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Observation of macro-heterogeneities in surface-stabilized smectic C* with antagonistically patterned substrates

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In our recent study, we considered equilibrium states in a monolayered sample of ferroelectric liquid crystal in smectic C* phase confined between two differently patterned substrates with strong anchoring under the applied electric field. By using the continuum theory for a "bookshelf" aligned sample for smectic C*, we derived an elliptic sine-Gordon equation. It was shown that due to the antagonistic boundary conditions at the substrates, competing boundary effects in the thin film generate a stable alignment of the smectic C* director. This alignment can be controlled by the electric field. The result obtained was explained basing on Frenkel-Kontorova's model, which was used to describe the map of the director alignment as the system of harmonically coupled "atoms" with the external potential produced by the substrates. In this study, we perform an experiment to verify our theoretical results. We prepared a cell with differently patterned substrates, and ferroelectric liquid crystal material CS-1024 (Chisso Co.) was injected into the empty cell by the capillarity flow. Patterned monolayers promoting planar alignment of CS-1024 in its smectic C* phase were created using microcontact printing of functionalized organothiols on gold films. By patterning the surface with planar alignment of monolayers, the location and formation of smectic C* director macro-heterogeneities can be controlled by the electric field. The observed macro-heterogeneities continue to exist when the electric field is turned off. Polarizing microscopy and fluorescent microscopy were used to observe the formation of macro-heterogeneities in the alignment of SmC* director field.

Keywords: ferroelectric liquid crystals, thin films, electro-optic response, micro-patterned surface.

1. Introduction

Ferroelectric liquid crystals in Smectic C* phase (SmC*) satisfy high demands for a variety of photonic devices, mainly due to its inherent spontaneous polarization. As the spontaneous polarization is always perpendicular to the tilt plane, which precesses along the helix axis, vector of the spontaneous polarization P_0 also changes its direction along the helix axis. Since the pitch of the helix p_0 ranges from the submicron to the micron size, this means that the spontaneous polarization within the bulk of SmC* is cancelled out on the mesoscopic scale of the pitch. Hence, the macroscopic polarization is cancelled. This helix can be elastically unwound by confining the pattern of SmC* within closely spaced substrates with their insides coated for imposing planar alignment of director. The director (which is also an optical axis) in such a sample is restricted to two orientations, the helix becomes unfavorable, and no polarization cancellation within the bulk of the sample occurs. This allows switching of the spontaneous polarization from UP to DOWN position, which is accompanied by a director reorientation of twice the tilt angle on the cone, giving maximum contrast of the cell for appropriately oriented crossed polarizers [1].

Earlier we employed the continuum theory for a "bookshelf" aligned sample of ferroelectric liquid crystal (FLC), and obtained an elliptic sine-Gordon equation [2]. We have shown that due to a micro-patterned structure of the substrates, competing boundary conditions in the thin film generate a specific alignment of liquid crystals (LCs), which can be controlled by the electric field. This theoretical finding was described within the framework of the Frenkel-Kontorova model [3].

Referring to the previously obtained results [2, 4], the present study is devoted to the experimental estimation of the continuum approach for bookshelf aligned SmC* LCs, confined between two differently patterned substrates.

2. Theory

Fig. 1 is the illustration of a SmC* sample confined between two micro-patterned substrates separated by a distance d. It is known that in each SmC* layer, long axes of the molecules are oriented parallel to a certain direction, which is characterized by the director field given by $n = a\cos\theta + c\sin\theta$, where a is the unit vector normal to the SmC* layer, c is the unit vector of the orthogonal projection of the director n

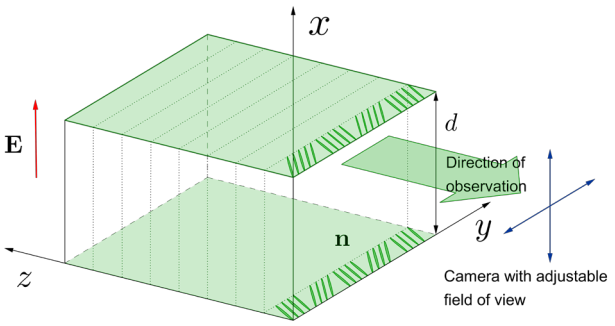


Fig. 1. (Color online) Geometry of the surface-stabilized FLC cell: smectic layers (dotted lines) are perpendicular to the substrates. Director n is in the yz-plane for $x=0$ and $x=d$. Electric field E is applied parallel to the x-axis.

onto the smectic plane [c-director]. Vectors a and n make angle θ, called the smectic cone angle. A detailed description of "bookshelf" aligned SmC* can be found, e.g., in ref. [5].

Following the continuum theory, earlier we derived the static c-equation under the one-constant approximation for the "bookshelf" geometry problem,

$$\frac{\partial^2\varphi}{\partial\tilde{x}^2}+\frac{\partial^2\varphi}{\partial\tilde{y}^2}=C_0\cos\varphi+2C_1\sin2\theta\sin2\varphi, \qquad (1)$$

where $\tilde{x}=x/d$ and $\tilde{y}=y/d$ are the scaled variables, φ is the angle between the x-axis and c-director; and quantities $C_0=P_0Ed^2/B$, $C_1=\varepsilon_0\varepsilon_aE^2d^2/4B$ [2]. Here ε_0 is the dielectric constant, ε_a is the dielectric anisotropy, and B is the constant relevant to the reorientation of c-director within the smectic planes. The c-director alignment at differently patterned substrates can be represented by the following boundary conditions:

$$\begin{aligned}\varphi(0,y)&=\pi\mathcal{H}\big(\sin(q_1y)\big)-\pi/2\\ \varphi(1,y)&=\pi\mathcal{H}\big(\sin(q_2y)\big)-\pi/2\\ \varphi(x,0)&=\pi/2,\quad \varphi(x,L)=\pi/2,\end{aligned} \qquad (2)$$

where $\mathcal{H}$ is the Heaviside step function with the adopted convention, $\mathcal{H}(0)=1$; q_1 and q_2 are the scaled wavenumbers associated with the periodicity of the substrates.

The analysis of the theoretical model indicates that electric field generates spatially-localized static excitations of the c-director, which can be regarded as static solitons (macro-heterogeneities). The formation of such solitons can be qualitatively described by the Frenkel-Kontorova model. Specific interaction between the director field of ferroelectric SmC* and patterned substrates demonstrates that the substrates play a twofold role: 1) they produce effective external potentials to the "atoms" of the primary chains (top and bottom boundaries); 2) constitute a mechanism for energy exchange between "atoms" of the Frenkel-Kontorova chain. The latter generates localized regions with the disturbed commensurability. Experimental evidence for the existence of this effect is qualitatively given in below.

3. Experimental

To examine our theoretical results, we studied experimentally a simplified scenario of FLC behavior confined between differently patterned surfaces. The antagonistic boundary conditions were rendered in the fabricated 5 μm-thick micropillar arrays of differing planar stripes. The patterned surfaces were prepared using microcontact printing of functionalized organothiols on thin gold films [6]. Glass slides were cleaned rigorously with detergent, MilliQ water (Millipore), methanol and piranha etch (30% hydrogen peroxide, 70% sulphuric acid). The substrates were dried in nitrogen and placed in a thermal evaporator (Edwards Auto 306). A 3 nm adhesion layer of Cr was deposited, followed by the deposition of a 25 nm Au film. Such thickness is sufficient to create a continuous gold film, which remains optically transparent, and hence it is suitable for polarizing microscopy studies.

A silicon wafer, etched with a series of micrometer-sized stripes was used as master for the formation of polydimethylsiloxane stamps. Two values of period of each stripe, 10 and 12 μm, were chosen. To get the hydrophillic surface, the wafers were treated by the acid Piranha solution. The wafer was silinezed to let stamp removal. Stripe structures on glass substrates were made by using negative tone photoresist SU82010 (Micro Chem Corp.). The polydimethylsiloxane material was poured onto the master in a mould, and cured at 65°C for 12 hours. After curing, polydimethylsiloxane material was removed. A 7 mM ethanolic solution of HS-$(CH_2)_{17}$-$(CF_2)_9$-CF_3 was prepared. The printing surface of the stamp was inked with this solution for several minutes and then carefully dried with nitrogen. The stamp was then placed onto the gold surface for 2 minutes. The gold surfaces were then immersed in a 3 mM ethanolic solution of 11-mercaptoundecanoic acid for 12 hours. This back fills the non-printed regions to produce a two-component patterned surface. The LC cells were formed with a planar alignment at top and bottom surface. The 5 μm cell gap was controllable and kept by means of the photolithographic polymer spaces. The microscopic textures of the surface-stabilized FLC cells were observed using a polarizing microscope. The FLC material CS-1024 (Chisso) was injected into the empty cell by the capillarity flow at a temperature above the clearing point (N*-Iso), and then slowly, at a rate of 0.1°C/min^{-1}, cooled down to the room temperature into the SmC* phase under the applied d.c. voltage ~2 V. Such cooling rate is needed to ensure that the SmC* molecules are strongly anchored to the patterned surfaces [7]. The CS-1024 has the following phase transition sequence: Crystal (–12°C) → SmC* (62°C) → SmA (82°C) → N* (90°C) → Iso. Table 1 lists the main physical properties of CS-1024.

Table 1. Physical properties of CS-1024 at 25°C.

P_0, nC/cm^2	θ, deg	ε_a	p_0, μm
–46.7	25	2.9	22

On further cooling, the uniform texture breaks down into two sets of domains with *c*-director boundary alignment such that $\varphi = \pi/2$ and $\varphi = -\pi/2$. To visualize the alignment of liquid crystalline molecules, CS-1024 was doped with the fluorescent dye *n,n*'-bis-2,5-di-*tert*-butylphenyl-3,4,9,10-perylenedicarboximide (BTBP; Aldrich Chemical Company, Inc.) at a concentration of 0.01% wt. This dye shows a bright fluorescence at 540 nm [7], so a DPSS laser at 532 nm was used for excitation of the BTBP molecules.

A polarized-light microscope (Optiphoto2-Pol, Nikon Eclipse E600, Tokyo, Japan) with digital camera were used to reveal the bistability when these the samples were driven by short d.c. electric pulses, the usual modality for polarization switching [9]. Depending on the field polarity, two different states were obtained, i.e., applying a positive voltage the SmC* molecules are rotated to the intrinsic maximum cone angle. Consequently, the transmission changes remarkably. The obtained UP- and DOWN-states of the director field were both stable after the field removal. This indicates that the sample of SmC* has a "bookshelf" structure [10].

To examine switching behavior of the micro-patterned cell, we use a function generator (Rohde & Schwarz, Germany) and power amplifier (Model 7500, Krohn-Hite Corporation, USA).

4. Results

By using a computer algebra system, we generated a triangular-mesh surface with 1.03 million elements. The convergence to the discretization error of 10^{-5} was achieved after 11 iterations. Fig. 2a displays the model distribution of *c*-director's azimuthal angle governed by equation (1) with boundary conditions (2). We observe that differently patterned substrates with surface-stabilized FLCs generate spatially localized static excitations of the *c*-director. Effects associated with the molecular twisting on the substrates were not considered.

Polarized light microscopy techniques, photomultiplier for detecting the change of light intensity and the heater stage were used to observe the formation of self-organizing macro-heterogeneities in the director (Fig. 2b). On applying the electric field along the *x*-axis, the corresponding twist of the P_0 vector field for one type of domains favors the director field alignment to the UP or DOWN position because the surface alignment is favorable to reorient the director field. The second type of domains is associated with the antagonistic surface alignment of the director field, so we observe a dark stripe. Fig. 2b captures the essential features of the SmC* director alignment, and reveals a good qualitative fit between the experimental data and theoretical issues.

Due to the adjustable camera tilt angle, we can observe the director field alignment. The low intensities in Fig. 2b correspond to *c*-director's $\varphi = 0$ or $\varphi = \pi/2$; the higher intensity corresponds to $\varphi = \pi/4$. The resulting effect is that the laser beam with the determined polarization will attract the twisted domain and repel the untwisted domain. Here, the low contrast ratio observed is due to the chosen direction of observation (Fig. 1).

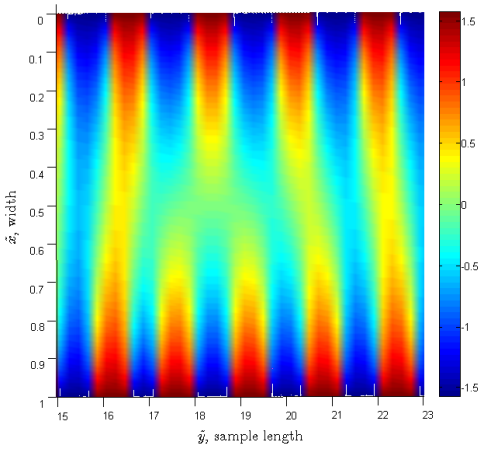
When the electric field is switched off, SmC* molecules rotate back to the initial alignment, decreasing the light transmission insignificantly due to differently patterned substrates.

The application of a square-wave electric field [4] with amplitudes up to 1 V·μm to the SmC* phase causes an irreversible structural transition, so that if the electric field is off, the texture does not return to its initial state. This effect would be further enhanced by improving preparation of cells and decreasing the gap between substrates.

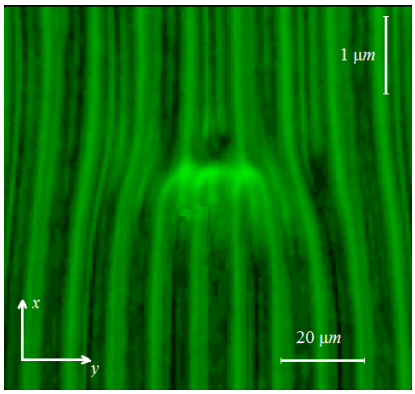
5. Discussion

Using the fluorescence confocal microscopy, we performed an experimental study of the scenario of macro-heterogeneities formation in surface-stabilized SmC*, where the fluorescence confocal microscopy image was obtained by the registered fluorescence signal from the SmC* layers. If the camera is tilted, the registered fluorescence signal from different parts of the layer can vary because of some light absorption, depolarization and defocusing.

We observed that SmC* layers, confined in a thin film geometry with differently patterned substrates, spontaneously



a



b

Fig. 2. (Color online) (a) Fragment of solution equation (1) with boundary conditions (2) with parameters represented in Table 1 and $B = 5$ pN. (b) Boundary-induced topological defects in the alignment of SmC* director between differently patterned substrates at 1 V. A DPSS laser at 532 nm was used for excitation of the BTBP.

assemble the director field into static solitons. Such a structure is the response to the antagonistic boundary conditions. It is clear from equation (1) that the interaction of the *c*-director with the electric field is due to the spontaneous polarization (C_0-term) and the dielectric anisotropy (C_1-term). For moderate electric fields the C_0-term is considerably greater than the C_1-term, meanwhile, we do not neglect the C_1-term because the C_0- and C_1-terms have different φ-dependences. Applying a moderate electric field $E = 200$ kV, we aim to avoid the appearance of boundary effects, associated with the molecular twisting and formation of chevron structures. So, the formation of the macro-heterogeneities is mainly due to the spontaneous polarization.

To summarize, we have shown that using cells with antagonistic boundary conditions, one can induce an assembly of static solitons representing excitations of the ferroelectric SmC* director field. However, achieving the time-periodic emergence of the c-director excitations, i.e., self-organizing macro-heterogeneities remains challenging due to the formation of topological defects in a "bookshelf" aligned sample of SmC*.

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