening and thinning dynamics reveals that different forces are driving these processes. For thinning, the driving characteristics are determined by intrinsic membrane properties, while for thickening they are very strongly dependent to the illumination conditions.

Figure 4 shows the schematic *cis*-isomer concentration-temperature phase diagram of photosensitive smectic samples: the line LM separates the bulk SmC^* phase from the higher temperature phase N^*. With increasing *cis*-isomer concentration β under illumination, the SmC^* melting temperature decreases from T_{b0} towards T_{b1}. The three upper thinner lines refer to SmC^* membranes with $N+1$, N, and $N-1$ layers. The lines shift to higher temperatures (and concentrations β) when N decreases. The main difference between these lines and the LM line is related to the nature of the domains they are separating.

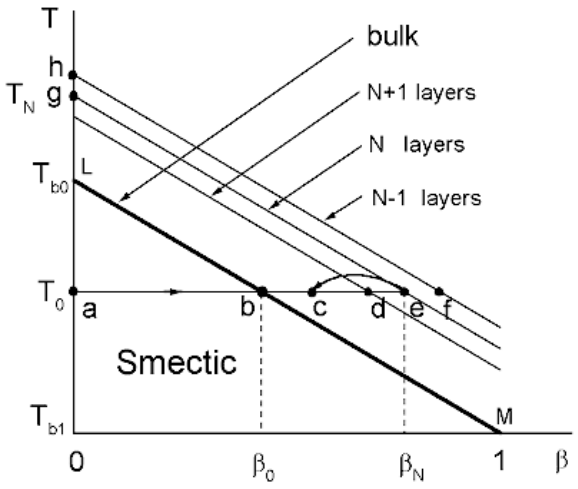

FIG. 4. Schematic representation of the phase diagram β-T. Solid line LM: phase transitions in bulk sample; transition temperatures for *trans*-isomer T_{b0} (state L, $\beta = 0$) and *cis*-isomer T_{b1} (state M, $\beta = 1$). State b: bulk melting point at $T = T_0$ under illumination ($\beta = \beta_0$). Thin straight lines: membrane instability limit for $N-1$, N, and $N+1$ layers. State e: instability limit for the N-layer membrane at T_0 ($\beta = \beta_N$). Jump from state e to c: LC matter flow towards S_{ill} decreases β.

The bulk sample exists on both sides of the LM line (SmC^* and N^*), whereas the N-layer membrane exists only on the left side of the corresponding thin line.

Membrane transformations under illumination are in some sense similar to those obtained under heating. In the initial state (point a, $T = T_0$, $\beta = 0$, Fig. 4) the profile of the smectic order parameter is nearly uniform across the membrane. Above the bulk transition temperature T_{b0} or above the concentration β_0, corresponding to melting bulk sample, the surface ordering as before maintains a finite value of the order parameter near the surface. However, the smectic ordering penetrates only on the value of the surface correlation length ξ. The smectic order profile inside the membrane depends actually on the ratio ξ/L, with L as the membrane thickness. With increasing β (or temperature) the profile of the smectic order parameter across the membrane becomes essentially inhomogenous due to the decreasing ξ. At sufficiently small $\xi \sim L/2$ (large β or high T) the order parameter reaches a low value in the middle of the membrane. Finally, the compression modulus inside the membrane tends to zero when β reaches the critical value β_N (point e, Fig. 4) or when T reaches T_N (point g) [8,10]. In the vicinity of the corresponding line, the disjoining pressure cannot be balanced by the internal elasticity, which results in instability of the N-layer membrane.

In a membrane the number of smectic layers N is a free thermodynamic parameter. At heating, the transition from unstable to stable state occurs through a thinning transition ($N \rightarrow N-1$) at T_N (point g, Fig. 4). Decreasing of thickness L transfers the membrane in a stable state due to the increasing ratio ξ/L. The membrane remains in point g, but for the $(N-1)$-layer membrane the point of instability is at a higher temperature (point h, Fig. 4). This process occurs through nucleation of a small dislocation loop. Inside the loop the number of smectic layers is less than in the surrounding part of the membrane. The difference in membrane tension τ ($\tau_{N-1} < \tau_N$ [1]) leads to increasing of the dislocation loop diameter and thinning of the whole membrane. A single example of the opposite thickening process attributed to a strong thermal heating has been recently detected under very specific conditions in the footprint of a synchrotron x-ray beam [22]. Our experiments have systematically shown the thickening process ($N \rightarrow N+1$) under light illumination. To our opinion, this is related to the existence of an additional thermodynamic parameter in the case of illumination: the concentration of *cis*-isomer β. With constant illumination, β increases, but it cannot overcome the β_N value. When β reaches β_N (state e, Fig. 4), the membrane has two possibilities: either rupturing or transiting to a stable state. The latter possibility corresponds to the transition from state e to c. It corresponds to the thickening process, which requires that new LC matter is provided by the meniscus (bulk reservoir) and travels through the nonilluminated area. Its flow enables the decrease of β in S_{ill}. The resulting state c of the

$(N + 1)$-layer membrane must be on the left side of the new instability point (state d). Let us now consider the possibility of thinning transition under illumination. After thinning ($N \rightarrow N - 1$) the membrane remains in the point e on the phase diagram (β is unchanged). But now the point of membrane instability is on the right side from point e, namely, in point f. The membrane state e after thinning would thus become a stable state. So, in the photosensitive membrane, both decreasing $N \rightarrow N - 1$ and increasing $N \rightarrow N + 1$ of the number of smectic layers can move the membrane to stable states. Competition of these two processes in the photosensitive membrane has to be considered.

Film tension increases when approaching the point of structure instability [23]. An evaluation with the help of the β-T phase diagram (Fig. 4) allows us to determine whether thickening or thinning moves the membrane further from the instability point. In membranes with $N \approx 80$ layers the temperature intervals between layer by layer transitions $\Delta T_N = T_N - T_{N+1}$ are about 0.01 °C [12]. The corresponding difference between concentrations for instability points for membranes with N and $N + 1$ layers may be denoted $\Delta\beta_N = \beta_N - \beta_{N+1}$. For a linear dependence of the instability temperature T_N on β as in Fig. 4, we obtain $\Delta\beta_N/\beta_N = \Delta T_N/(T_N - T_0)$. On the other hand, one new layer with *trans* isomer can decrease the net *cis* concentration by a value $\delta\beta_N = \beta_N/(N + 1)$. For the transition to a thicker membrane to lead to a stable state and to be energetically favorable, the shift from the instability point due to a decrease $\delta\beta_N$ of β should exceed $\Delta\beta_N$. With our values, $T_N - T_0 \approx 10$ °C, $N = 82$, and $\Delta T_N \approx 0.01$ °C, the difference in β between neighboring instability points is $\Delta\beta \approx 10^{-3}\beta_N$ and $\delta\beta_N \approx 10^{-2}\beta_N$. Approximately the same value $\Delta\beta_N$ exists between the instability points in membranes with $N - 1$ and N layers. So, an increase in the number of layers (thickening) leads to an essentially larger shift of the membrane from the instability point than thinning ($\delta\beta_N > \Delta\beta$), and thus it decreases the energy essentially more than thinning.

Let us estimate the critical radius R_c of the platform. Creation of a platform with radius R requires positive energy $2\pi RE$, where E is the energy per unit length of an elementary thickness step (dislocation). The interaction energy of surfaces in thick membranes is of the order or less than $10^{-3}\gamma$ [23], with γ as the film surface tension. Assuming this to be the energy difference between states before and after thickening, since at approaching instability points the interaction energy tends to zero [23], we obtain for the energy of a circular platform $10^{-3}\pi R^2\gamma$ and thus $R_c \approx 2 \times 10^3 E/\gamma$. Taking $\gamma = 20$ dyn/cm and $E = 6 \times 10^{-7}$ dyn [21], we obtain $R_c \approx 0.6$ μm. We observed formation of platforms with initial radius about 1 μm, in accordance with the above estimation.

In conclusion, a photosensitive smectic membrane under illumination can undergo thickening with an increase of the number of smectic layers. This process is opposite to the well-known thinning transitions upon heating. Thickening can occur through a layer by layer process and can be light controlled. Successive transitions between stable and unstable states result from the continuous illumination with an increase of the *cis*-isomer concentration, followed by the formation of additional layers with decrease of the *cis*-isomer concentration. Photosensitive membranes turn out to be very suitable objects to investigate membrane instabilities and to manipulate membrane thickness and properties by varying illumination and temperature.

Région Nord-Pas de Calais is acknowledged for setup funding and the Russian Foundation for Basic Research (Grant No. 05-02-16675) for support.

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