

# Phase switching of ordered arrays of liquid crystal emulsions

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We report a fabrication method for producing interference-based electrooptic phase gratings that switch between diffracting and transparent states. The phase grating consists of a hexagonal close-packed array of monodisperse emulsion drops of nematic liquid crystal, embedded in a polymer matrix. Monodisperse droplet size allows for fast switching at low electric fields.

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Polymer dispersed liquid crystals (PDLC) are a well established technology for electrooptic devices used in displays and light switches. They rely on dispersions of nematic liquid crystal material in a polymer matrix. In the absence of an electric field, the director field  $\mathbf{n}(\mathbf{r})$ , which characterizes the local average orientation of the rodlike nematic mesogens, is randomly oriented, leading to a mismatch between the average index of refraction of the liquid crystal and that of the polymer; this results in strong scattering making the film opaque. An external electric field aligns the nematic director parallel to the direction of light propagation, and, if the average index of refraction of the aligned liquid crystal matches that of the polymer, scattering is eliminated making the film transparent [1]. To control the direction of the light, a holographic version of this same technology (H-PDLC) incorporates a periodic modulation of the liquid crystal; switching then induces a phase grating, leading to controllable diffraction of the light [2].

Formation of PDLCs usually involves the phase separation of liquid crystal during the curing of the polymer matrix; H-PDLCs are formed when intensity gratings from crossed laser beams are imposed on the film during curing. Because of the strong pinning of the liquid crystal to the polymer matrix, PDLCs require relatively large switching fields. An alternate fabrication technique, which can significantly reduce the switching fields, relies on the formation of well defined liquid crystal droplets suspended in a polymer matrix. However, these liquid crystal emulsions are typically comprised of a highly polydisperse mixture of droplets limiting their use to controlling the transmission of light, and precluding their use in any H-PDLC application.

In this letter we report a unique technique for producing phase gratings from liquid crystal emulsions. We accomplish this by using monodisperse liquid crystal droplets formed into a precisely ordered two-dimensional hexagonal close-packed monolayer. The spacing of this grating is controlled by the droplet size. This allows us to switch both the intensity and the direction of the light, producing a very simple new material equivalent to a H-PDLC. Moreover, very low switching voltages ( $0.1 \text{ V}/\mu\text{m}$ ) and relatively fast switching speeds can be achieved by exploiting the interference effects of these phase gratings.

Monodisperse droplets of nematic liquid crystal where

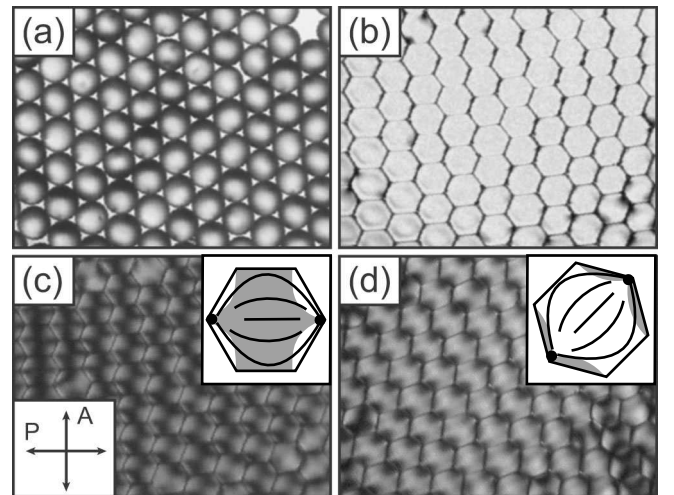


FIG. 1: Photomicrographs of the crystalline monolayer before (a) and after drying (b). The bipolar character of the droplets having two surface disclinations and parallel boundary conditions on the director is indicated by the texture when viewed between crossed polarizers shown in (c) with the droplet axis along the polarizer  $P$  and (d) rotated by  $45^\circ$ . The insets in (c) and (d) indicate the director pattern inside each droplet. The gray shaded regions indicate approximate regions of extinction.

produced by extrusion through a thin capillary, typically  $3 - 10 \mu\text{m}$  in diameter, into a coflowing fluid consisting of water with 1% polyvinyl alcohol (PVA) [3]. When a droplet at the tip of the capillary grows to reach a critical size, viscous drag exceeds surface tension and break-off occurs, producing highly monodisperse emulsions, with polydispersities below 3%. After generating the emulsion, the PVA concentration is increased to 4%. A small quantity of this concentrated emulsion is placed on an ITO coated glass cover slip and the water is slowly evaporated. At sufficiently high concentration the droplets spontaneously order into a hexagonal close-packed (HCP) monolayer as shown in Fig. 1(a). As the remaining water is driven off, the liquid crystal drops are distorted and compressed into a flat film consisting of hexagonally shaped liquid crystal drops embedded in a polymer matrix, as shown in Fig. 1(b). These results are typical: a thickness of  $7 \mu\text{m}$  is achieved for drops on a HCP lattice with a spacing of  $15 \mu\text{m}$ . A second ITO

coated glass plate is placed over the dried film to apply an electric field  $E$  to the liquid crystal droplets normal to the film.

The liquid crystal drops are stabilized against coalescence by the thin polymer walls that both encapsulate the liquid crystal and impose strong tangential boundary conditions,  $\mathbf{n}$ . To accommodate these boundary conditions,  $\mathbf{n}$  adapts a bipolar structure consisting of two disclinations located on opposite sides of the drop, see insets of Fig. 1(c) and 1(d). The line joining these defects defines the polar axis of the droplets, which forms the macroscopic optic axis of the drops. To minimize distortions in  $\mathbf{n}$ , the polar axis is confined to the plane of the film along the direction connecting next-nearest neighboring droplets. The three-fold degeneracy in this direction is broken by slight variations in the drying process that produce a uniformly aligned film as shown in the polarized photomicrographs in Figs. 1(c) and 1(d). The observed textures are those of bipolar droplets having their polar axis in the plane of film, and aligned nearly parallel and at  $\sim 45^\circ$  with respect to the polarizer direction [4].

To demonstrate the functionality of the liquid crystal droplet array as a tunable phase grating, the diffraction pattern from a laser incident normal to the film is measured as a function of the applied E-field. When no voltage is applied, the scattering pattern consists of a combination of diffraction peaks and diffusively scattered light, due to small variations in the director field of different droplets and director fluctuations. Upon application of a small electric field ( $E = 0.05 \text{ V}/\mu\text{m}$ ) a well defined diffraction pattern is obtained as shown by the image in the inset of Fig. 2(a). As many as 7 orders of diffraction peaks are visible reflecting the long-range hexagonal order of the film. The voltage dependencies of the intensity of the central undiffracted beam [Fig. 2(a)] and of a first order diffraction peak [Fig. 2(b)] are collected with a photodiode. The intensity of the first order diffraction peak shows an absolute maximum at  $E = 0.061 \text{ V}/\mu\text{m}$  and decreases at higher E-fields. The small remaining mismatch of the refractive index of the PVA  $n_p = 1.484$  and the ordinary refractive index of the liquid crystal  $n_o = 1.530$  precludes the complete disappearance of the diffraction peaks; this could easily be improved by tuning the materials to reduce the index mismatch. At lower voltages the observed oscillations are similar to those reported for one-dimensional liquid crystal gratings [5]. The intensity of the undiffracted beam behaves in a complementary way, showing minima when the intensity of the diffraction peaks is maximal.

The variations in the transmitted and diffracted intensities with applied field forms the basis of the switching of this H-PDLC. The number of maxima observed can be understood in terms of a simple model based on the interference of light passing through a phase grating that consists of alternating periodic regions of a fixed refractive index  $n_p$  (polymer) and electric-field-dependent refractive index  $n(E)$  (liquid crystal). The

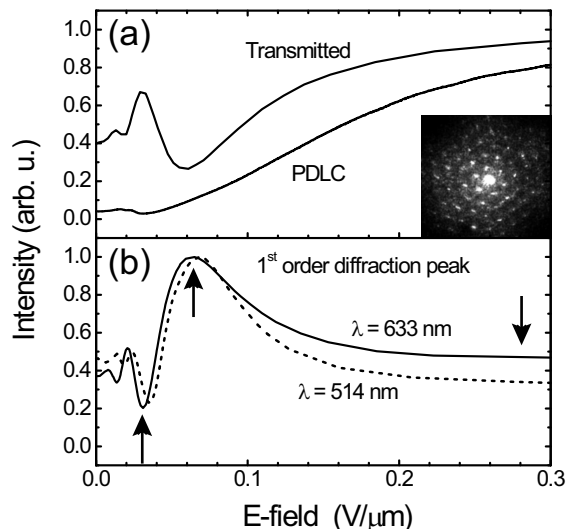


FIG. 2: (a) Transmitted intensity of an ordered two-dimensional film and of a PDLC as a function of electric field. (b) First order diffraction peak intensity versus electric field at two different wavelengths:  $\lambda = 633 \text{ nm}$  (solid) and  $\lambda = 514 \text{ nm}$  (dashed). Consecutive arrows indicate the E-fields between which switching the diffraction intensity ON and OFF is possible. The inset in (a) shows a typical diffraction pattern exhibiting high order peaks, indicating long range HCP order.

position of the diffraction peaks is fixed by the periodicity of the grating. By contrast, the intensity of the diffraction peaks depends on the optical path difference  $\Delta = k(n(E) - n_p)d$ , yielding high intensities when it becomes a multiple of  $2\pi$ . Using  $d = 7 \mu\text{m}$ , a vacuum wavelength of  $\lambda = 2\pi/k = 633 \text{ nm}$ , and the maximum index difference  $\Delta n \equiv (n_e - n_p) - (n_o - n_p) = 0.212$ , we estimate that we should observe 2.4 oscillations in the intensity. Experimentally three maxima are observed [Fig. 2(b)], matching the expected number given the uncertainty in sample thickness. The origin of these oscillations is confirmed by using a laser with a shorter wavelength,  $\lambda = 514 \text{ nm}$ . In this case, we expect 2.9 oscillations; we observe an additional interference minimum [Fig. 2(b)], confirming our interpretation.

The optical path difference giving rise to the oscillations depends on the droplet size, which is well defined in our monodisperse samples. In conventional PDLCs, interference effects are smeared out due to the broad distribution of droplet sizes. To demonstrate this we measure the transmission of a PDLC film consisting of polydisperse droplets with sizes between fractions and tens of microns. The corresponding transmission is shown in Fig. 2(a). No diffraction peaks are observed when switching between scattering ( $E = 0 \text{ V}/\mu\text{m}$ ) and transparent ( $E \gtrsim 0.4 \text{ V}/\mu\text{m}$ ) states.

The unique interference effects caused by the ordered

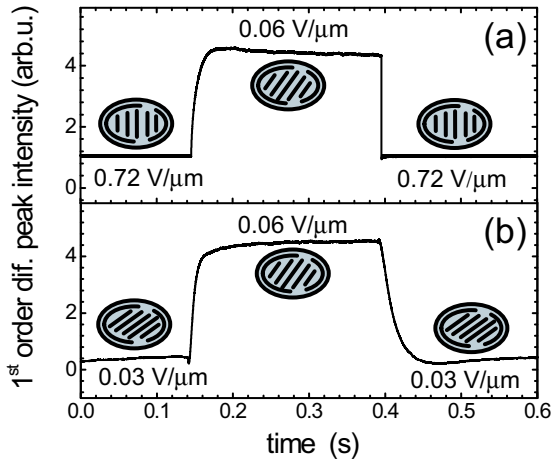


FIG. 3: Response and relaxation dynamics of the first order diffraction peak corresponding to switching between (a)  $E = 0.061 \text{ V}/\mu\text{m}$  and  $E = 0.720 \text{ V}/\mu\text{m}$  and (b)  $E = 0.029 \text{ V}/\mu\text{m}$  and  $E = 0.061 \text{ V}/\mu\text{m}$ . The schematic droplets show the mean orientation of the polar axis at the different  $E$ -fields.

array of liquid crystal droplets provide additional flexibility in the switching behavior. Switching can be achieved in a much narrower  $E$  interval by switching between adjacent minimum and maximum of the first order diffraction peak; a variation of 80% in the diffracted intensity can be achieved with a  $E$  difference of only  $0.03 \text{ V}/\mu\text{m}$ . These small field differences reflect the fact that  $\mathbf{n}$  does not need to be rotated by a full  $\pi/2$ , but instead must be rotated only enough to change from a constructive to destructive interference condition. This happens between  $E = 0.029 \text{ V}/\mu\text{m}$  and  $E = 0.061 \text{ V}/\mu\text{m}$  or between  $E = 0.061 \text{ V}/\mu\text{m}$  and  $E = 0.4 \text{ V}/\mu\text{m}$  [arrows Fig. 2(b)].

The interference effect also significantly improves the switching times since  $\mathbf{n}$  must change over an angular interval much less than  $\pi/2$ . To demonstrate this, we apply square wave  $ac$  voltages with two different amplitudes and measure the optical response of the first order diffraction peak. The frequency of the square wave signal is  $1 \text{ KHz}$  and its amplitude is switched with a modulation frequency  $f_{mod} = 2 \text{ Hz}$ . The fastest response is obtained by switching between the maximum of the diffraction intensity ( $E_{ON} = 0.061 \text{ V}/\mu\text{m}$ ) and the final minimum of the diffracted intensity at high voltage ( $E_{OFF} = 0.72 \text{ V}/\mu\text{m}$ ). We emphasize that the OFF state occurs at the

high field where index matching reduces almost all scattering. The fall time is  $\tau_f = 0.2 \text{ ms}$  and is rapid because the change in orientation of  $\mathbf{n}$  is controlled by the electric field as is shown in Fig. 3(a). However, the rise time is  $\tau_r = 20 \text{ ms}$ , which is much slower than the fall time, since now the change in orientation of  $\mathbf{n}$  is controlled by the elastic response of the droplet [Fig. 3(a)]. Nevertheless this switching time is decreased by more than order of magnitude over that obtained when switching between the maximum field and the  $E = 0$  state, where a switching time of  $0.85 \text{ s}$  is obtained; here the polar axis must travel through a much larger angle, taking a much longer time.

Similar switching can be achieved between  $E$ -fields that give rise to an adjacent minimum ( $E_{OFF} = 0.029 \text{ V}/\mu\text{m}$ ) and maximum ( $E_{ON} = 0.061 \text{ V}/\mu\text{m}$ ) of the diffracted intensity. In this case, however, the ON state is driven by the electric field, while the OFF state is controlled by the restoring elastic energy; the fall and rise times are  $\tau_f = 60 \text{ ms}$  and  $\tau_r = 45 \text{ ms}$ . Despite the fact that the electric field drives the rise time,  $\Delta E$  is now  $\sim 20$  times smaller; since the response time is proportional to  $\Delta E^{-2}$  [6], it should be  $\sim 400$  times longer, consistent with our observations. By contrast, the slower off time reflects the weaker restoring force of the elastic energy [Fig. 3(b)]. The switching speed and  $\Delta E$  requirements depend delicately on the orientation of  $\mathbf{n}$  and the total change required [7].

The use of monodisperse droplets results in new phenomena that can be used to switch between diffracting and transparent states in shorter times and at lower electric fields. Improvement of the relaxation times can be achieved through the use of smaller droplet sizes, since the characteristic relaxation time scales as  $a^2$ . Alternatively, by incorporating a polymer gel within the liquid crystal droplets the switching time can be improved because of the increased elastic energy, but the field requirements will be increased. A qualitative improvement of the switching can be achieved through the use of a three-dimensional ordered structure that will exhibit true Bragg switching of the light.

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