Electro-Optics of Bipolar Nematic Liquid Crystal Droplets

A. Fernández-Nieves, D. R. Link, D. Rudhardt, and D. A. Weitz
Department of Physics and DEAS, Harvard University, Cambridge, Massachusetts 02138, USA

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We directly visualize the response and relaxation dynamics of bipolar nematic liquid crystal droplets to an applied electric field E. Despite strong planar anchoring, there is no critical field for switching. Instead, upon application of E, the surface region first reorients, followed by movement of the disclinations and the bipolar axis. After removing E, elastic forces restore the drop to its original state. The collective electro-optic properties of ordered hexagonal-close-packed monolayers of drops are probed by diffraction experiments confirming the proposed switching mechanism.

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Electro-optical devices based on two- and three-dimensional arrays of polymer-encapsulated nematic liquid crystal [1] offer considerable promise for large-area flexible displays that can be assembled on plastic substrates [2]. Conventional polymer dispersed liquid crystal (PDLC) devices work by switching between strongly scattering and transparent states. Light normally incident on a PDLC film is scattered by droplets of nematic liquid crystal in the polymer matrix due to their different refractive indices. A transparent state is achieved when a sufficiently large electric field is applied to reorient the nematic director field in the droplets, index matching the droplets and polymer matrix. When the field is removed the film relaxes to the scattering state to minimize elastic distortions and satisfy boundary conditions.

The electro-optical response of the devices depends critically on boundary conditions at the nematic polymer interface. In nondroplet devices boundary conditions are typically determined by a polymer surface coating that provides for zenithal anchoring of the director at a fixed pretilt angle θ with respect to the interface; the extreme cases of $\theta = 0$ and $\theta = \pi/2$ are, respectively, planar and homeotropic alignment. Mechanical or optical rubbing of the interface provides for additional azimuthal anchoring of the director at a fixed angle φ in the plane of the interface. In droplet based technologies planar anchoring is achieved through appropriate materials selection, but encapsulation of the liquid crystal precludes the use of rubbing to fix the azimuthal anchoring. Nonetheless, it has been found experimentally that the polymerization of monomer in a monomer-liquid crystal mixture results in liquid crystal droplets in a polymer matrix with strong azimuthal anchoring [3]. Alternative dispersion strategies such as the formation of PDLCs from emulsions, requires that the droplets be strongly deformed either during the drying process or by stretching of the dried films to give anisotropy to droplets, essential for the relaxation dynamics [4].

Under conditions of planar anchoring PDLCs are generally modeled as a collection of bipolar droplets, with the nematic director, $\mathbf{n}$, aligned, on average, between two disclinations positioned at opposite poles of the droplet. Disclinations, which are singular points about which $\mathbf{n}$ rotates through a multiple of π radians, are required by the topological constraints enforced by the confinement of the liquid crystal, and the parallel boundary conditions. Switching of bipolar droplets is generally thought to require application of an electric field, E, greater than a critical Fréedericksz field, E_F [4]. Below E_F there is no change in the director field, while above E_F the director begins to reorient in the field. This reorients $\mathbf{n}$ along $\mathbf{E}$, changing the effective index of refraction of the nematic droplets, reducing the scattering of transmitted light and switching the device on. The increased scattering of the incident light for $E < E_F$ switches the device off.

However, computer simulations based on Franck-Leslie-Ericksen continuum theory [5] suggest that it is possible to switch droplets continuously, without a Fréedericksz transition. These simulations depend critically on the boundary conditions, strong zenithal and weak azimuthal, of the director field in the droplets. The lack of a critical switching voltage is qualitatively different than expectations based on all current experimental observations and may prove useful in generating gray-scale levels in display applications.

In this Letter, we study an ordered array comprised of nearly identical, well-defined bipolar nematic droplets, and show that the switching mechanism for this system is outside of the current understanding of droplets [4–7]. We propose that this is due to strong planar anchoring and negligible azimuthal anchoring. We study individual droplets and show that there is no critical Fréedericksz field. Instead, it is the surface region that responds first to the applied field, driving the average bipolar director field to reorient with E; moreover, this response occurs for vanishingly small E. By exploiting the periodic packing of the uniformly sized droplets, we measure the Bragg-reflected light to determine the mean orientation of the bipolar structure and to probe the dynamics of the relaxation when E is switched off. These dynamics are slow because the full bipolar structure must reorient. The basic behavior is adequately captured by a simple model based on shape anisotropy [8] and by the computer simulations [5]. Our results provide clear experimental evidence of the switching mechanism for simple bipolar droplets and provide a switching geometry that does not require a critical field, which has both fundamental and practical implications.

Monodisperse emulsions are prepared by extrusion of penthylcyanobiphenyl (5CB), a nematic liquid crystal, through a thin capillary (3–10 μm in diameter) into coflowing water with 1% polyvinyl alcohol (PVA), yielding droplets with polydispersities below 3% [9]. A small volume of emulsion is placed on a glass slide coated with indium tin oxide (ITO); as the water evaporates, the liquid crystal droplets self-assemble into a hexagonally close packed (HCP) monolayer. The PVA prevents the drops from coalescing while enforcing planar boundary conditions on **n**. An ITO coated glass top is added to apply an electric field, in the form of a 1 kHz bipolar square wave, along the film normal.

A photomicrograph of a typical film in the absence of an applied field ($E = 0$) is shown in Fig. 1(a). The film has a total thickness of 39 μm, and contains a single layer of hexagonally shaped droplets of thickness $d = 7$ μm, enclosed by PVA walls on an $a = 18$ μm hexagonal-close-packed lattice; the drops are somewhat larger than those typically used in PDLC devices. Note that there is 32 μm of PVA on top of the film. The color is consistent with a uniaxial birefringent slab with $\Delta n = 0.21$ and a thickness of 5 μm, in agreement with experiment. The droplets are bipolar with the line connecting the two disclinations residing in the x-y plane 45° from the crossed polarizers. The polar axis is nearly perfectly aligned because of the slight elongation of the droplets during drying. The bipolar structure of all droplets is verified by textural observations between crossed polarizers [10]. Thus, this film is an ideal structure with which to investigate the switching mechanism of bipolar liquid crystal drops.

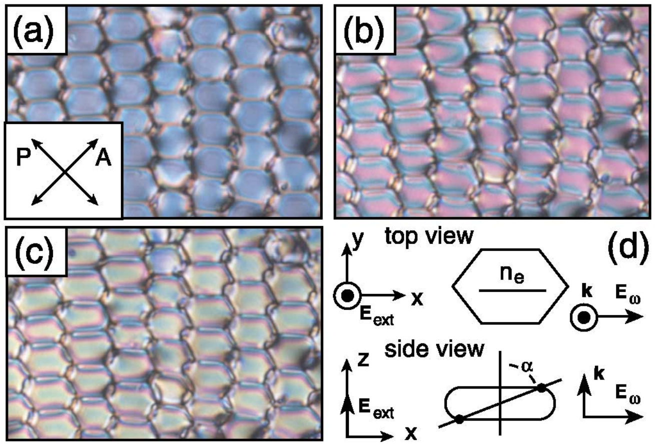

FIG. 1 (color). Photomicrographs of the hexagonal-close-packed monolayer taken between crossed polarizers (indicated by P and A) for different fields: (a) $E = 0$, (b) $E = 0.03$ V/μm, and (c) $E = 0.15$ V/μm. (d) The schemes show the experimental geometry. Anisotropy in the drop shape fixes the polar axis of the drops in the$x$-y plane in the absence of an E field. For $E \neq 0$ the axis rotates through an angle α reducing the birefringence of the drops as indicated by the color change. For the diffraction experiment, light is incident along **k** with polarization direction $\mathbf{E}_\omega$ along the drop polar axis. At $E = 0$ the effective refractive index for $\mathbf{E}_\omega$ equals the extraordinary index of refraction n_e of the liquid crystal.

Unexpected behavior is observed upon application of an electric field: The polar axis rotates continuously out of the x-y plane, decreasing the average birefringence of the droplets, as shown by the change in color in Figs. 1(b) and 1(c). There is no critical field for the switching in contrast to the response typically reported for PDLC and related devices [4,6,7]. For $E \gtrsim 2.0$ V/μm optical birefringence disappears completely and the nematic director is aligned with **E**.

To elucidate the switching mechanism of these bipolar drops, we focus on the behavior of a single drop. We observe three distinct steps in the response to the application of an arbitrarily small electric field. Surprisingly, in the first step, the polar axis remains fixed, but the director field changes near the interface of the drop, where boundary conditions should pin **n**. This is shown by the difference in intensity of the transmitted light near the droplet boundary between the photomicrograph in Fig. 2(a), which has $E = 0$, and that in Fig. 2(b), which is taken 1/30 s after application of a field of $E = 0.13$ V/μm. Second, the bipolar axis moves out of the x-y plane with the disclinations moving toward the top and bottom of the drop, as shown in Fig. 2(c), taken 4/30 s after application of the field. Third, equilibrium is reached with the electric and elastic restoring forces balancing each other. This equilibrium is characterized by a bulk that is more tilted than the edges, as can be seen by recognizing that the birefringence in the center of the drops in Figs. 1(b) and 1(c) is less than that on the edges. This behavior implies that the director first rotates out of the film plane at the drop edge, producing a twist in **n** without changing the bipolar axis, which remains at $\alpha = \pi/2$; this is shown in Figs. 2(d) and 2(e).T he angle of the bipolar axis, α, is defined in Fig. 1. The initial switching at the edge can occur because of the unique geometry and boundary conditions on **n** at the droplet surface; **n** rotates parallel to the interface, thus maintaining the parallel boundary condition. This twist induces the subsequent movement of the disclinations and the rotation of the bipolar axis as shown in Fig. 2(f).

We also can use the images of the individual droplets to investigate the relaxation of the director field when the applied electric field is switched off. When a large E field of $E = 2.1$ V/μm is applied, the bipolar axis is aligned with the field and the disclinations are on the top and bottom of the droplet, as shown in Fig. 2(g). The relaxation sequence is shown in Figs. 2(h) and 2(i), taken 1/30 s and 2/30 s, respectively, after removing the field. The disclinations are clearly seen moving along the top and

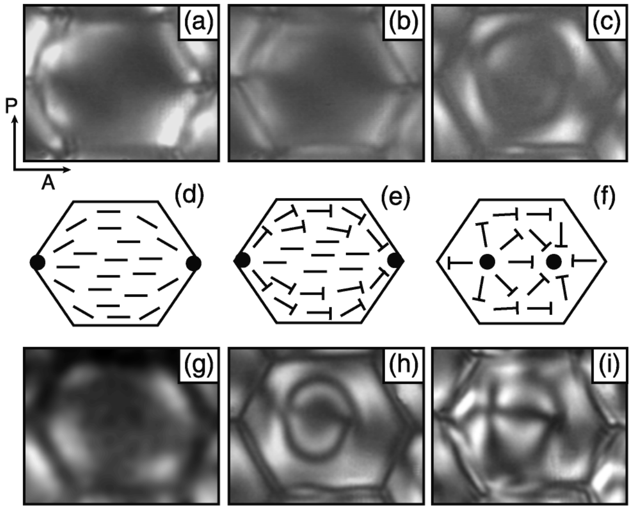

FIG. 2. Polarized optical microscopy observations of an individual drop during application and after removal of an electric field. The photomicrographs in (a)–(c) show a sequence of images taken after application of an $E = 0.13$ V/μm field. The times are (a) $t = 0$, (b) $t = 1/30$ s, and (c) $t = 4/30$ s. Sketched below each of the photomicrographs, (d)–(f), is a scheme depicting the director structure inside the drop during switching. A time sequence during the relaxation after removal of an $E = 2.1$ V/μm field is shown in the photomicrographs in (g)–(i). The time after removal of the field are (g) $t = 0$ s, (h) $t = 1/30$ s, and (i) $t = 2/30$ s. The system continues to relax back to the state shown in (a) after $t = 0.85$ s. Image (g) appears black under conditions similar to the other photomicrographs and has been electronically enhanced for clarity.

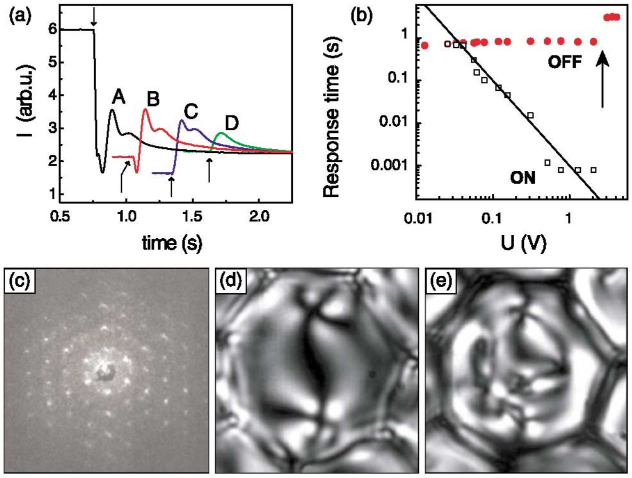

FIG. 3 (color online). Time dependence of the transmitted intensity and orientation of droplet axis. (a) The arrows indicate the times at which the square wave voltage signal is turned off from (*A*) 0.12 V/μm, (*B*) 0.056 V/μm, (*C*) 0.041 V/μm, and (*D*) 0.026 V/μm. The number of extremes in the transmitted signal is reduced as the applied field decreases. (b) Square symbols, on times, indicate the total time for the film to become transparent after an external field is applied and the round symbols, off times, give the time for the diffraction pattern, shown in (c), to return upon removal of the field. The jump in the relaxation time at high fields, see the arrow in (b), occurs when the relaxation process switches from the simple movement of two disclinations, (d), to a coarsening followed by the movement of the final pair, (e).

bottom surfaces to the vertices of the hexagonal drop. The fact that they are on the surface of the drops can be confirmed by changing the focal plane of the microscope. After ~0.85 s, the disclinations have returned to the *x*-*y* plane, where the elastic distortions are minimized, and $\alpha = \pi/2$. We observe that approximately 2/3 of the total relaxation time is spent near the final droplet configuration indicating that the angular velocity of the relaxation is peaked at small α and thus at short times.

To understand the relaxation process, we exploit the uniformity in size, shape, and orientation of the droplets, to study Bragg diffraction from the films. A linearly polarized HeNe laser, with a wavelength of $\lambda = 632.8$ nm, is incident along the film normal, with the polarization vector aligned nearly parallel to the polar axis of the droplets, as shown in Fig. 1. The resultant diffraction pattern, shown in Fig. 3(c), has sixfold symmetry, reflecting the hexagonal order of the droplets. It exhibits as many as 10 orders of diffraction, reflecting the high degree of order of the packing. Using a photodiode, the intensity of the coherent transmitted beam is measured as a function of time after the field is switched off, and is shown in Fig. 3(a), where the curves *A* through *D* reflect decreasing *E* fields, and where the arrows indicate when the field is switched off. For fields greater than $E = 0.11$ V/μm, six relative extremes in the intensity of the transmitted light are observed between the initial and final intensities. These oscillations result from an interference effect and are consistent with a simple model of a phase grating comprised of alternating periodic regions of a fixed refractive index of the polymer coating, n_p, and a refractive index of the liquid crystal, $n(\alpha)$, which varies with the applied *E* field [11]. The maximum change in $n(\alpha)$ induces a maximum phase shift $\delta = 2\pi d[n(\alpha) - n_p]/\lambda$ of 5π, in agreement with the three oscillations observed. As the *E* field is reduced below $E = 0.11$ V/μm, α increases and fewer extremes are observed, as shown in curves *B*, *C*, and *D* in Fig. 3(a).

This technique of monitoring the transmitted intensity allows us to measure the total time that it takes for the device to switch on or off. As is expected for a dielectric switching process, the on times decrease as E^{-2} as shown by the open squares in Fig. 3(b); the solid line has a slope of -2. For the off times, solid circles, there is very little dependence on the field strength even though the total angle through which the director field must relax is increasing with the field. This reflects the fact that the relaxation time is determined by the shape anisotropy of the droplets and is thus dominated by the last several degrees [8]; this can be confirmed in the video microscopy images.

However, above a critical field E_c of roughly 3 V/μm there is a surprising discontinuous threefold increase in the off time. Images taken during the relaxation at fields just below and just above this critical field are shown in Figs. 3(d) and 3(e) for the same droplet. The images show that above E_c there is a dense collection of disclinations present during the relaxation that are absent at slightly lower fields: an indication that at high fields the zenithal anchoring is broken. These disclinations first coarsen through pairwise annihilation events until only two disclinations remain. This final pair of disclinations move to opposite sides of the droplet. Above E_c, the addition of the coarsening dynamics triples the total relaxation time.

This relaxation process rules out all other possible boundary conditions on the droplets except strong planar and weak azimuthal anchoring, confirming our model for the switching mechanism. Strong azimuthal anchoring cannot be present as it would both imply a Fréedericksz transition, as is observed in other PDLC systems, and would also forbid the generation of multiple disclinations after breaking zenithal anchoring; only π-wall defects would be allowed. Similarly, this observation confirms strong zenithal anchoring in our droplets; systems with weak zenithal anchoring, such as polyurathane matrices [12], would not be expected to exhibit a surface switching transition with field. It is the combination of strong planar anchoring in the absence of azimuthal anchoring that allows for thresholdless switching of droplets.

A more complete description of the dynamics can be expected within the Franck-Leslie-Ericksen continuum theory, and recent simulations capture the absence of a critical field for switching. They also capture a relaxation angular velocity that is peaked at low times [5], consistent with our experimental observations. Moreover, the simulations show that, upon balance of electric and elastic forces, the bulk is more tilted than the droplet edges, again consistent with our observations. However, the simulations are restricted to two dimensions; hence the essential physics of the response dynamics, which are governed by a twist in the x-y plane, cannot be described. A full three-dimensional implementation of the continuum theory equations is essential to fully capture the physics of the problem.

The critical switching field observed in most PDLCs implies they do not follow the same switching dynamics as our droplets. Instead, confocal microscopy studies of PDLC film morphology suggest that polymer filaments can penetrate droplets [13] and presumably pin the director at fields below E_F. We further speculate that this may also be the case in smaller droplets where the filaments cannot be directly visualized and that the slow relaxation dynamics of typical PDLC devices does not arise from the movement of the two defects. Our results provide a clear picture of the switching of bipolar nematic droplets when planar anchoring is not accompanied by azimuthal anchoring. This mechanism is clearly at odds with the observations for PDLC devices; thus any modeling of the electro-optic properties of such devices must reflect the fact that a relaxation process consisting of the rotation of a bipolar drop is valid only for the case of negligible azimuthal anchoring, precluding the occurrence of this mechanism when there is a Fréedericksz transition.

A full understanding of the switching mechanism of bipolar drops, such as those studied here, must recognize the fundamental difference with the E-field response and relaxation of nematic films, where the Fréedericksz transition requires application of fields above a critical value for the system to respond. However, the absence of a critical value reduces the electric field needed for switching; this is important for practical applications [7]. Finally, we note that films of monodisperse, aligned bipolar drops are potentially valuable for display applications, particularly where encapsulation of the nematic liquid crystal is essential to assure uniform birefringence in flexible displays.

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